PREDISPERSED SOLVENT EXTRACTION OF HEAVY METALS USING COLLOIDAL LIQUID APHRONS

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To my parents

For raising me to believe that anything was possible

and

To my husband

For making everything possible

ABSTRACT

Predispersed solvent extraction (PDSE) is a modified solvent extraction technique which uses colloidal liquid aphrons to extract metal ions from aqueous solutions. Colloidal liquid aphrons (CLAs) are micrometer-sized organic droplets encapsulated within a thin soapy shell. The small size and special structure of CLAs make them of interest to removing low concentrations of heavy metals from aqueous solutions. Large interfacial area and electrostatically-charged surfaces are two important properties of CLAs, which distinguish PDSE from conventional solvent extraction. This thesis examined the application of PDSE to remove heavy metals, such as copper and nickel, from dilute aqueous solutions. The final goal of this study was to selectively separate these metals from a synthetic wastewater stream with the minimum reagent and energy consumption. The first step to reach this target was to remove copper and nickel from single cation bearing solutions and determine the important experimental parameters and optimum operational conditions.

It was observed that PSDE was able to remove more than 95 % of copper and nickel cations from dilute aqueous streams when optimum conditions were met for each metal ion. CLAs were formed by dropwise addition of organic phase (containing extractant, diluent, and oil soluble surfactant) into foaming aqueous phase (containing water soluble surfactant). LIX 984N was used as both copper and nickel extractant, and this was diluted in kerosene; sodium dodecyl sulphate (SDS) was used as an anionic water soluble surfactant in the generation of CLAs. In the case of copper extraction, cationic hexadecyl trimethylammonium bromide (CTAB) and non-ionic polyethylene glycol sorbitan monostearate (TWEEN 60) were also used as water soluble surfactants in the formation of the aqueous phase

The optimum conditions for copper extraction were determined to be an extractant concentration of 0.5 % (w/v); phase volume ratio (PVR) of 4; and initial copper solution pH of 3-5.5. It was also noted that using an anionic surfactant (SDS) resulted in higher extraction efficiency when compared to cationic and non-ionic surfactants; the concentration of SDS did not have any significant effect on the copper extraction. In addition, the experimental observations showed that the extraction process was very fast, with less than one minute contact time required to extract copper ions. However, in order to have rapid phase separation between metal loaded organic and

metal free aqueous, either centrifugation or a flotation column with the addition of flocculant should be utilized.

In case of nickel extraction, the optimum extraction conditions were found to be different with regard to initial nickel concentration in the aqueous solution. At the lowest nickel concentration (20 ppm), the extraction was mostly affected by the equilibrium pH. PVR and SDS concentration were other significant parameters in the nickel extraction. At 100 ppm, once again the equilibrium pH was the most significant factor on the nickel extraction; extractant concentration and PVR were the second and third most significant factors, respectively. At 300 ppm, due to the high metal content, the extractant concentration was found to be the most significant parameter, followed by equilibrium pH and PVR. Although different optimum conditions were determined for these three solutions, the optimum equilibrium pH for all of them was found to be 5.

Once the significant experimental parameters were determined for individual extraction of copper and nickel, the selective extraction of these metal ions from a ternary system, containing different concentrations of calcium, was investigated. Due to the high selectivity of LIX 984N for copper extraction, copper could be extracted in a wide range of operational conditions; hence, the extraction process was optimized based on nickel extraction. It was determined that in order to have selective extraction, first, copper should be extracted at lower pH values; and then by increasing the equilibrium pH and extractant concentration, nickel can be extracted from the copper free aqueous solution. Similar to single cation extraction processes, pH had a significant effect on the selective extraction and the extraction efficiency of each metal was mostly controlled by the equilibrium pH. The presence of calcium ion in the system negatively affected the nickel extraction, in which by increasing the calcium concentration, either extractant concentration or equilibrium pH should be increased to obtaining nickel removal greater than 95%.

Beside the extraction processes, a number of experiments were conducted to characterize CLAs, as well as recycling and regeneration. It was observed that the size of CLAs varied from sub-micrometer to few hundred micrometers, which was affected by PVR and water soluble surfactant concentration. Higher PVR or higher SDS concentration resulted in smaller CLAs. Finally, size distribution analysis and extraction experiments were performed on the stripped and recycled organic phase. The results showed that CLA could be regenerated from recycled organic phase,

and these regenerated CLAs showed no significant difference in size distribution and extraction efficiency when compared to freshly made CLAs.

RÉSUMÉ

L'extraction par solvant prédispersé (ESPD) est une modification de la technique d'extraction par solvant utilisant des aphrons de liquide colloïdal (ALC) pour extraire les ions métalliques de solutions aqueuses. Les ALC sont des gouttelettes organiques de la taille du micromètre encapsulées dans une mince membrane savonneuse. Leur petite taille et leur structure spéciale les rends intéressants pour l'extraction de faibles concentrations de métaux lourds présents dans des solutions aqueuses. Leur grande aire d'interface ainsi que la charge électrostatique de leur surface sont deux propriétés importantes, et distinguent ESPD de la technique d'extraction par solvant conventionnelle. Cette thèse examine l'application de la technique ESPD à l'extraction des métaux lourds tels le cuivre et le nickel à partir de solutions aqueuses diluées. Le but ultime de cette étude est de sélectivement séparer ces métaux à partir d'une solution synthétique d'eau usée en utilisant un minimum de réactifs et d'énergie. La première étape à accomplir était l'extraction du cuivre et du nickel séparément à partir de solutions porteuses de cations uniques ainsi que de déterminer l'importance des paramètres expérimentales et les conditions d'opérations optimales.

Il a été observé que la technique ESPD était capable d'extraire plus de 95 % des cations de cuivres et de nickel à partir de solutions aqueuses diluées lorsque les conditions optimales sont présentes pour chaque ion métallique. Les ALC ont été formés par l'addition goutte à goutte de la phase organique (contenant l'agent d'extraction, le diluant et l'agent de surface soluble dans l'huile) dans une émulsion de la phase aqueuse (contenant l'agent de surface soluble dans l'eau). LIX 984N a été utilisé pour l'extraction du cuivre et du nickel, cet agent d'extraction a été dilué avec du kérosène. Du dodécyle sulfate de sodium (DSS) a servit d'agent de surface anionique soluble dans l'eau lors de la génération des ALC. Dans le cas de l'extraction du cuivre, du hexadécyle triméthylammonium de brome cationique (HTBC) et du glycol polyéthylènique monostéarate de sorbitanne non-ionique (TWEEN 60) ont aussi été utilisés comme agents de surface soluble dans l'eau pour la formation de la phase aqueuse.

Il a été déterminé que les conditions optimales pour l'extraction du cuivre sont : une concentration d'agent d'extraction de 0.5 % (m/v); un ratio de phase volumique (RPV) de 4; un pH initial de 3-5.5 pour la solution de cuivre. Il a été noté que l'utilisation d'un agent de surface anionique (DSS)

résulte en une meilleure efficacité d'extraction lorsque comparée a un agent de surface cationique ou non-ionique. Cependant, la concentration de DSS n'a pas eu d'effet significatif sur l'extraction du cuivre. De plus, les observations expérimentales ont montré que le procédé d'extraction est très rapide avec un temps de contact requis de moins d'une minute pour l'extraction des ions de cuivre. Par contre, afin d'obtenir une séparation rapide de la phase organique contenant le cuivre et la phase aqueuse sans métal, la centrifugation ou la flottation par colonne avec addition de floculant doit être utilisée.

Dans le cas de l'extraction du nickel, les conditions optimales sont différentes dépendamment de la concentration initiale de nickel dans la solution aqueuse. Avec une concentration minimale de nickel (20 ppm), l'extraction est principalement affectée par le pH d'équilibre. Le RPV et la concentration de DSS sont les autres paramètres importants pour l'extraction du nickel. À 100 ppm, le pH d'équilibre est toujours le facteur le plus important sur l'extraction du nickel, alors que la concentration de l'agent d'extraction et le RPV sont respectivement le second et troisième facteurs plus importants. À 300 ppm, à cause de la forte concentration de métal, la concentration de l'agent d'extraction est le facteur le plus significatif, suivi par le pH d'équilibre et le RPV. Même si différentes conditions optimales ont été déterminées pour ces trois solutions, le pH d'équilibre optimal est de 5 pour chacune d'elle.

Une fois les paramètres expérimentaux significatifs identifiés pour l'extraction du cuivre et du nickel de façon individuelle, l'extraction sélective de ces ions métalliques a été testée dans un système tertiaire contenant différentes concentrations de calcium. À cause de la bonne sélectivité du LIX 984N pour l'extraction du cuivre, ce dernier peut être extrait sur un large plage de conditions opérationnelles. Le procédé a donc été optimisé pour l'extraction du nickel. Pour obtenir une extraction sélective, le cuivre doit être extrait en premier à un pH faible pour ensuite augmenté le pH d'équilibre et la concentration de l'agent d'extraction pour extraire le nickel de la solution aqueuse exempte de cuivre. De façon similaire au procédé d'extraction de cations simple, le pH a un effet significatif sur la sélectivité de l'extraction. De plus, l'efficacité de l'extraction de chaque métal est principalement contrôlée par le pH d'équilibre. La présence d'ions de calcium dans le système affecte négativement l'extraction du nickel. Avec une augmentation de la concentration en calcium, soit la concentration de l'agent d'extraction ou le pH d'équilibre doivent être augmenté pour obtenir une extraction de plus de 95 % du nickel.

En plus du procédé d'extraction, plusieurs expériences ont été réalisées pour la caractérisation des ALC de même que leur recyclage et régénération. Il a été observé que la taille des ALC variait d'un peu moins d'un micromètre à plus de 100 micromètres. Celle-ci étant affectée par le RPV et la concentration d'agent de surface soluble dans l'eau. Un RPV ou une concentration de DSS plus élevé produisant des ALC plus petits. Finalement, l'analyse de la distribution dimensionnelle et des expériences d'extraction avec la phase organique dégarnie et recyclée ont été réalisées. Les résultats ont montrés que les ALC peuvent être régénérés à partir de la phase organique recyclée et que ces ALC régénérés ne montrent pas de différence significative dans leur distribution dimensionnelle ou dans leur efficacité d'extraction lorsque comparés à des ALC produit à partir de solution fraîche.

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CONTRIBUTION OF AUTHORS

The thesis is presented as a "manuscript-based thesis" consisting of four manuscripts, three published, and one under revision. All the manuscripts are co-authored by Professor Kristian E. Waters in his capacity as research supervisor. The full bibliographic information of manuscripts is as follows:

1. Molaei, A., & Waters, K. E. (2015). Aphron applications - A review of recent and current research. Advances in Colloid and Interface Science, 216, 36-54.

2. Molaei, A., & Waters, K. E. (2015). Copper ion removal from dilute solutions using colloidal liquid aphrons. Separation and Purification Technology, 152, 115-122.

3. Molaei, A., Kökkılıç, O., & Waters, K. E. (2017). An investigation into predispersed solvent extraction of nickel (II) ions from dilute aqueous solutions. Separation and Purification Technology, 174, 396-407.

4. Molaei, A., Kökkiliç, O., Waters, K.E. (2017). Selective removal of copper and nickel ions from synthetic process water using predispersed solvent extraction. Chemical Engineering Research and Design, under review.

All the experiments and chemical analysis were conducted by the candidate. Manuscript 3 and 4 (Chapters 5 and 6) includes Dr. Ozan Kökkılıç (Research Associate, Department of Materials Engineering, Mc Gill University) recognizing his contribution in design of experiments and statistical analysis. Beyond the noted contributions of the co-authors the whole work presented in this dissertation was performed and written by the candidate.

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NOMENCLATURE AND ABBREVIATIONS

A/O	Acid to organic phase ratio
ANOVA	Analysis of variance
AASX	Air assisted solvent extraction
CASX	Compressed air assisted solvent extraction
Ca. Con.	Concentration of calcium ions
CCD	Central composite design
CGA	Colloidal gas aphron
CLA	Colloidal liquid aphron
CMC	Critical micelle concentration
CTAB	Hexadecyl trimethyl ammonium bromide
DOE	Design of experiments
Eq. pH	Equilibrium pH
Ex. Con.	Extractant concentration
ICP-OES	inductively coupled plasma optical emission spectroscopy
PDSE	Predispersed solvent extraction
ppm	Parts per million = mg L^{-1}
PVR	Phase volume ratio = V_{org} / V_{aq}
rpm	Revolutions per minute
RSM	Response surface methodology
S. Con.	Water soluble surfactant concentration
SDBS	Sodium dodecyl benzene sulfonate
SDS	Sodium dodecyl sulfate

SX   Solvent extraction

Tween 60   polyethylene glycol sorbitan monostearate

V_{aq} Volume of aqueous phase

V_{org} Volume of organic phase

CHAPTER 1. INTRODUCTION

1.1 INTRODUCTION

In the mining and mineral processing industry, wastewater treatment is considered to be one of the main challenges. According to the last survey released by Statistics Canada ("Industrial Water Use-2011," 2014), the total water intake by the mining industries in Canada in 2011 was 429.2 million cubic meters of which 60.6 % was withdrawn by the metal mines. Furthermore, the total volume of water discharged by the mining industries was reported to be 587.9 million cubic meters and approximately 60 % of this amount was the water discharged from metal mines. The discharge volumes were higher than the intake volumes of water due to the necessity of many operators to de-water their mines of groundwater in order to carry out their operations. It was also reported that 83.3 % and 10 % of wastewater was discharged into surface water bodies and tailing ponds respectively, and almost 30 % of this was not treated before discharge ("Industrial Water Use-2011," 2014). This water discharged to the environment each year may contain dissolved heavy metals which can be very harmful to humans and other living organisms.

Serious environmental regulations and cost benefits lead companies to focus on treatment of wastewater and reduce the heavy metals ion content to the permitted levels. There are different treatment methods for heavy metal containing wastewater including: solvent extraction, chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation, flocculation, flotation and electrochemical methods (Fu & Wang, 2011; Kentish & Stevens, 2001). All these techniques can be employed to remove heavy metals from wastewater, however the selection of the most appropriate method depends on the initial metal concentration, the component of the wastewater, capital and operational costs, plant flexibility and reliability, environmental consideration, to name but a few (Fu & Wang, 2011; Kurniawan *et al.*, 2006).

Solvent extraction (SX) is one of the more favored separation processes in hydrometallurgy, which is used in the extraction of various metals such as uranium, copper, zinc, nickel and cobalt from concentrated solutions (Chauhan & Patel, 2014; Flett, 2005; Kordosky, 2002; Lo *et al.*, 1983; Pradhan & Mishra, 2015; Thorsen, 1983). In this technique, the target metal ions are transferred from an aqueous solution into an organic solvent which comprises the metal extractant.

Although this technique is one of the most established techniques in hydrometallurgy, it is not economically feasible in removing low concentration heavy metals from wastewater due to high organic consumption and solvent loss. Solvent extraction is most effective and economically feasible in removing metals at concentrations greater than 500 ppm, which is above the concentration of heavy metals in wastewater streams (Kentish & Stevens, 2001).

Predispersed solvent extraction (PDSE) is a modified solvent extraction technique in which the organic phase is comminuted into small multilayer droplets called colloidal liquid aphrons (CLAs) prior to extraction (Sebba, 1985). A CLA consists of an oily core (containing the organic phase) which is encapsulated by a soapy shell (containing water soluble surfactant). CLAs possess two properties which distinguish the PDSE technique from conventional solvent extraction. The first property is high stability of CLAs provided by the soapy shell of surfactant which allows for storage of the CLA dispersion for months (even years) without any noticeable deterioration in their characteristics. The second property is the large surface area of CLAs which is a result of the micrometer size. This large surface area improves mass transfer (extraction) rate of PDSE compared to conventional solvent extraction (Michelsen *et al.*, 1986; Sebba, 1985, 1987). Furthermore, this large surface area of CLAs makes predispersed solvent extraction applicable to treat the dilute solutions with low organic/aqueous ratio and because it eliminates the mixing stage in the solvent extraction process large energy saving can be achieved using this technique. Research comparing PDSE with solvent extraction showed that PDSE was 5-10 times more effective in extraction of organic compound from water than SX (Michelsen *et al.*, 1986). It was also reported that, on the extraction of ethanol from water PDSE resulted in 20 % higher extraction compared to conventional solvent extraction.

Since the first application of PDSE in removal of organic solutes from water in 1980s (Sebba, 1985) many potential applications of this technique was found in metal recovery (Hahm *et al.*, 2003; Luo *et al.*, 2013); oil recovery (Sebba, 1985, 1987); acid recovery (Hong *et al.*, 2001; Kim *et al.*, 2004); and water remediation (Yan *et al.*, 2011). However, in case of heavy metals extraction, there is not much research especially the selective extraction of heavy metals from wastewater streams. Furthermore, any research on the recyclability of organic phase used in generation of CLAs which offers a full process of extraction, stripping and reusing of organic phase, was not offered. Hence, the main motivation of this dissertation was to develop an extraction

process to selectively extract heavy metal from wastewater solutions which meet the following conditions:

- Be selective.

Selectivity is one of the dominant advantages of solvent extraction that should be preserved in any modified solvent extraction technique.

- Be able to extract low concentration of metals without a high organic consumption.

One of the main disadvantages of solvent extraction is that, because of high organic consumption it is not economically feasible to apply to wastewater streams of low metal ion concentration. The alternative technique must be able to extract lower concentrations of metals using lower concentrations of extractant.

- Be adaptable with existing solvent extraction equipment.

One of the big challenges in applying alternative methods is the compatibility of this new technique with the equipment and instruments that already exist, which decreases the capital costs, time and space required for a new setup.

- Be cost effective and environmental friendly.

Recyclability of organic is one of aspects of being cost effective and environmental friendly, because the organic phase is one of the major operational cost in solvent extraction, which on the other hand is a source of pollution if releases into the environment.

Based on the literature, predispersed solvent extraction seems to meet all of these requirements but it was not proved in case of heavy metal extraction. Therefore, the main goal of this thesis is to determine the potential of PDSE in selective extraction of heavy metals such as copper and nickel from dilute wastewater streams while possessing the above properties.

1.2 THESIS OBJECTIVES

The general objective of this thesis research was to apply the predispersed solvent extraction technique to threat dilute wastewater streams which contain low concentration of base metals such as copper and nickel.

Specific objectives are addressed as follows:

1.2.1 Generation and characterization of colloidal liquid aphrons

For this objective, the generation of colloidal liquid aphrons under different conditions was studied and the produced CLAs characterized through their size and stability.

1.2.2 Application of predispersed solvent extraction to extraction of heavy metals such as copper and nickel

This objective investigated the predispersed solvent extraction of copper and nickel individually, and studied the effect of different experimental parameters on the extraction.

1.2.3 Selective extraction of metals from process water

For this purpose, the selective PDSE of copper and nickel from a synthetic process water containing calcium as an impurity was studied and optimum conditions to extract each of these metals established.

1.2.4 Examining the recyclability of colloidal liquid aphrons

This objective explored the stripping and reusing of the organic phase used in the formulation of CLAs after the extraction process.

1.3 THESIS STRUCTURE

The thesis is presented as a "manuscript-based thesis" consisting of seven chapters. Chapters 2, 3, 4 and 5 being published, submitted to a journal or in preparation for submission

The outline of each individual chapter is as follows:

Chapter 1:

This chapter includes introduction, objectives and structure of the thesis.

Chapter 2:

Background information on heavy metals, treatment methods of heavy metal bearing wastewater, and detailed information about solvent extraction are presented in this chapter.

Chapter 3:

This chapter gives a detailed information about aphron structure, properties and applications. This chapter was published as a review paper in Advances in Colloid and Interface Science Journal as follows:

Molaei, A., & Waters, K. E. (2015). Aphron applications - A review of recent and current research. Advances in Colloid and Interface Science, 216, 36-54.

Chapter 4:

The removal of copper ions from dilute solutions using colloidal liquid aphrons is investigated in this chapter. This chapter was published in Separation and Purification Technology as follows:

Molaei, A., & Waters, K. E. (2015). Copper ion removal from dilute solutions using colloidal liquid aphrons. Separation and Purification Technology, 152, 115-122.

Chapter 5:

This chapter presents the results on predispersed solvent extraction of nickel (II) ions from dilute aqueous solutions. This chapter was published in Separation and Purification Technology as follows:

Molaei, A., Kökkılıç, O., & Waters, K. E. (2017). An investigation into predispersed solvent extraction of nickel (II) ions from dilute aqueous solutions. Separation and Purification Technology, 174, 396-407.

Chapter 6:

Selective removal of copper and nickel ions from synthetic process water using predispersed solvent extraction is detailed in this chapter. This chapter was submitted to Chemical Engineering Research and Design.

Chapter 7:

This chapter presents the major conclusions of the thesis, highlights contributions to original knowledge and suggests areas in need of further research.

Appendix:

The appendix presents two conference papers which were presented and accepted for oral presentation at International Mineral Processing Congress (IMPC) in 2014 and 2016, respectively and speciation diagrams of copper, nickel and calcium.

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CHAPTER 2.   LITERATURE REVIEW

2.1   HEAVY METALS

There is no clear definition for heavy metals, with different definitions being found in the literature. In the Webster Dictionary a heavy metal is defined as: "A metal of high specific gravity; especially: a metal having a specific gravity of 5.0 or over" (Hawkes, 1997). According to Srivastava and Majumder (2008): "Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0". A general definition was also given by Hawkes, which comprises heavy metals as: "a block of all the metals in Groups 3 to 16 that are in periods 4 and greater that may also be stated as the transition and post-transition metals" (Hawkes, 1997).

According to these definitions many toxic elements which may exist in the wastewater streams such as zinc, copper, nickel, mercury, cadmium, lead, and chromium (Fu & Wang, 2011) are considered as being heavy metals.

Heavy metals can be discharged into environment directly or indirectly from mining, metal, tannery, battery, pharmaceutical, plastic, agricultural, glass, and wood industries, to name but a few (Bradl, 2005). They can be transported by runoff water, contaminating downstream water sources. Because heavy metals are not biodegradable, and tend to accumulate in microorganisms, they are considered to be toxic or carcinogenic. (Borba *et al.*, 2006; Fu & Wang, 2011; Hawkes, 1997; Paulino *et al.*, 2006; Srivastava & Majumder, 2008).

Although some of heavy metals are essential for life, an excessive amount of these metals can cause serious health problems for the human body. For example, excessive amounts of copper in water can cause such problems as vomiting, convulsions, cramps, or even death (Fu & Wang, 2011; Paulino *et al.*, 2006). Nickel is known to be a human carcinogen and it may cause serious lung and kidney problems, pulmonary fibrosis, gastrointestinal distress, and skin dermatitis if it exceeds the critical level (Borba *et al.*, 2006; Fu & Wang, 2011). Canada, as one of the major nickel producers in the world, is faced with an increase in aquatic contamination of nickel sediments (Salomons *et al.*, 2012) (see Figure 2.1).
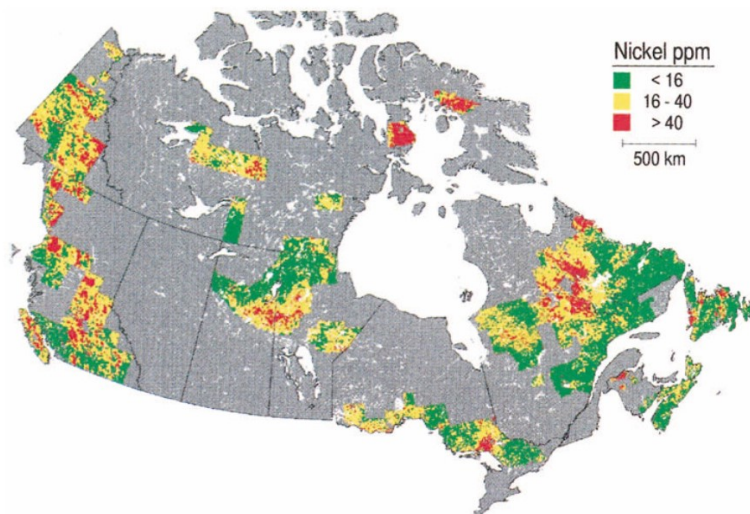
Figure 2.1. Nickel distribution in aquatic sediments in Canada (Salomons *et al.*, 2012)

Due to the toxicity of heavy metals, (including: copper, nickel, zinc, mercury, lead, cadmium, and chromium) even in low concentrations, they are of particular concern requiring treatment, and the concentration of these heavy metals in wastewater is highly regulated. Table 2.1 shows the authorized limits of a number of heavy metals in Canada's industrial waste discharges.

Table 2.1. Authorized limits of heavy metals in Canada's waste discharge regulations (*Metal Mining Effluent Regulations*, 2016)

Heavy metal	Maximum authorized concentration (mg L^{-1})
Copper	0.3-0.6
Nickel	0.5-1
Zinc	0.5-1
lead	0.2-0.4

These regulations require companies to treat wastewater and develop/use technologies that are effective at removing heavy metals from low concentrations. Some of the current heavy metal removing technologies include solvent extraction (Alguacil, 2002; Alguacil & Navarro, 2002; Dukov & Guy, 1982; Fouad, 2009; Navarro & Alguacil, 1999; Sridhar *et al.*, 2009; Xie & Dreisinger, 2010; Yun *et al.*, 1993), chemical precipitation (Alvarez *et al.*, 2007; Chen *et al.*, 2009; Fu *et al.*, 2007; Ghosh *et al.*, 2011), ion-exchange, (Argun, 2008; Berber-Mendoza *et al.*, 2006; Dąbrowski *et al.*, 2004; Rodríguez-Iznaga *et al.*, 2002; Ye *et al.*, 2011), adsorption (Inglezakis *et*

al., 2007), membrane filtration (Guha *et al.*, 1994; Kumar & Sastre, 1999; Raghuraman *et al.*, 1994; Valenzuela *et al.*, 1997), coagulation-flocculation (Amuda *et al.*, 2006; Bratskaya *et al.*, 2009; Johnson *et al.*, 2008), flotation (Matis *et al.*, 2003; McIntyre *et al.*, 1983; Polat & Erdogan, 2007), and electrochemical methods (Casqueira *et al.*, 2006; Heidmann & Calmano, 2008; Khelifa *et al.*, 2005; Merzouk *et al.*, 2009; Ölmez, 2009; Shafaei *et al.*, 2010). Table 2.2 summarize the advantages and disadvantages of these treatment methods.

Table 2.2. Chemical treatment methods for heavy metal contaminated wastewater (Fu & Wang, 2011; Kentish & Stevens, 2001; Tarkan & Finch, 2005a)

Process	Major advantages	Major disadvantages
Chemical precipitation	Well established, low effluent concentration	High chemical dosages, several unit operations, Limited to high metal concentration, production of sludge
Flotation	High selectivity, High efficiency, high overflow rates, low detention periods, low operating cost	High initial capital cost, high maintenance and operation costs
Electro-chemical	Rapid, well controlled, Low chemical consumption	Energy intensive, high capital costs, reduced efficiency at dilute concentrations
Ion-exchange	High selectivity, high effectiveness for metal concentration <100 mg L^{-1}	Chemical regeneration requirements, adsorbent expense, prone to fouling in mixed waste, not suitable for large scale
Adsorption	Simple metal remove process, low adsorbent cost, effective for <100 mg L^{-1}	Selectivity, recurring cost of new adsorbent, disposal cost of spent adsorbent
Coagulation-flocculation	Good sludge settling and dewatering characteristics.	Can't treat the heavy metal wastewater completely and must be followed by other treatment techniques, chemical consumption, increased sludge volume generation
Membrane Filtration	High Efficiency, easy operation, space saving	High cost, process complexity, membrane fouling and low permeate flux
Solvent extraction	Well-established, selective, continuous concentrated metal solution recycle, suitable for large-scale operations	Capital costs, large volume of organic solvent, risk of cross-contamination of aqueous phase, limited to high metal concentrations (>500 mg L^{-1})

2.2 SOLVENT EXTRACTION

Solvent extraction (SX) is a common hydrometallurgical process for selectively concentrating metals. Solvent extraction or liquid-liquid extraction is based on the transfer of a solute substance (metal ions) from one liquid phase (aqueous phase) into another liquid phase (organic phase), according to its solubility.

Application of solvent extraction in hydrometallurgical processes was first proposed in 1942 in the Manhattan project to extract uranium from a nitric acid solution, using ether as extractant (Chauhan & Patel, 2014). In 1950s, the solvent extraction technique was used to recover uranium from sulphuric acid solutions produced in the leaching of uranium ores using extractants such as alkyl amines and di (2-ethylhexyl) phosphoric acid (DEHPA). Nowadays, SX has become a common separation technique for recovering different metals, including: Cu, Ni, Co, Zn, U, Mo, W, V, Zr, Hf, Nb, Ta, Ga; rare earths; the platinum group metals (PGMs); metalloids such as B and Ge; reprocessing of nuclear fuels; purification of wet process phosphoric acid; and nitric acid recovery (Flett, 2005).

The popularity of solvent extraction is not only due to its versatility, but also its simplicity, selectivity, speed, and applicability to both the trace and macro level. In addition, the operation of solvent extraction can operate on a continuous basis and easily be automated with no solid handling requirement, which all contribute to low operating costs and high online availability.

The commercial solvent extraction process used to separate valuable metals in hydrometallurgy usually follows leaching, and is completed by stripping process. Figure 2.2 shows a simple flowsheet of a hydrometallurgical circuit which includes leaching, solvent extraction, stripping, and electro-winning.
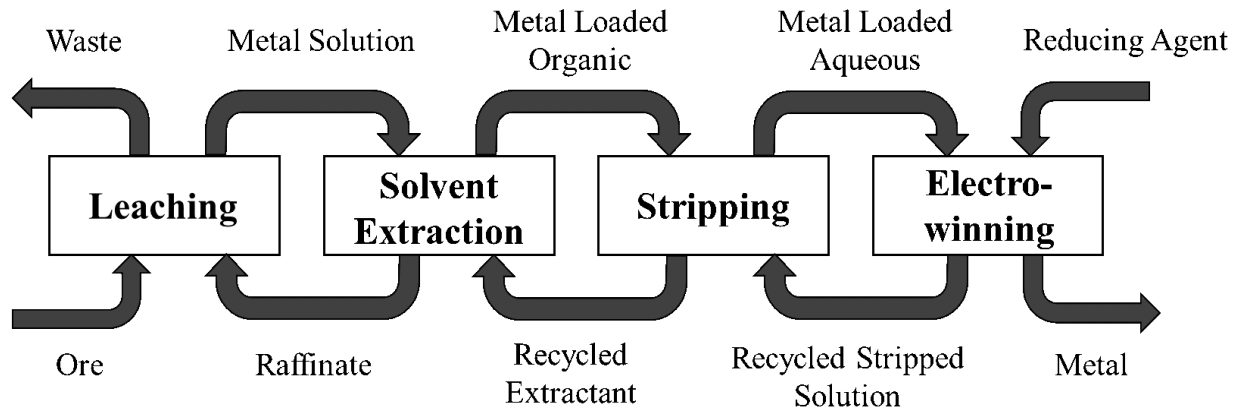
Figure 2.2. Flowsheet of a hydrometallurgical circuit including solvent extraction

At the front end of this circuit, the metal-bearing leached solution is mixed with the organic phase, which contains metal extractant in either a mixer- settler, a column, or centrifugal contactors.

In the hydrometallurgical industry, mixer-settler units have traditionally been used for commercial-scale solvent extraction. Figure 2.3 illustrates a schematic view of a mixer-settler unit.
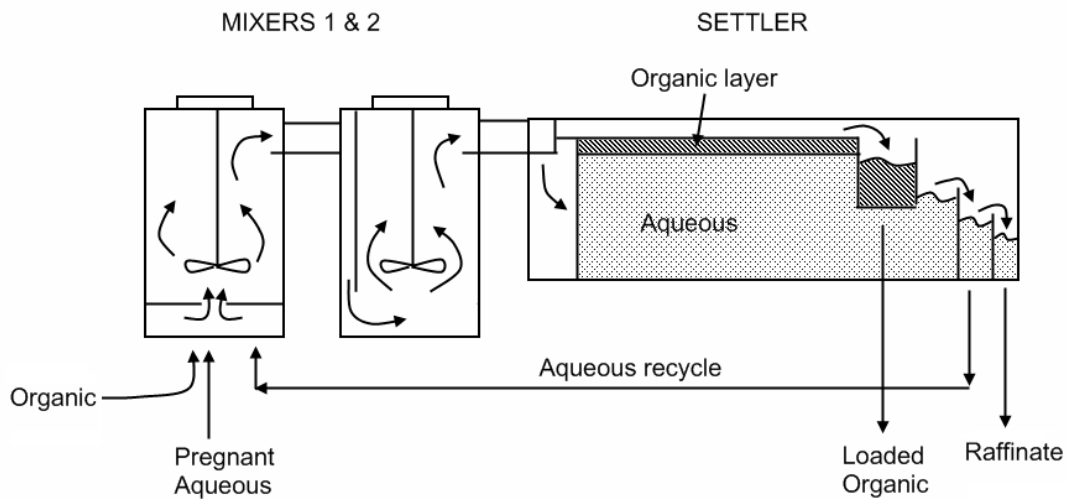
Figure 2.3. Schematic view of a mixer-settler (Littlejohn, 2007)

In the mixing unit, the desired metal is selectively transferred to the water-immiscible organic phase which contains the metal's extractant. In the settling unit, the phase separation is conducted and the metal free aqueous phase is recycled back to the leaching unit and organic phase is

transferred to stripping unit. In the stripping unit, the metal loaded organic phase is contacted with a stripping agent (most commonly an acid) to obtain a pure, concentrated aqueous solution of the metal to be sent to electro-winning unit.

SX Columns were designed to provide continuous contact between the two phases. The main application of the columns is in pharmaceutical, nuclear, and petro-chemical industries (Aguilar Sanjuán & Cortina, 2008). Figure 2.4 shows a schematic view of a solvent extraction column.
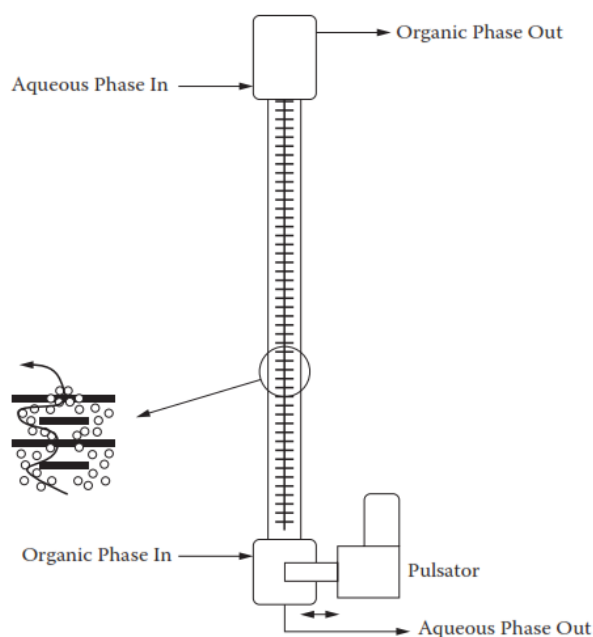
Figure 2.4. Schematic view of a solvent extraction column (Aguilar Sanjuán & Cortina, 2008)

 Centrifugal contactors (extractors), generally comprise a combination of a high-speed mixer and a centrifugal separator in a single unit. These contactors have various designs such as the one shown in Figure 2.5 (Aguilar Sanjuán & Cortina, 2008).
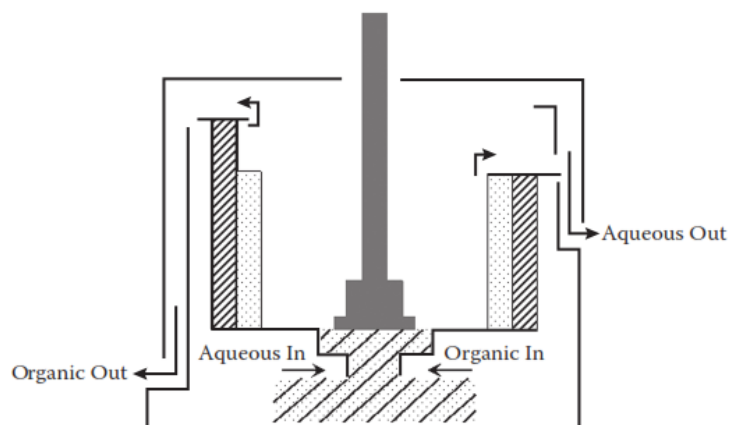
Figure 2.5. Schematic view of a centrifuge contactor (Aguilar Sanjuán & Cortina, 2008)

2.2.1 Solvent extraction reagents

A key element in the successful application of solvent extraction is the adoption of appropriate organic reagents, ensuring a high degree of selectivity for the desired metals. Selection of reagents is the most important stage in a solvent extraction circuit, not only because of the high cost of the reagents, but also due to the impact of reagents on the process and other operational parameters, such as pH and temperature. The solvent extraction reagents are generally selected with regard to the nature of ions present in the pregnant feed solution. Good mass transfer and phase separation characteristics are also important in the selection of reagents (Demopoulos, 1981; Wilson *et al.*, 2014).

Reagents used in solvent extraction usually consist of an extractant dissolved in a diluent. Other components can also be added to the organic phase, such as synergists (to improve extraction or separation factors); phase modifiers (to enhance phase separation or to increase the solubility of certain species); antioxidants (to retard or prevent degradation of components of the organic phase), and phase-transfer catalysts (to improve the reaction kinetics) (Aguilar Sanjuán & Cortina, 2008).

2.2.1.1 Extractants

Extractants are the most important components of the organic phase, as the solvent extraction of metals occurs by reaction of metal ions with an extractant. Since the metals usually exist as

hydrated ions in aqueous solutions with little or no tendency to transfer to the organic phase, in order to transfer these ions into the organic phase, the ionic charge needs to be neutralized and some or of the all water molecules must be replaced. These requirements can be met by complexing the ion with an ion of opposite charge to neutralize the charge, and replace the water molecules around the metal ions. In order to achieve this, three type of extractants can be used: acidic, basic, and solvating (Ritcey & Ashbrook, 1984).

Acidic extractant extracts metals via a cation-exchange mechanism, in which the hydrogen ion of the extractant is exchanged with the metal ion in the aqueous phase. Organic acids (such as: carboxylic acids, organophosphorus acids, and sulphonic acids) belong to this group of extractants. Chelating extractants are also cation exchangers; however, despite the acidic extractants that form ion-pairs with the metal ions, chelating extractants form coordination complexes. The cation-exchange reaction in both type of extractants can be expressed by Equation 2.1.

$$M^{z+}_{(aq)} + z\ HA_{(org)} \longleftrightarrow MR_{z\ (org)} + z\ H^{+}_{(aq)} \qquad \text{Equation 2.1}$$

where M represents metal and HA represents the extractant.

Equation 2.1 indicates that the metallic ions exchange with the H^{+} ions, and the equilibrium state is determined by the concentration of hydrogen ions, thus, the acidity of the aqueous phase increases during extraction. Every extractant has a maximum efficiency at a specific pH value, therefore, the pH of solution during the solvent extraction process should be controlled (Havlík, 2008).

Chelating extractants generally contain donor groups which form complexes with metal ions, and are often derived from analytical reagents, such as: β-diketones, 8-hydroxyquinoline, and hydroxyoximes (Aguilar Sanjuán & Cortina, 2008; Demopoulos, 1981).

Basic extractants are mostly used for solvent extraction of anionic species from acidic solutions or from strong alkali leach liquors. These extractants are protonated forms of primary, secondary, and tertiary high molecular weight amines and quaternary compounds. The extraction mechanism between these extractants and anionic metal complexes is based on the electrostatic interactions resulting in the formation of ion-pair between them. A general reaction in basic extraction using quaternary ammonium salt is given in Equation 2.2 (Aguilar Sanjuán & Cortina, 2008; Demopoulos, 1981; Lo *et al.*, 1983; Rousseau, 1987).

$$MX_n^{(n-z)-}{}_{(aq)} + R_4NX_{(org)} \longleftrightarrow R_4N^+MX_{z+1\ (org)} + (n-z)\ X^- \qquad\qquad \text{Equation 2.2}$$
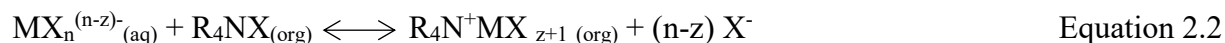
where z is the charge number of the metal cation M^{z+}, and X^- is a univalent anion.

Extraction using solvating extraction operates by replacing the solvating water molecules around the aqueous metal complex, which makes the metal species more lipophilic. For this purpose, the solvating extractant must have lone pair of electrons, which can be donated to the metal ion. Solvating extractants can be divided into two groups: organic ones (carbon–oxygen compounds) such as: alcohols, ethers, esters, amides and ketones; and oxygen/sulfur-phosphorus compounds such as: alkylphosphates, alkylphosphonates, alkylphosphinates, and alkylphosphine oxides (Aguilar Sanjuán & Cortina, 2008; Kislik, 2012; Rousseau, 1987; Tavlarides *et al.*, 1987). Equation 2.3 shows an extraction reaction using solvating extractant where S represent the solvating agent.

$$MX_{z\ (aq)} + mS_{(org)} \longleftrightarrow MX_zS_{m\ (org)} + m\ H_2O_{\ (aq)} \qquad\qquad \text{Equation 2.3}$$
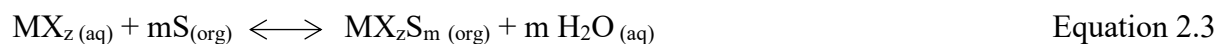
Table 2.3 and Table 2.4 detail a listing of commercial reagents and their applications.

Table 2.3. Acidic and chelating solvent extraction reagents (Aguilar Sanjuán & Cortina, 2008; Flett, 2005; Szymanowski, 1993)

Class of extractant	Type	Examples	Commercial use
Acid extractants	Carboxylic acids	Naphthenic acids, Versatic acids	Copper/nickel separation, nickel extraction, yttrium recovery
	Alkyl phosphoric acids	Mono/Di-alkyl phosphoric acids, sulphur analogues, (DP-8R, DP 10R, TR-83, MSP-8, D2EHPA, DEHPA)	Fe removal, Sb, Bi removal from copper electrolytes, uranium extraction, rare earth extraction, cobalt/nickel separation, zinc extraction, etc.
	Alkyl phosphonic acids	2-ethylhexyl phosphonic acid 2-ethylhexyl ester and sulphur analogues, (PC- 88A, Ionquest 801)	Cobalt/nickel separation, rare earth separation
	Alkyl phosphinic acids	Di-alkyl phosphinic acids and sulphur analogues (PIA-8, CYANEX 272, 302 and 301)	Cobalt/nickel separation, zinc and iron extraction
	Aryl sulphonic acids	Dinonyl naphthalene, sulphonic acid (Synex 1051)	Magnesium extraction
Chelating acid extractants	Hydroxyoximes	α-alkaryl hydroxyoximes, β-alkaryl hydroxyoximes, LIX 63, 64, 65N, 70, 71, 73, 84, 622, 860, 864 , 984	Copper extraction, nickel extraction
	8-hydroxyoxine	Kelex 100, 120, LIX 26	Gallium extraction, proposed for copper
	β-diketones	LIX 54, Hostarex DK16	Copper extraction from ammoniacal solution
	Bis-dithiopho-sphoramide	DS 5968, DS 6001	Zinc extraction, cobalt/nickel/ manganese separation
	Hydroxamic acids	LIX 1104	Nuclear fuel reprocessing, iron extraction, Sb and Bi extraction from copper refinery liquors
	Alkaryl sulfonamides	LIX 34	Development reagent

Table 2.4. Basic, solvating and non-ionic solvent extraction reagents (Aguilar Sanjuán & Cortina, 2008; Flett, 2005; Szymanowski, 1993)

Class of extractant	Type	Examples	Commercial use
Basic extractants	Primary amines	Primene JMT, Primene 81R	No known commercial use
	Secondary amines	LA-1, LA-2, Adogen 283	Uranium extraction, proposed for vanadium and tungsten extraction
	Tertiary amines	Various Alamines, in particular Alamine 336	Uranium extraction, cobalt extraction from chloride media, tungsten extraction, vanadium extraction, etc.
	Quaternary amines	Aliquat 336, Adogen 464	Vanadium extraction, other possible uses for chromium, tungsten, uranium
	Quaternary amine + nonyl phenol	LIX 7820	Anionic metal, cyanide extraction
	Mono N-substituted amide		Iridium separation from rhodium
	Trialkyl guanidine	LIX 79	Gold extraction from cyanide solution
Solvating extractants and non-ionic extractants	Phosphoric, phosphonic and phosphinic acid esters and sulfur analogues	TBP, DBBP, TOPO, CYANEX 921,923,471X, Hoechst PX324, 320, BaySolvex VP-AC 4046 (DBBP), VP-AC 4014 (DPPP), VP-Al 4059, (DEDP)	Refining of U3O8, nuclear fuel reprocessing, Fe extraction, Zr/Hf separation, Nb/Ta separation, rare earth separation, gold extraction
	Various alcohols, ketones, esters, ethers,	MIBK, etc	Nb/Ta separation, Zr/Hf separation
	Sulfoxide sulphides	SFI-6, Hoe F 3440	Palladium extraction in PGM refining
	Bi-imidazoles and bi-benzimidazoles Pyridine, dicarboxylic ester	ZNX 50, CLX 50	Zinc extraction and separation from iron in chloride media, Copper extraction from chloride media

2.2.1.2   Commercial extractants for copper and nickel extraction

The solvent extraction of copper ions is typically conducted using LIX extractants, which are mixed with diluents with the ratio of 1:7-1:10 (extractant/diluent ratio) (Free, 2013). LIX extractants such as LIX 63, LIX 84I, LIX 860, LIX 64, LIX 65N, LIX 70, and LIX 984N belong to the hydroxyoxime family of chelating extractants. LIX 984 N is a strong copper extractant with very good extraction efficiency (Aminian & Bazin, 2000; Asghari *et al.*, 2009; Devi & Nayak, 2014; Kul & Çetinkaya, 2009; Pradhan & Mishra, 2015; Sridhar *et al.*, 2009; Watling *et al.*, 2009). LIX 984 N is a 1:1 volume blend of LIX 860N-I (5-nonylsalicylaldoxime) and LIX 84-I (2-hydroxy-5-nonylacetophenone oxime) with a specific gravity of 0.935–0.955 g cm^{-3} at 25 $^{\circ}$C and a flash point greater than 76 $^{\circ}$C. Figure 2.6 shows the chemical structures of LIX 84 and LIX 860N.
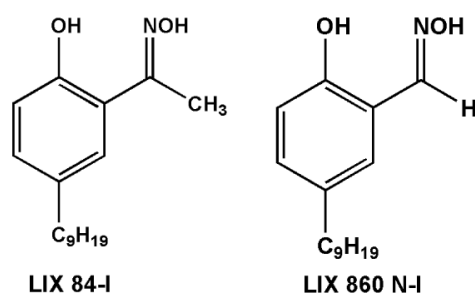
Figure 2.6. Chemical structure of LIX 84 and LIX 860N (Pradhan & Mishra, 2015)

In the case of nickel extraction, because nickel is mostly found with cobalt, the general trend is to extract cobalt using an amine extractant (from chloride-based solutions) or organophosphorus acids (from sulphate-based solutions). In some cases, nickel is extracted using hydroxyoximes (*e.g.* LIX family), phosphoric acids (*e.g.* D2EHPA), and carboxylic acids (*e.g.* Versatic acid), or a mixture of them (Bhaskara Sarma & Reddy, 2002; Devi & Nayak, 2014; Free, 2013; Guimarães *et al.*, 2014; Hutton-Ashkenny *et al.*, 2015; Li *et al.*, 2011; Sridhar *et al.*, 2009; Zhang *et al.*, 2012; Zhu *et al.*, 2012).

2.2.1.3   Diluents

Diluents are organic liquids (most commonly inexpensive hydrocarbon mixtures) in which the extractant and other additives (synergists, modifiers, *etc.*) are dissolved to form the solvent. The

main role of diluents in the solvent structure is to reduce the viscosity of the extractant, which facilitates pumping, processing, and settling of the extractant. In most of the cases, the diluent comprises the major portion of solvent. Diluents must meet general requirements such as (Aguilar Sanjuán & Cortina, 2008; Ritcey & Ashbrook, 1984; Rousseau, 1987):

- Being soluble for extractant and other additives (*e.g.* phase modifiers)

- Having a high flash point (>60 $^\circ$C) to minimize fire hazards and losses by volatilization

- Having a specific gravity of ~ 0.8 to allow for rapid phase separation

- Being insoluble in the aqueous phase

- Having a low surface tension

- Being cheap, available, and less toxic

A wide range of diluents are available for solvent extraction, which often consist of paraffins, naphthenes, and alkyl aromatics with one of the more common diluents used in solvent extraction being kerosene. The low polarity of this diluent facilitates the formation of H-bonds and other forms of secondary bonding between extractant molecules (Wilson *et al.*, 2014). Furthermore, the low dielectric constant of kerosene is favorable for solvent extraction. This is because, an increase in the dielectric constant of a diluent will increase the interaction between the diluent and the extractant, resulting in a decrease in the availability of the extractant for metal extraction (Devi & Nayak, 2014; El-Nadi, 2010; Rezaei & Nedjate, 2003).

2.2.2   Solvent extraction in wastewater treatment

Although solvent extraction is a well-established technology in heavy metal removal, it has a limited application in wastewater treatment (Khwaja *et al.*, 2000; McDonald & Bajwa, 1977; Yun *et al.*, 1993). Solvent extraction is not economically efficient for treating wastewater containing low metal concentrations (<500 mg L^{-1}). The reason is that to extract metal ions from dilute streams, a high aqueous to organic ratio is required and this results in high organic losses through entrainment in the solvent extraction process (Kentish & Stevens, 2001; Lazaridis et al., 2004). Therefore, alternative methods such as membrane filtration, ion exchange, and biosorption can be used to treat dilute solutions (see Figure 2.7). Another option for treating dilute wastewater

solutions is to use modified solvent extraction techniques such as: air assisted solvent extraction (AASX) and predispersed solvent extraction (PDSE). These modified techniques were designed to increase the contact between the organic phase and the aqueous phase and to provide higher aqueous/organic ratio having a reduced loss of organic phase. Another advantage of using modified techniques over the more traditional technologies is their adaptability to existing solvent extraction units, which is both time and cost effective.
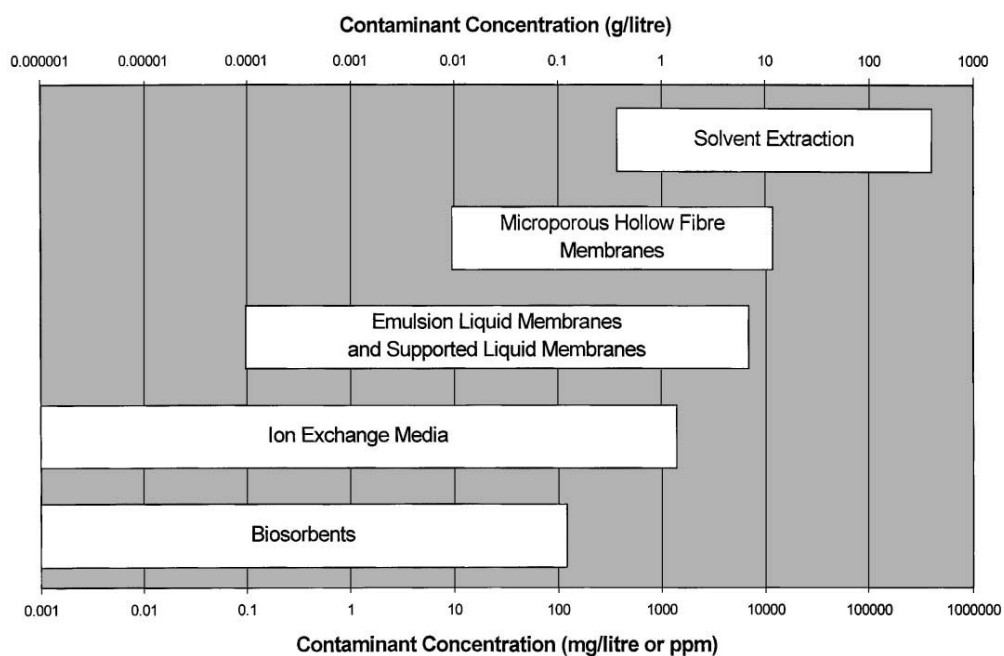
Figure 2.7. Wastewater treatment methods based on the contaminant concentration (Kentish & Stevens, 2001)

2.2.3   Modified solvent extraction techniques

2.2.3.1   *Air assisted solvent extraction*

The air assisted solvent extraction (AASX) technique was first proposed by Chen *et. al* (2003), and it is based on the use of solvent-coated bubbles to increase the contact between organic phase and aqueous phase. Figure 2.8 shows a schematic view of AASX process.
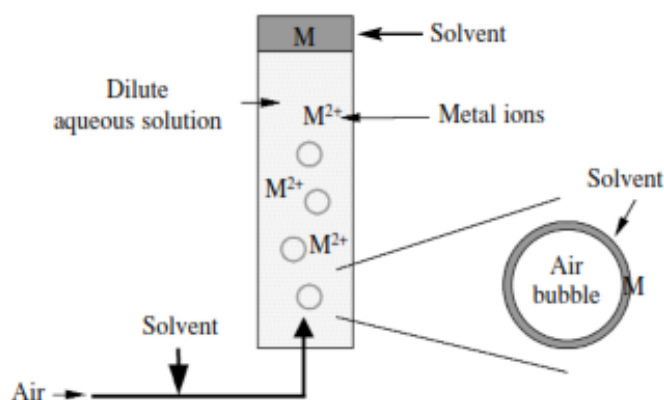
Figure 2.8. Schematic view of AASX (Chen *et al.*, 2003)

AASX was applied to the extraction of copper and zinc (Tarkan & Finch, 2005a, 2005b) and it was reported that AASX can provide high aqueous/organic (a/o) ratio, and consequently, high concentration enrichment. It was also found that the phase separation is very fast in AASX compared to conventional SX (Tarkan & Finch, 2005a). However, a maximum Cu extraction of 40 % can be reached using this method with 1:1 LIX 973N/kerosene ratio, 75:1 aqueous/organic ratio, and 500 mg L^{-1} initial copper concentration (Tarkan & Finch, 2005a). One of the drawbacks of AASX is that the rate of solvent coated air cell formation and addition is limited by the rate of air flow rate.

Later, Li *et al.* (2008) presented an improved AASX technique which was called compressed air-assisted solvent extraction (CASX). This technique is based on the pressurization of solvent with compressed air followed by releasing air-oversaturated solvent into the metal-containing wastewater. This technique could overcome the problems associated with the formation of solvent coated bubbles. The application of CASX to the extraction of Cr(VI) and Cd(II) from wastewater was studied and the effects of operating conditions such as pH, compressed air pressure, extraction time, extractant/diluent ratio, and solvent dosage on the extraction efficiency were investigated (Lee *et al.*, 2009; Li *et al.*, 2008). CASX achieved 100 % Cd extraction using 1:1 D2EHPA/kerosene ratio, aqueous/organic ratio of 250:1 with 50 mg L^{-1} initial Cd concentration at an equilibrium pH of 6. A schematic view of CASX is shown in Figure 2.9.
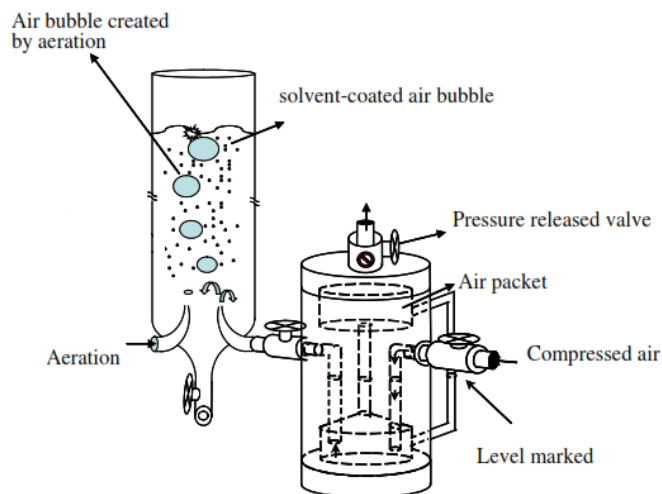
Figure 2.9. Schematic view of compressed air-assisted solvent extraction (Li *et al.*, 2008)

2.2.3.2   Predispersed solvent extraction

Predispersed solvent extraction (PDSE) was first proposed in 1985 by Sebba (1985), as an alternative technique to solvent extraction and to overcome some limitations of SX, such as: the requirement of mixing-settling stage; high metal concentration, and low aqueous to organic ratio (Lee *et al.*, 2000; Matsushita *et al.*, 1992; Sebba, 1985; Yundong *et al.*, 2000).

In PDSE the organic phase (which contains the extractant) is predispersed into micrometer sized globules called colloidal liquid aphrons (CLA) (Birajdar *et al.*, 2015). Compared to conventional SX, the rate of extraction and the ratio of aqueous phase to organic phase in PDSE can be very high. This is due to the small size of CLAs (from sub-micrometer to approximately 100 μm), which provides high interfacial area between extractant molecules and metal ions (Sebba, 1987).

Successful practices of PDSE show the potential of this technique to be used in separation of different materials. For example, it was reported by Michelsen *et al.* (1986) that the effectiveness of PDSE for the removal of an organic compound (o-dichlorobenzene) from water was 5 to 10 times greater than conventional solvent extraction using the same quantity of the solvent. In addition, a considerable drop in solvent to feed ratio (1:500) was observed. It was also reported by Wallis *et al.* that the PDSE method resulted in 20 % higher ethanol extraction with CLAs in comparison with conventional solvent extraction (Wallis *et al.*, 1986). Furthermore, PDSE showed

great potential applications in extraction of antibiotics (Lye & Stuckey, 2000) and organic pollutants (Hong *et al.*, 2001; Kim *et al.*, 2004); separation of bio-based products (Birajdar *et al.*, 2015); removal of metals (Hahm *et al.*, 2003; Luo *et al.*, 2013); oil recovery (Sebba, 1985, 1987); and water remediation (Yan *et al.*, 2011).

The focus of this thesis research was to investigate the use of PDSE as an extraction technique for treating dilute wastewater streams. The following chapter gives a comprehensive review of the current state of the art for this technique, and aphrons in general (both gas and liquid).

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CHAPTER 3. APHRON APPLICATIONS - A REVIEW OF RECENT AND CURRENT RESEARCH

3.1 ABSTRACT

Colloidal aphrons are multi-layered stable bubbles (CGAs) or droplets (CLAs), surrounded by a thin surfactant film. The small size of the aphrons creates a system with a high interfacial area which can be pumped like water without collapsing. The high stability of colloidal aphrons due to a thin soapy shell surrounding the core, and high interfacial area make them of interest in many processes such as mineral processing, protein recovery, drilling fluids, separation of organic dyes from wastewater, predispersed solvent extraction of dilute streams, clarification and purification of suspensions, soil remediation, material synthesis and immobilization of enzymes. This chapter aims to provide a comprehensive database in generation, characterization and applications of colloidal gas and liquid aphrons from more than 140 published works so far. The chapter also reports scale up, industrial applications, technical limitation regarding aphron applications and future research scopes.

3.2 INTRODUCTION

Aphrons are multi-layered stable bubbles or droplets, surrounded by a thin surfactant film. Aphrons were first proposed by Sebba (1984 & 1987) and the term originates from the Greek word for foam. Aphrons are foams in which the liquid shell is made from two different phases, such that they are also termed biliquid foams (Fink, 2012b; Sebba, 1979). The aphron consists of a spherical core, which can be gas or liquid, encapsulated in a thin shell of surfactant molecules. The hydrophobic, non-polar ends of surfactants are orientated towards the core and the hydrophilic ends go into a second phase. The second phase is often water which comprises an aphron stabilizer, a thickening agent and surfactant molecules at the outer boundary. The surfactants of the second phase orient their hydrophobic ends into the third outer phase which includes an additional layer of surfactant molecules whose hydrophilic ends extend into the bulk fluid. The surrounding phase prevents coalescence of adjacent aphrons (Fink, 2012b; Sebba, 1979).

3.3   COLLOIDAL GAS APHRONS

Colloidal gas aphrons (CGAs) as described by Sebba, can be termed a microfoam system, with colloidal properties consisting of closely packed spherical bubbles, 10-100 μm in size, and classified as kugelschaums or 'ball foams'. According to Sebba, gas aphrons are composed of two main parts: a gaseous core and a thin multi-layered aqueous surfactant shell that is composed of two surfactant layers. There is then a third surfactant layer that stabilizes the structure (Larmignat *et al.*, 2008; Sebba, 1987). Figure 3.1 illustrates the schematic view and a micrograph of CGAs.
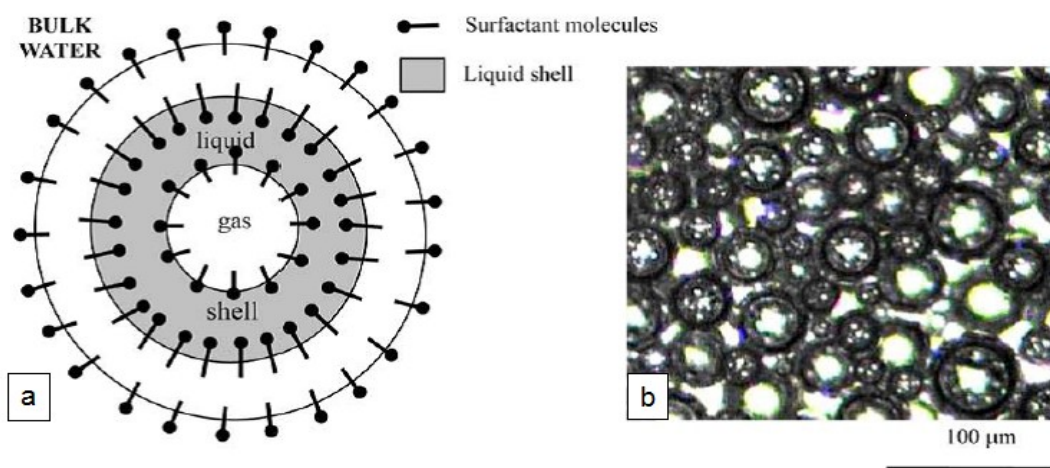
Figure 3.1. Schematic view of a CGA based on the structure proposed by Sebba (a) and a micrograph of actual CGAs (b) (Tseng *et al.*, 2006)

CGAs are first generated by stirring an aqueous surfactant solution contained in a baffled vessel, using a spinning disk impeller at high speed (5000-10000 rpm) (Sebba, 1984; Sebba, 1985a; Sebba, 1987) (Figure 3.2).
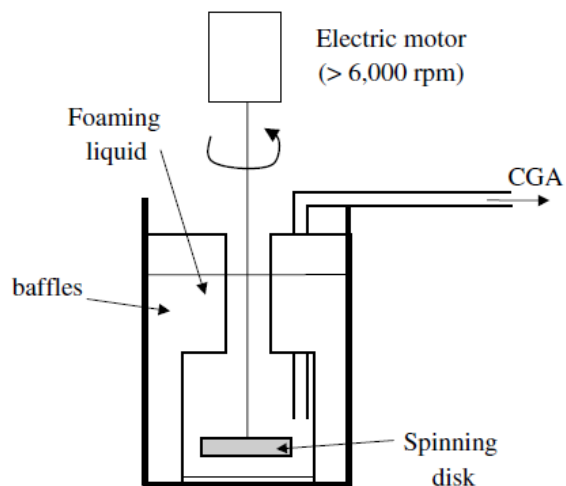
Figure 3.2. Schematic view of the CGA forming process (Tseng *et al.*, 2006)

As well as this classical method, various other techniques have been exploited to produce gas aphrons including sonication and homogenization (Bjorndalen & Kuru, 2008; Wan *et al.*, 1999; Xu *et al.*, 2008). Table 3.1 describes different methods of CGAs production as detailed by Hashim *et al.* (2012).

Table 3.1. Methods of CGAs generation (adapted from Hashim *et al.*, 2012)

Method	Instruments used	Principle	Diameter of CGAs	Gas hold-up	Production efficiency	Reference
Classical method	High speed stirrer in a baffled beaker	Above 4000 rpm, the liquid surface contacts the baffles and are forced to re-enter the bulk liquid carrying a thin film of gas. This thin film is unstable and breaks into minute gas bubbles encapsulated by a soapy shell- aphrons.	> 25 μm	> 60 % of gas in solution	1 KWh for 10000 L CGAs	Sebba (1985a)
Sonication	Sonicator	Sonicator with 0.5 inch ultrasound probe operated at a power of 300 W for 3 min. High frequency sound waves produce CGAs in a surfactant solution.	26 μm for 1 % L-150A 46 μm for 1 % SDS	40 % for 1 % L-150 A; 42 % for 1 % SDS	2.5×10^7 mL^{-1} for 1 % L-150A; 8.3×10^6 mL^{-1} for 1% SDS	Xu *et al.* (2008)
Homogen-ization	Homogen-izer	At > 4000 rpm speed, high speed rotor automatically draws solution axially into dispersion head and then forces it radially through the slots in rotor-stator arrangement. The turbulence forms CGAs.	68 μm 1 % L-150A solution 72 μm for 1 % SDS	15 % for 1 % L 150 A; 11 % for 1 % SDS	6.25×10^5 mL^{-1} for 1 % L-150A; 4.36×10^5 mL^{-1} for 1% SDS	Xu *et al.* (2008)

There are several properties of colloidal gas aphrons that make them of interest in a wide range of applications. These properties include: large interfacial area due to the small size of CGAs; relatively high stability due to multilayer surfactant film surrounding the gaseous core (which delays their coalescence); similar flow properties to those of pure water; and easy separation from the bulk liquid phase (Fink, 2012b; Jauregi *et al.*, 1997; Larmignat *et al.*, 2008). The CGA system contains up to 65 % air by volume (Bhatia *et al.*, 2005; Wang *et al.*, 2001) and has a specific gravity of approximately 0.35 (Hashim *et al.*, 2012). CGAs also retain the same charge as the surfactant solution from which they are generated (Hashim *et al.*, 2012). Colloidal gas aphrons can survive a compression of at least 27.3 MPa, which is ten times greater than the highest pressure conventional bubbles can survive (Fink, 2012b; Growcock *et al.*, 2007).

Based on these properties, many potential applications have been found for aphrons such as the removal of metals (Caballero *et al.*, 1989; Cabezón *et al.*, 1994; Ciriello *et al.*, 1982; Diaz *et al.*, 1990; Wang *et al.*, 2001) and dyes (Basu & Malpani, 2001; Fuda *et al.*, 2004; Huang *et al.*, 2002; Roy *et al.*, 1992b) from aqueous solutions, protein recovery (Jarudilokkul *et al.*, 2004; Jauregi *et al.*, 1997; Jauregi & Varley, 1998; Noble *et al.*, 1998; Noble & Varley, 1999) and flotation of cells and minerals (Amiri & Woodburn, 1990; Caballero *et al.*, 1989; Cilliers & Bradshaw, 1996; Hashim *et al.*, 1995; Subramaniam *et al.*, 1990; Waters *et al.*, 2008). They can also be used as carrier or mass transfer agent in different processes such as in-situ biodegradation, bacteria transportation and oxygen transfer (Bredwell *et al.*, 1997; Bredwell *et al.*, 1995; Bredwell & Worden, 1998; Dai *et al.*, 2004; Jackson *et al.*, 1998; Jenkins *et al.*, 1993; Michelsen *et al.*, 1984; Mulligan & Eftekhari, 2003; Wagner & Pöpel, 1996; Worden & Bredwell, 1998), and they have been successfully applied in dust collection processes (Jarudilokkul *et al.*, 2008).

3.1.1 Characterization of colloidal gas aphrons

Colloidal gas aphrons are most commonly characterized in terms of the stability, gas holdup and size distribution.

3.1.1.1 Stability

The most important property of aphrons is their stability. They are very stable and their stability depends on the thickness and viscosity of the encapsulating shell. Aphrons are not stable if the shell is thinner than 4 µm or thicker than 10 µm (Ivan *et al.*, 2001). The second parameter that controls an aphron's stability is shell viscosity. The shell must have a certain viscosity to minimize the phenomenon known as the "Marangoni effect" that causes transfer of water from the shell into the bulk liquid resulting in thinner and less stable aphrons (Gaurina-Međimurec & Pašić, 2009; Growcock *et al.*, 2004b; Scriven & Sternling, 1960; Sebba, 1987).

In the case of ionic surfactants, the stability of CGA dispersions is mainly due to electrostatic interactions and surface forces. A delay in coalescence of the aphrons occurs at the gas–liquid interface of adjacent aphrons as a result of the repelling effect of charged or polar groups in the surfactant molecules. When CGAs are made from non-ionic surfactants, the electrostatic interactions will not be the main stabilizing force, thus other forces (*i.e.* steric forces) will

contribute to the stability of these dispersions. In most studies, the stability of CGAs has been determined in terms of half-life ($t_{1/2}$), which is the time taken for half of the initial volume to become a clear liquid due to drainage and bubble collapse or coalescence (Jauregi & Varley, 1999). In the study carried out by Matsushita *et al.* (1992), the effect of stirring time and speed, and surfactant type and concentration on the half-life of CGAs was investigated. It was found that the stability of CGAs in terms of half-life increased significantly (from 210 s to 300 s) by increasing stirring speed (from 5000 rpm to 5500 rpm). However, increasing stirring time did not have any effect on CGA stability. Furthermore, it was reported that surfactant type and concentration greatly affected the half-life of CGAs. Different values of half-life (from 144 s for 0.5 g L^{-1} G1300 to 486 s for 2.5 g L^{-1} cetyl trimethyl ammonium bromide) were obtained during stability measurements using different surfactant types and concentrations. The stability of CGAs can also be determined directly by measuring the drained volume of liquid CGAs with respect to time, termed the rate of liquid drainage (Longe, 1989). Amiri and Woodburn (1990) analysed the rate of rise of CGA bubbles using a graduated cylinder to determine the stability of CGAs. Many other studies were carried out in order to investigate stability of CGAs in terms of the drainage rate which mostly highlighted the difference between CGAs and conventional foams (Bhatia *et al.*, 2005; Feng *et al.*, 2009; Jianhong *et al.*, 2009; Moshkelani & Amiri, 2008; Save & Pangarkar, 1994; Yan *et al.*, 2005a).

The effect of different parameters such as the type and concentration of surfactant (Chaphalkar *et al.*, 1993; Jauregi *et al.*, 1997; Matsushita *et al.*, 1992; Roy *et al.*, 1992b; Save & Pangarkar, 1994; Subramaniam *et al.*, 1990; Yan *et al.*, 2005a), stirring speed (Bhatia *et al.*, 2005; Jauregi *et al.*, 1997; Matsushita *et al.*, 1992; Sebba, 1985a) and stirring time (Bhatia *et al.*, 2005) in CGAs generation, temperature (Yan *et al.*, 2005a), pH of continuous phase and additives such as salts, enzymes, polymers and solvents (Save & Pangarkar, 1994) on the stability of colloidal gas aphrons have been investigated by many researchers. It was found that maximum stability is achieved at surfactant concentrations above the critical micelle concentration (CMC) (Chaphalkar *et al.*, 1993; Matsushita *et al.*, 1992; Save & Pangarkar, 1994) and the critical speed for CGA generation was found to be 5000 rpm (Jauregi *et al.*, 1997; Matsushita *et al.*, 1992). It was reported that salt concentration (ionic strength) had a significant effect on the stability of CGAs generated from ionic surfactants in the classical method (Jauregi & Varley, 1999), however pH did not have any

remarkable effect on the CGA stability (Jauregi *et al.*, 1997; Save & Pangarkar, 1994). The various applications of surfactants based on their ionic charge are detailed in Tables 3.2, 3.3 and 3.4.

Table 3.2. Anionic surfactant applications

Anionic surfactant	Applications	References
SDS (sodium dodecyl sulfate)	Mineral Processing	Cabezón *et al.* (1994); Waters *et al.* (2008)
	Biological separation	Dermiki *et al.* (2009); Lye & Stuckey (2000)
	Water purification	Hashim & Gupta (1998)
	Soil remediation	Couto *et al.* (2009); Roy *et al.* (1995a); Roy *et al.* (1995b); Roy *et al.* (1994)
	Predispersed solvent extraction (PDSE)	Matsushita *et al.* (1992)
	Enzyme immobilization	Lamb & Stuckey (1999); Lamb & Stuckey (2000a); Lamb & Stuckey (2000b); Lye *et al.* (1996)
	Drilling fluids	Nareh'ei *et al.* (2012)
SDBS (sodium dodecyl benzene sulfonate)	Mineral Processing	Wang *et al.* (2001)
	Water purification	Basu & Malpani (2001); Ciriello *et al.* (1982); Mansur *et al.* (2006); Subramaniam *et al.* (1990)
	PDSE	Hahm *et al.* (2003); Hong *et al.* (2001); Lee *et al.* (2000); Luo *et al.* (2013); Matsushita *et al.* (1992)
	Mass transfer	Save & Pangarkar (1995); Save *et al.* (1993)
	Drilling fluids	Bjorndalen *et al.* (2014); Bjorndalen & Kuru (2008)
AOT (sodium bis-(2-ethyl hexyl) sulfosuccinate)	Protein Recovery and Biological separation	Alves *et al.* (2006); Fuda & Jauregi (2006); Fuda *et al.* (2004); Jauregi *et al.* (1997); Jauregi & Varley (1998); Noble *et al.* (1998); Noble & Varley (1999)
	Enzyme immobilization	Lamb & Stuckey (2000a)
SLS (sodium lauryl sulfate)	Mineral Processing	Diaz *et al.* (1990)
potassium oleate	Mineral Processing	Cabezón *et al.* (1994)
Aerosol OT	Water purification and effluent treatment	Subramaniam *et al.* (1990)
LUX flakes	Water purification and effluent treatment	Subramaniam *et al.* (1990)

Table 3.3. Cationic surfactant applications

Cationic surfactant	Applications	References
CTAB (cetyl trimethyl ammonium bromide)	Protein Recovery and Biological separation	Alves *et al.* (2006); Dermiki *et al.* (2008); Fuda *et al.* (2005); Fuda & Jauregi (2006); Noble *et al.* (1998); Spigno *et al.* (2010)
	PDSE	Matsushita *et al.* (1992)
	Mass transfer	Save *et al.* (1993)
HTAB (hexadecyl trimethyl ammonium bromide)	Mineral Processing	Caballero *et al.* (1989)
	Biological separation	Basu & Malpani (2001)
	Water purification	Mansur *et al.* (2006)
	Soil remediation	Roy *et al.* (1995b)
	PDSE	Hahm *et al.* (2003); Hong *et al.* (2001)
	Drilling fluids	Bjorndalen & Kuru (2008)
BDHA (Benzyl dimethyl-n-hexadecyl ammonium chloride)	Water purification and effluent treatment	Subramaniam *et al.* (1990)
BHDC (benzyl dimethyl hexa-decyl ammonium chloride)	Water purification and effluent treatment	Hashim *et al.* (1995); Hashim *et al.* (1998)
CPC (cetyl pyridinium chloride)	Biological separation and Water purification	Save & Pangarkar (1995)
	Mass transfer	Bredwell *et al.* (1995)
CTAC (cetyl trimethyl ammonium chloride)	Biological separation and Water purification	Save & Pangarkar (1995)
DTAC (dodecyl trimethyl ammonium chloride)	Biological separation and Water purification	Save & Pangarkar (1995)
DTAB (dodecyl trimethyl ammonium bromide)	PDSE	Matsushita *et al.* (1992)
	Enzyme immobilization	Lamb & Stuckey (2000a)
EHDA (ethyl hexadecyl dimethyl ammonium bromide)	Removal of heavy metals	Ciriello *et al.* 1982)

Table 3.4. Non-ionic surfactant applications

Non-ionic surfactant	Applications	References
Tweens (Polysorbates)	Biological separation	Dermiki *et al.* (2009); Jarudilokkul *et al.* (2004)
	Water purification	Mansur *et al.* (2006)
	Mass transfer	Bredwell & Worden (1998); Srivastava *et al.* (2000); Worden & Bredwell (1998)
	PDSE	Luo *et al.* (2013)
Tergitols	Soil remediation	Roy *et al.* (1995b)
	PDSE	Lee *et al.* (2000); Matsushita *et al.* (1992)
	Water purification	Yan *et al.* (2011)
	Mass transfer	Srivastava *et al.* (2000)
Brij (Polyoxyetylene sorbitan momooleate)	PDSE	Hahm *et al.* (2003)
	Enzyme immobilization	Lamb & Stuckey (2000a)
Triton	Protein Recovery and Mass transfer	Bredwell *et al.* (1995); Noble *et al.* (1998)
Softanol	Biological Separation	Lye & Stuckey (2000)
	Enzyme immobilization	Lamb & Stuckey (2000b)

The effect of surfactant type and concentration on the stability of CGAs is given in Table 3.5.

Table 3.5. Effect of surfactant type and concentration on the stability of CGAs

Surfactant	Concentration	pH	Half-life (s)	Reference
	0.25 g L^{-1}	-	216	
CTAB	0.5 g L^{-1}	-	354	Matsushita *et al.* (1992)
	1 g L^{-1}	-	396	
	2.5 g L^{-1}	-	486	
CPB	0.5 g L^{-1}	-	426	Matsushita et al. (1992)
DTAB	0.5 g L^{-1}	-	174	Matsushita et al. (1992)
SDS	0.5 g L^{-1}	-	312	Matsushita et al. (1992)
SDBS	0.5 g L^{-1}	-	408	Matsushita et al. (1992)
Tergital	0.5 g L^{-1}	-	162	Matsushita et al. (1992)
	3.5 mM	-	340	
SDS	8.7 mM	-	535	Yan *et al.* (2005a)
	41.7 mM	-	330	
	0.9 mM	-	446	
HTAB	4.5 mM	-	525	Yan et al. (2005a)
	9.1 mM	-	141	
	0.2 mM	-	413	
Tween 80	1 mM	-	498	Yan et al. (2005a)
	5 mM	-	471	
	0.5 g L^{-1}	7	387	
Rhamnolipid	1 g L^{-1}	7	502	Feng *et al.* (2009)
	4 g L^{-1}	7	529	
LUX flakes	5.1 g dm^{-3}	9	738	Subramaniam *et al.* (1990)
Aerosol OT	2 g dm^{-3}	9	510	Subramaniam et al. (1990)
SDBS	1.2 g dm^{-3}	9	540	Subramaniam et al. (1990)
BDHA	1.3 g dm^{-3}	9	510	Subramaniam et al. (1990)
CTAC	2 kmol m^{-3}*10^3	-	300	Save & Pangarkar (1994)
DTAC	2 kmol m^{-3}*10^3	-	270	Save & Pangarkar (1994)
CPC	2 kmol m^{-3}*10^3	-	290	Save & Pangarkar (1994)
SDBS	2 kmol m^{-3}*10^3	-	320	Save & Pangarkar (1994)
SLS	2 kmol m^{-3}*10^3	-	300	Save & Pangarkar (1994)

3.1.1.2 Size distribution

Colloidal gas aphrons have a wide size range (10-100 μm). Aphron size has a significant effect on their stability. Large aphrons can survive for longer than small aphrons (Belkin *et al.*, 2005). They are less stable when smaller than ~ 50 μm in diameter.

Various methods have been employed to determine aphron size distributions. Techniques such as laser diffraction to measure the aphrons' diameter (*d*) (Bredwell *et al.*, 1995; Chaphalkar *et al.*, 1993; Kommalapati *et al.*, 1996; Roy *et al.*, 1992b), and light microscopys and image analysis (Jauregi *et al.*, 1997; Save & Pangarkar, 1994) are the most commonly used methods for determining aphron sizes. Jauregi *et al.* (2000) measured the size distributions of aphrons using microscopy connected to a CCD camera. Basu & Malpani (2001) took photomicrographs with a stereo-zoom microscope to estimate the Sauter mean diameter of CGAs. By using light microscopy, the average aphron diameter was found to be between 30 μm and 90 μm (Jauregi *et al.*, 1997; Save & Pangarkar, 1994) while an average diameter of up to 120 μm has been obtained from laser-based techniques (Bredwell *et al.*, 1995; Chaphalkar *et al.*, 1993; Kommalapati *et al.*, 1996; Roy *et al.*, 1992b). Aphron size depends on the type and concentration of surfactant, ionic strength, and the presence of other molecules or particles (Jauregi & Dermiki, 2010).

3.1.1.3 Gas hold-up

Gas hold-up is the gas volumetric ratio, a measure of the air quantity incorporated into the dispersion and the hold-up just before collapse (ε_0). It is defined as the ratio between the gas volume (V_g) and the dispersion final volume (V_{a0}). Gas hold-up can be described by Equation 3.1, where V_{l0} is the initial volume of the liquid, h_0 is the height of the dispersion and h_{l0} is the height of the initial volume of liquid (Jauregi & Varley, 1999).

$$\varepsilon_0 = \frac{V_g}{V_{a0}} = \frac{(V_{a0} - V_{10})}{V_{a0}} = \frac{(h_0 - h_{10})}{h_0}$$

Equation 3.1

In order to measure gas content of a microbubble an oscillation U-tube densitometer can be used (Bjerknes *et al.*, 1997; Parmar & Majumder, 2013). The CGA system contains up to 65 % gas hold-up (Bhatia *et al.*, 2005; Hashim *et al.*, 2012; Wang *et al.*, 2001) and as a comparison, in

mineral processing the gas hold-up range for column flotation is commonly 10-20 % (Bhole & Joshi, 2007; del Villar *et al.*, 2010; Fuerstenau *et al.*, 2007).

3.2   COLLOIDAL LIQUID APHRONS

Colloidal liquid aphrons (CLAs) are believed to be micrometer-sized solvent droplets encapsulated by a thin soapy (aqueous) shell. A mixture of non-ionic and ionic surfactants makes CLAs stable by forming three distinct interfaces (a monolayer and a separate bilayer) in the soapy shell (Figure 3.3). It is possible to generate CLAs with a diameter varying from less than 1 µm to 100 µm (Sebba, 1987) using different surfactant types and concentrations. Similar to CGAs, CLAs show a remarkable resistance to coagulation and can be stored for long periods of time without any noticeable coalescence, and can also be transported through pumping without destroying the structure (Sebba, 1987).
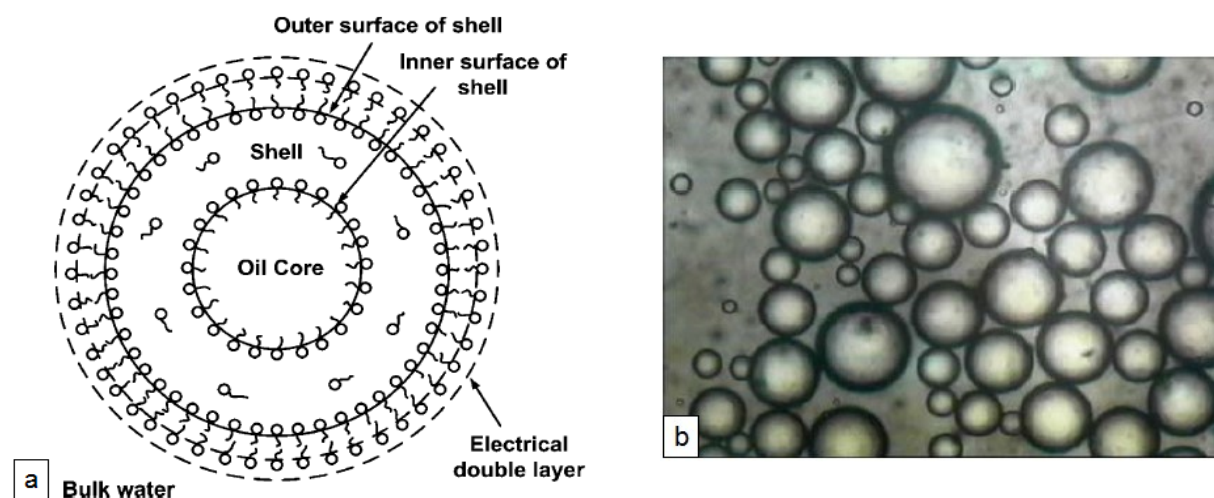
Figure 3.3. Structure of a colloidal liquid aphron (a) (Yan *et al.*, 2005b) and micrograph of diluted CLAs (b) (Luo *et al.*, 2013)

In order to produce CLAs, the oil (internal phase) must be broken down to the required globule size and then the globules encapsulated in the soapy film. This is achieved when the oil contains a dissolved surfactant, and is spread across the surface of water having a water-soluble surfactant dissolved in it (Sebba, 1987). One of the most commonly used methods to generate CLAs is the slow drop-wise addition of an organic phase (containing non-ionic surfactant) into a foaming solution of the surfactant.

Colloidal liquid aphrons have several properties, such as high stability and large interfacial area which make them of interest to separation processes (Lee *et al.*, 2002). Several potential applications for CLAs include: predispersed solvent extraction (PDSE) such as the extraction of antibiotics (Lye & Stuckey, 2000) and organic pollutants (including organic dyes) (Michelsen *et al.*, 1986; Zhang *et al.*, 1996); soil remediation (Vidrine *et al.*, 2000); and enzyme immobilization (Lamb & Stuckey, 1999; Lamb & Stuckey, 2000a; Lamb & Stuckey, 2000b; Lye *et al.*, 1996). They also have been successfully applied to reducing toxicity in the downstream separation of fermentation products (Hong *et al.*, 2001).

3.2.1 Characterization of colloidal liquid aphrons

The properties of the aphrons depends upon the formulation and method of generation (Matsushita *et al.*, 1992), however the characteristics of CLAs can be affected by the nature of the continuous phase in which they are dispersed. Sebba was the first to investigate the structure of CLAs using fluorescent dyes (Sebba, 1987). Other techniques, including transmission electron microscopy (TEM) (Jauregi *et al.*, 2000; Lye & Stuckey, 1998; Yan *et al.*, 2005b), differential scanning calorimetry (DSC) (Lye & Stuckey, 1998) and light scattering (Chaphalkar *et al.*, 1993; Lye & Stuckey, 1998; Matsushita *et al.*, 1992) have also been utilized to characterize liquid aphrons.

3.2.1.1 Stability

The influence of surfactant type and concentration, pH of continuous phase and additives such as enzymes, polymers, and salts on the stability of CLAs were studied by Matsushita *et al.* (1992) and Sebba (1987). The stability of CLAs when dispersed in various continuous phases was also investigated by Lye & Stuckey (1998). Optimum stability can be obtained by using relatively polar solvents with non-ionic surfactants having a high hydrophilic/lipophilic balance (HLB) number. Scarpello & Stuckey (1999) studied the stability of CLAs generated from an Aliquat 336/n-octanol/Softanol 120 solvent phase and proposed a semi-empirical design equation for the prediction of CLA half-life. The half-life of CLAs increased with decreasing size, which was proposed to be due to a lower energy of collision of CLAs with decreasing size. Results demonstrated that the stability of CLA both with and without Aliquat 336 reached a maximum value at an ionic strength of 0.06 M NaCl.

3.2.1.2 Size distribution

The size and structure of the CLAs are influenced by surfactant type and concentration, the physical properties of the components and additives and also by the CLA generation conditions such as oil addition rate, mixing time and speed, phase volume ratio and vessel geometry (Lye & Stuckey, 1998). Light scattering is one of the more effective methods to determine the size of dispersed CLAs (Lye *et al.*, 1996; Lye & Stuckey, 1998; Lye & Stuckey, 2000; Matsushita *et al.*, 1992; Scarpello & Stuckey, 1999; Yan *et al.*, 2011; Yan *et al.*, 2005b; Zhang *et al.*, 1996).

Zhang *et al.* (1996) investigated the effects of surfactant type and concentration, and storage times on the size distribution of CLAs. The size distribution based on volume fraction was found to display a bimodal trend. Sizes of CLAs were in the ranges 1 µm to 3 µm and 10 µm to 30 µm in diameter. CLAs produced using the non-ionic Brij 35 in water had the largest average diameter compared with those generated from the anionic SDBS. Furthermore, by increasing the surfactant concentration of the water-soluble surfactant smaller CLAs obtained, which had a broader range of size distribution. It was found that the average size distribution of CLAs in water became smaller over time. Scarpello & Stuckey (1999) also studied the size distribution of colloidal liquid aphrons with and without Aliquat 336 which resulted in bimodal size distributions. CLAs generated from Aliquat 336 displayed a relatively tight size distribution, with a mean diameter of 8 µm while CLAs generated in the absence of Aliquat 336 showed slightly wider distributions, with a mean diameter of 20 µm.

3.2.1.3 Phase volume ratio

The phase volume ratio (PVR) is an important property of CLAs that distinguishes them from micro emulsions and is defined as the volume ratio of the dispersed oil (organic) phase to the continuous aqueous phase. According to Sebba (1987) at low PVR values the aphrons are spherical and the system flows like a Newtonian liquid. At a PVR greater than 3 or 4, the CLAs become crowded and distort into polyhedral shapes. In such cases, the CLAs display flow characteristics corresponding to a Bingham-plastic system, and at a PVR above 20 they exhibit gel-like properties.

Matsushita *et al.* (1992) studied the effect of several solvents and a variety of surfactants on CLAs phase volume ratio and stability. They produced very stable CLAs with a variety of non-polar solvents with a maximum PVR of 20 without coalescence or phase inversion. It was found that as

the solvent became more polar, both the stability and the maximum obtainable PVR decreased until stable liquid aphrons could not be formed. In a study carried out by Yan *et al.* (2005b), the effect of PVR on the size of CLAs was investigated. The findings showed a mean diameter of 15.5, 10.7 and 4.6 µm for a PVR of 2, 4 and 8, respectively. These results indicated that diameter size of CLAs decreases with increasing PVR.

Figure 3.4 shows light micrographs of CLA dispersions at a PVR of 4 and 8. As demonstrated in the figure, the CLAs in the dispersed phase show a core–shell structure, that is, the oil core consisting of light organics (dark color) covered by the water continuous phase (light color). As seen in the figure the droplet size of PVR 8 is smaller than that of the PVR 4 which shows the reduction of CLA sizes as a result of increasing PVR (Yan *et al.*, 2011).
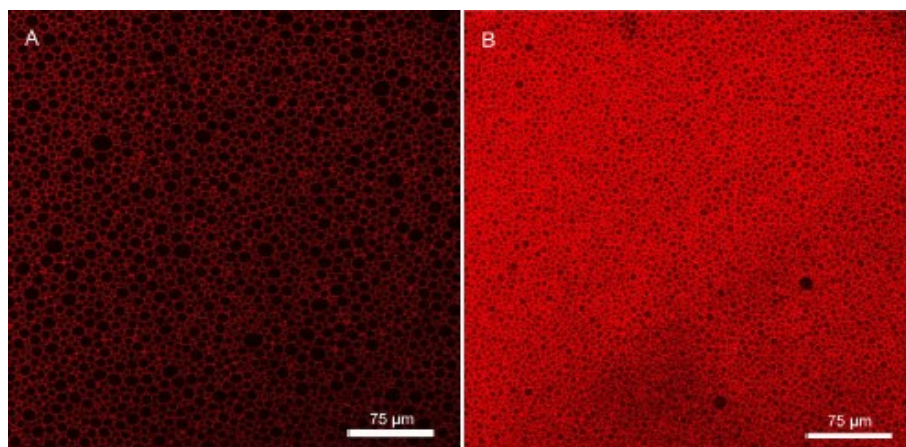
Figure 3.4. Optical micrographs of CLAs. (A) PVR 4; (B) PVR 8 (Yan *et al.*, 2011)

3.3 EVIDENCE FOR SEBBA'S STRUCTURE

Sebba's proposed structure was based on experiments carried out on the coalescence and stability of CGAs. He claimed that the significant delay in coalescence and higher stability of CGAs compared with conventional foams are due to their multilayered structure. Since 1982, most researchers accepted this hypothesis without any direct evidence, and characterized CGAs generated from a number of surfactants in terms of stability, size and gas holdup. However, there have been a few studies investigating the structural feature of CGAs that support Sebba's theory. The first study was carried out by Amiri & Woodburn (1990). They tried to characterize the

structure of CGAs by estimating the surfactant shell thickness and calculating the aphron rise velocity. Their experimental observations showed that the thickness of CGAs is equivalent to 350 molecules of surfactant arranged in consecutive layers, which supports the original theory of a multilayered aphron structure.

Later, Jauregi *et al.* (2000) studied the dispersion and structural features of CGAs by predicting aphron size and drainage rate, and conducting experiments using electron microscopy and X-ray diffraction. According to both experimental and modelling data, they concluded that CGA dispersions had different structural and dispersion features from either conventional foams or non-coalescing gas-liquid dispersions. They explained these differences as being evidence for the existence of multilayers of surfactant, further supporting Sebba's hypothesis. They also used electron microscopy and X-ray diffraction in order to determine the thickness of the surfactant shell and the number of surfactant layers existing in the CGA structure. The electron microscopy observations showed the existence of an interface which was composed of more than one layer (Figure 3.5), and it was determined from small angle x-ray diffraction results that regardless of the surfactant concentration, aphrons showed similar scattering which was equivalent to seven layers of surfactant.
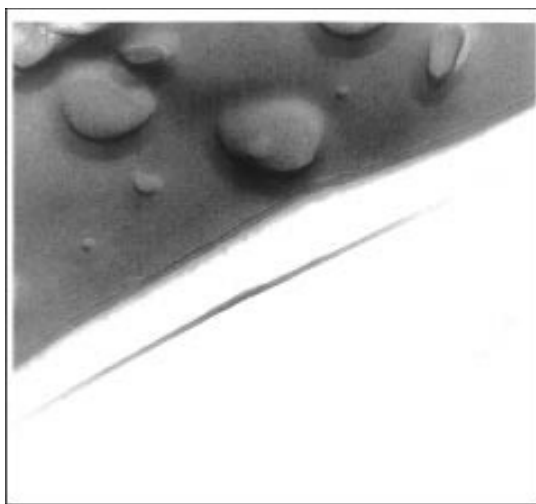
Figure 3.5. Electron micrograph of CGA (34 mM AOT in an acetate buffer, 0.1 M and pH 4) (Jauregi *et al.*, 2000)

All the evidence above indicates remarkable differences between CGAs and conventional foams. However, there is as yet no direct evidence on Sebba's proposed structure. The rest of this chapter covers the synthesis, properties, and applications of aphrons, as they have become known in the

literature. The term "aphrons" will be used as there is evidence that they exhibit properties which distinguish them from conventional foams, even if there are still questions as to what these mean for the structure.

3.4   APPLICATIONS OF APHRONS

3.4.1   Applications of colloidal gas aphrons

In general, the potential applications of CGAs can be classified into six categories: (1) protein recovery and biological separation (Alves *et al.*, 2006; Amiri & Valsaraj, 2004; Basu & Malpani, 2001; Dermiki *et al.*, 2008, 2009; Fuda *et al.*, 2005; Fuda & Jauregi, 2006; Fuda *et al.*, 2004; Jarudilokkul *et al.*, 2004; Jauregi *et al.*, 1997; Jauregi & Varley, 1996; Jauregi & Varley, 1998; Noble *et al.*, 1998; Noble & Varley, 1999; Singh *et al.*, 2007; Spigno *et al.*, 2010; Spigno & Jauregi, 2005; Weber & Agblevor, 2005); (2) mineral processing/ particle separation (Cabezón *et al.*, 1994; Cilliers & Bradshaw, 1996; Diaz *et al.*, 1990; Mansur *et al.*, 2006; Wang *et al.*, 2001; Waters *et al.*, 2008); (3) water purification and effluent treatment (Basu & Malpani, 2001; Ciriello *et al.*, 1982; Grimes, 2002; Hashim & Gupta, 1998; Hashim *et al.*, 1995; Roy *et al.*, 1992b; Rubio *et al.*, 2002; Subramaniam *et al.*, 1990; Watcharasing *et al.*, 2008); (4) soil remediation (Boonamnuayvitaya *et al.*, 2009; Couto *et al.*, 2009; Kommalapati *et al.*, 1998; Roy *et al.*, 1995a; Roy *et al.*, 1995b; Roy *et al.*, 1992a; Roy *et al.*, 1994); (5) material synthesis (Abdullah *et al.*, 2006; Davey *et al.*, 1998; Riviello *et al.*, 1994); and (6) drilling fluids and firefighting (Belkin *et al.*, 2005; Fink, 2012a; Gaurina-Međimurec & Pašić, 2009; Growcock *et al.*, 2007; Ivan *et al.*, 2001; Ivan *et al.*, 2002a; Nareh'ei *et al.*, 2012). In most of these applications, CGAs are pumped through columns, pipes, and fittings (Larmignat *et al.*, 2008).

3.4.1.1   Protein recovery and biological separation

Jauregi *et al.* (1997) were the first to investigate CGAs applied to protein recovery. The CGAs used in their studies were created from an anionic surfactant (AOT) and were characterized in terms of stability and gas hold-up for a range of process parameters relevant to protein recovery. A statistical experimental design was developed in order to study the effect of different factors including surfactant and salt concentration, pH, stirring time and temperature on the stability and gas hold-up of CGAs. By analyzing the results, it was found that the stability of aphrons depends

primarily on salt and surfactant concentration, and that gas hold-up was dependent mainly upon salt and surfactant concentration as well as stirring time. Furthermore, several interactions such as time-temperature interaction were demonstrated to be significant. Power consumption was another parameter studied in this work in order to determine the optimum conditions for the production of CGAs. The protein recovery process is illustrated in Figure 3.6.
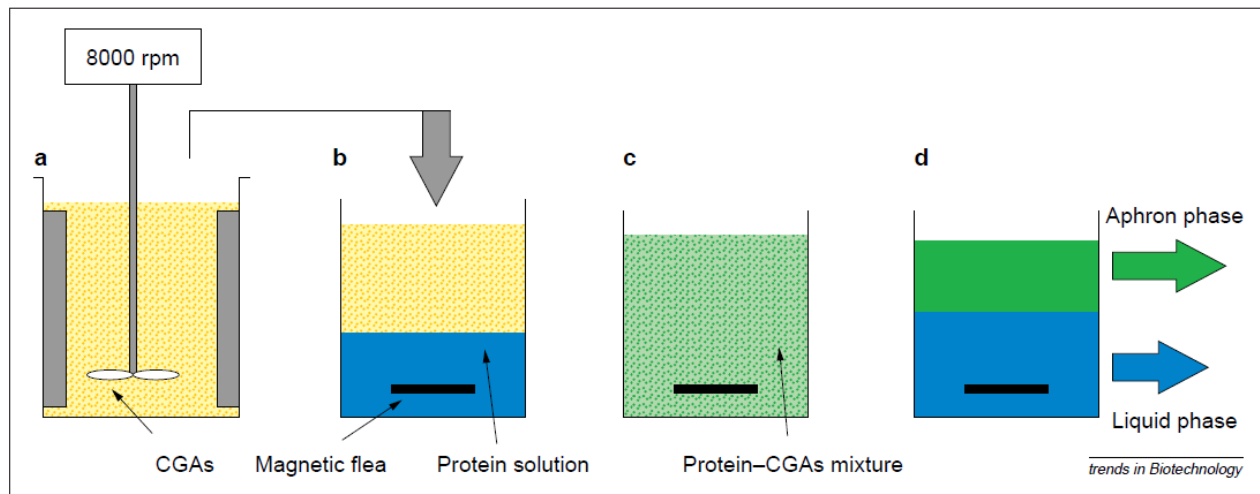
Figure 3.6. The recovery of proteins using CGAs (a) Generation of CGAs; (b) adding CGAs to a protein solution; (c) mixing CGAs and protein solution using a magnetic stirrer; (d) separating the aphron and liquid phases (Jauregi & Varley, 1999)

Jauregi and Varley (1998) applied colloidal gas aphrons to the recovery of proteins from aqueous solutions. Lysozyme was recovered from an aqueous solution using CGAs generated from AOT. They investigated the influence of a wide range of parameters including initial concentration of protein and surfactant, surfactant/protein molar ratio, pH, and ionic strength on the process efficiency to optimize the final recovery. At optimum conditions, lysozyme recovery, enrichment ratio, and separation ratio were 95 %, 19 and 302, respectively. These results indicated the potential of the CGA technique.

Another study on the application of the gas aphrons for the separation of proteins from aqueous solution was carried out by Noble & Varley (1999). In this study, the effect of various process conditions on the recovery of three proteins (conalbumin, ribonuclease A and α-chymotrypsinogen A) by means of AOT were investigated. High enrichment ratios (up to 8) and high recovery of the

protein (85 %) were obtained under optimum conditions. Furthermore, the main parameters influencing the partitioning of protein into the aphron phase was determined to be the pH of the system, the initial concentration of surfactant and the volume of aphrons added to the protein solution. According to their study, separation of the three proteins illustrated the same trends as the AOT-lysozyme system studied by Jauregi and Varley (1998).

Two separation techniques (foam separation and CGAs), were used by Noble *et al.* (1998) to recover proteins. The potential advantages of each method were described and a comparison between the concentration and selectivity achieved with each method for a range of proteins was undertaken. In this study, different kinds of surfactants (anionic, cationic and non-ionic) were employed to generate CGAs for the recovery of a range of proteins. Under appropriate conditions, high recoveries could be achieved in both CGA and foam separation. However, in cases where the relative surface activities between proteins are similar, protein recovery using CGAs may prove to be a good alternative to foam separation. For CGAs generated from anionic surfactants, high enrichment and recovery of protein was obtained at optimum conditions. The optimum conditions were defined as initial surfactant to protein molecular ratio of 30-110 and 12-30 molecules of surfactant per protein molecule for the AOT/α-chymotrypsinogen and AOT/lysozyme systems, respectively. For a CGA system using non-ionic and cationic surfactants some enrichment and recovery of the proteins was observed, however this was less than that obtained in the case of anionic surfactant. The reason for this, the authors concluded, was that it may be due to the reduction in interactions of the proteins with cationic and non-ionic surfactants compared to anionic ones.

Jarudilokkul *et al.* (2004) investigated the separation of proteins by CGAs produced from different non-ionic surfactants. In this work, the selection of a suitable non-ionic surfactant was conducted by evaluating the stability and protein recovery values. Polyoxyethylene sorbitol anhydride monolaurate (Tween 20) was found to be an appropriate surfactant. The stability of the CGAs was determined at different surfactant concentrations, stirring speeds, times, and concentrations of NaCl as an additive. The optimal conditions for CGA preparation was found to be 10 mM Tween 20 in distilled water, with a stirring speed of 5500 rpm and stirring time of 5 min. Furthermore, factors affecting protein separation such as initial protein concentration, CGA volume ratio and pH were examined. It was demonstrated that the hydrophobicity of Tween affected CGA stability

and the electrostatic interaction between CGA and proteins played an important role in the separation.

The effect of gas transfer on separation of whey protein with aphron flotation was studied by Amiri and Valsaraj (2004). For this purpose, they investigated the effect of the spinning disc position on aphron generation and the mode of surfactant addition on aphron flotation of whey protein at two different temperatures (22 ˚C and 30 ˚C). Experimental observations indicated that gas transfer into the dispersion during aphron generation is a controlling step for aphron flotation. It was found that there is an optimum depth (approximately 30 % below the solution surface) for the position of the spinning disc as in this position highest separation efficiency and highest stability for CGA system were achieved. In addition, it was suggested that in order to improve aphron flotation recovery the continuous injection of surfactant is more efficient than batch addition.

Fuda *et al.* (2004) used CGAs prepared from AOT for the separation of lactoferrin and lactoperoxidase from sweet whey. In order to investigate the effect of different conditions on protein separation a number of process parameters including pH, ionic strength and the initial volume of whey were varied. At an optimum pH of 4 with an ionic strength of 0.1 mol L-1, the recovery of lactoferrin and lactoperoxidase was 90 % and also their concentration in the aphron phase was 25 times greater than in the liquid phase. It was shown that aphrons acted as ion exchangers and the selectivity of the process and the surface properties of microbubbles could be largely manipulated by changing the main operating parameters such as pH, type of surfactant and ionic strength.

Fuda *et al.* (2005) utilized CGAs prepared from a cationic surfactant (CTAB), to selectively separate β-Lactoglobulin from sweet whey. Similar to the pervious experiments (Fuda *et al.*, 2004), the main factors influencing the partitioning were pH, ionic strength, and mass ratio of surfactant to protein (MCTAB/MTP). Under optimum conditions (2 mM L^{-1} CTAB, MCTAB/MTP = 0.26–0.35, pH 8, and ionic strength = 0.018 M L^{-1}), 80-90 % β-lactoglobulin was removed from the liquid phase as a precipitate, while approximately 75 % lactoferrin and lactoperoxidase, 80 % bovine serum albumin, 95 % immunoglobulin, and 65 % α-lactalbumin were recovered in the liquid fraction. Based on the experimental results, the separation of β-lactoglobulin into the aphron phase is predominantly driven by electrostatic interactions between proteins and individual surfactant molecules.

Later, Fuda and Jauregi (2006) attempted to gain a better understanding of the mechanism of protein separation by CGAs generated from ionic surfactants (AOT, CTAB), performing a mechanistic study to determine the main parameters influencing selectivity. Experimental observations indicated that electrostatic interactions were the main drivers responsible for selectivity; however, these were not the only factor controlling the selectivity. In order to determine the protein–surfactant interactions and the effect of surfactant on protein conformation, zeta potential and fluorescence intensity measurements of proteins upon surfactant addition across a pH range from 3-8 were carried out. These measurements demonstrated that although electrostatic interactions mainly controlled the protein separation using ionic CGAs, the selectivity of the separation was finally determined by conformational features and that competitive adsorption effects should also be considered.

Spigno *et al.*, in two separate studies (Spigno *et al.*, 2010; Spigno & Jauregi, 2005), reported the recovery of gallic acid (GA) using CGAs. In the first study, CGAs from a cationic surfactant (CTAB) were used to recover antioxidants from wine-making waste extracts that occurred naturally in an anionic form. The effect of pH, solvent type (buffered aqueous solution or ethanol solution) and CTAB to GA molar ratio on recovery were investigated and the optimum recovery (63 %) was achieved from an aqueous solution of GA with a CTAB to GA molar ratio of 16. In the second study, attempts focused on determining the optimum operating conditions to maximize the recovery of gallic acid, while preserving its antioxidant properties. Zeta potential analyses were carried out to characterize the surface charge of GA, CTAB and their mixtures at three different pH ranges. Based on the experimental observations, the recovery of gallic acid was profoundly affected by pH, ionic strength, surfactant/GA molar ratio, mixing conditions and contact time. GA interacted intensely with CTAB at pH ranges greater than its pKa (3.14) where it is ionized and negatively charged. However, at pH higher than 7 GA becomes oxidized and loses its antioxidant power. They also performed some scale-up tests using a flotation column which resulted in higher recovery and reproducibility.

Alves *et al.* (2006) used CGAs as a method to selectively recover norbixin from a raw extraction solution of annatto pigments in KOH solution. In order to generate CGAs they used CTAB and under the optimum condition (CTAB to norbixin molar ratio of 3) they reached 94 % recovery while the pH of the norbixin–surfactant mixture did not have any influence on the recovery. They

also proposed a new mechanism of separation based on the separation results using the cationic surfactant and an anionic surfactant (AOT) and measurements of surfactant to norbixin ratio in the aphron phase. Electrostatic interactions between the surfactant and norbixin molecules resulted in the formation of a colored complex, and effective separation of norbixin.

Dermiki *et al.* (2008) investigated the potential to apply colloidal gas aphrons to the downstream processing in the recovery of astaxanthin from the cells of *Phaffia rhodozyma*. The experiments were carried out with standard solutions of astaxanthin (astaxanthin dispersed in aqueous solutions and astaxanthin dispersed in ethanolic/aqueous solutions) and CGAs produced from CTAB. They achieved up to 90 % recovery under optimum conditions: pH 11 and 0.2 M L^{-1} NaOH. They also investigated three different chemical methods for the separation of astaxanthin from the fermentation broth with regard to their influence on the subsequent separation of astaxanthin with CGAs. In the first method, CGAs were introduced directly to the broth; in the second approach, CGAs were applied to the clarified suspension of cells; and in the last one, an *in situ* approach, CGAs were generated within the clarified suspension of cells. Experimental results obtained from the first method indicated up to 78 % recovery under the same conditions found to be optimal for the standard solutions. In addition, a recovery of up to 97 % total carotenoids could be achieved from the clarified suspension after pretreatment with NaOH. Therefore, CGAs proved to be greatly effective in the recovery of bioactive components from a complex feedstock.

Dermiki *et al.* (2009) again applied CGAs to the recovery of astaxanthin to determine the mechanism. Colloidal gas aphrons were generated using cationic (CTAB), anionic (SDS) and non-ionic (TWEEN 60 and mixtures of TWEEN 60-SPAN 80) surfactants, with a stirring speed of 8000 rpm and 5 min stirring time. In order to determine the optimum condition, experiments were performed at different pH and volumetric ratios of astaxanthin to CGA, and with two different astaxanthin standard suspensions including astaxanthin dispersed in aqueous solutions and astaxanthin dispersed in ethanolic/aqueous solutions with different compositions of ethanol (20/80 (v/v) and 40/60 (v/v)). When astaxanthin was dispersed in aqueous solutions, the separation appeared to be driven largely by electrostatic interactions. As demonstrated by zeta potential measurements, although astaxanthin was a highly hydrophobic molecule, its hydroxyl groups can become ionised under strong alkaline conditions, resulting in an overall negative charge. Therefore, the recovery was higher by using cationic surfactant for the negatively charged

astaxanthin particles. When ethanol was present, the highest recovery was achieved with CGAs generated from the non-ionic surfactant, which indicates that the separation occurred mainly due to hydrophobic interactions since zeta potential measurements indicated that the presence of ethanol reduces the surface charge of astaxanthin particles, leading a reduction in the electrostatic interactions.

3.4.1.2   *Mineral processing and hydrometallurgy*

Caballero *et al.* (1989) were pioneers of using colloidal gas aphrons in mineral processing and particle separation. They applied CGAs in coflotation and solvent sublation processes, and compared the experimental results to those obtained by conventional flotation. In the solvent sublation of methyl orange with HTAB in 2-octanol, a yield greater than 95 % was reached between 6 and 7 min; while with the conventional technique approximately 20 min was required to obtain a slightly lower yield. In the coflotation of Cu with $Fe(OH)_3$ and HTAB, up to 95 % of the separation recovery was achieved in less than one minute whereas this recovery can be obtained by conventional methods in approximately 25 minutes.

Diaz *et al.* (1990) utilized CGAs in the separation, pre-concentration and multi-elemental determination of Cu, Co, Cd and Ni by co-flotation of $Fe(OH)_3$ in natural waters and synthetic media. The CGAs were generated from sodium lauryl sulfate (SLS) and the experiments were performed in columns (Figure 3.7). The separation process was optimized by means of both Univariate and Simplex Methods (COFLOT computer program). The results obtained after 5 min of flotation, indicated greater than 90 % recovery for all the elements at initial concentrations of less than 10 ppb.
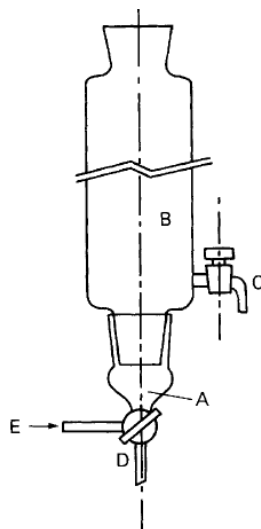
Figure 3.7. Experimental device used for the flotation process. (A) Detachable section; (B) variable size column; (C) stopcock; (D) three-way stopcock; and (E) CGA inlet (Diaz *et al.*, 1990)

The separation and pre-concentration of heavy metals using CGA in connection with co-flotation processes was carried out by Cabezon *et al.* (1994). In this study, the mixture of anionic surfactants consisting of SDS and potassium oleate was utilized to produce CGAs, and $Fe(OH)_3$ was used as a collector. The separation process was optimized using the Simplex Method (COFLOT computer program) and the effects of different process parameters including pH, pump position, co-precipitant and induction time on the separation process were investigated. Experimental observations reported over 90 % recovery for the elements (Cu, Co, Cd, and Ni) in 5 minutes flotation for all the samples, which were different in salinity, concentration and volume.

Wang *et al.* (2001) used CGAs in the flotation of Cu (II) in order to explore a new method for separation of heavy metal ions from dilute solution. SDBS was used to generate CGAs, and flotation tests were performed in a glass column (0.1 m height, 0.05 m diameter). After flotation, the CGA phase was collected from the top of the column, and Cu (II) concentration in the column was determined by atomic adsorption spectrometry. The effects of CGA flow rate, surfactant concentration and the amount of CGA introduced to the system on the flotation efficiency were investigated. The results indicated that pH had a profound effect on the flotation by CGAs as the flotation efficiency at pH= 5-6 was 20-30 %. In contrast, the flotation efficiency at pH > 7, could be as high as 99 % under the optimum operating conditions which were: SDBS concentration= 0.4 g L^{-1}; CGA flow rate and amount= 0.02 L min^{-1} and 0.35 L respectively.

Comparative experiments of conventional batch flotation and CGA flotation using a spinning disc impeller were carried out by Cilliers & Bradshaw (1996). The samples used in the flotation were composed of fine (< 38 µm) pyrite and quartz particles. Sodium normal propyl xanthate (SNPX) and Dow 400 were used as collector and frother respectively. The flotation was performed using different impellers under the following conditions: pH 4 and 8; copper sulphate addition between 0 and 50 g ton^{-1}. The CGA flotation yielded higher grades (50 % sulphur) than the conventional floatation (35 %) although the flotation rate was somewhat lower. The results obtained indicated that CGA flotation system may be applied for the selective recovery of finely ground minerals, which was then investigated by Waters *et al*. (2008).

Charged CGAs were used by Waters *et al*. (2008) in laboratory scale flotation tests (Figure 3.8) to separate fine particles of copper oxide from silica, with the result compared to conventional batch flotation. The CGAs used in these experiments were prepared from the anionic surfactant SDS and a novel, two-stage flotation technique was employed in which the CGA-generated froth did not overflow the column lip, but was allowed to drain before being collected. The two-stage CGA flotation system resulted in a CuO grade of 81.8 % and a recovery of 76.5 %, compared with the conventional batch flotation that yielded a concentrate grade of 59.1 % CuO at a recovery of 58.3 %. The zeta potential analysis of the CuO and SiO$_2$ particles was conducted in order to investigate the effect of electrostatic interactions on the separation. According to zeta potential results, the attraction force between the anionic CGAs and the CuO particles is initially due to electrostatic interactions in contrast to conventional flotation system in which the interaction between the bubbles and surfactant-adsorbed particles is hydrophobic in nature.
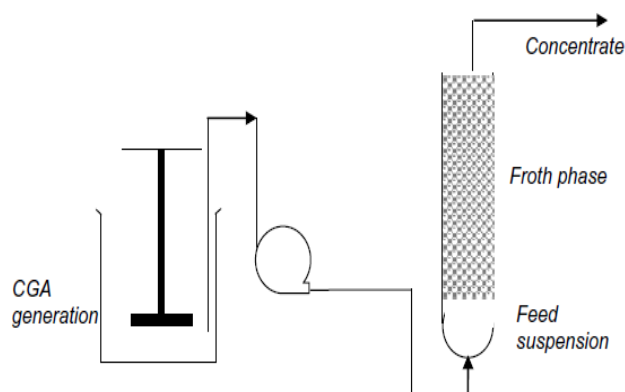
Figure 3.8. Schematic view of the CGA flotation column system (Waters *et al*., 2008)

Johnson *et al.* (2009) studied the interactions between silica glass colloidal probes and CGAs using atomic force microscopy (AFM). CGAs were generated using an anionic surfactant (SDS) and a cationic surfactant (DTAB) in an aqueous environment. For the CGAs produced using SDS, a significant repulsive force between the glass probe and CGAs was observed prior to contact. In contrast, only attractive forces between glass probe and CGAs from DTAB were observed prior to contact. Zeta potential analysis was carried out in order to understand the mechanism of fine particles removal from suspension using charged CGAs. According to zeta potential measurements in the absence of surfactant, silica surfaces are negatively charged in the pH range of 3-10. The addition of SDS did not have any significant effect on the zeta potential, which indicated that adsorption onto the particle surface, did not occur. However, when DTAB was added, the zeta potential became more positive, indicating that adsorption occurred. It was concluded that silica particles could be removed using positively charged CGAs from DTAB but not when using negatively charged CGAs created from SDS. The results suggested that electrostatic interactions were responsible for the selective attachment of silica particles to CGAs. Part A of Figure 3.9 shows a silica glass microsphere attached to the apex of a cantilever and in part B an image of typical CGAS created using a 1 g L^{-1} solution of SDS, photographed using a conventional light microscope is illustrated.
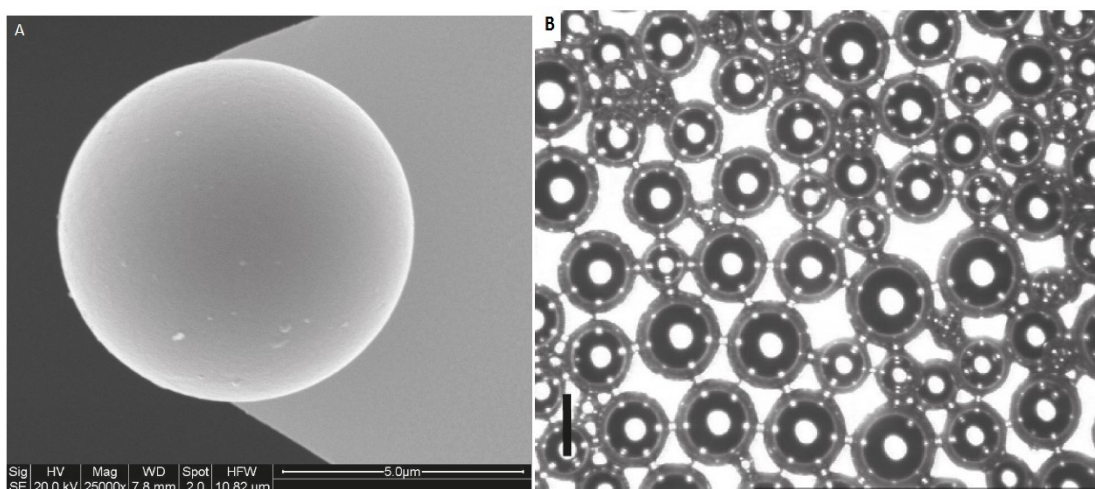
Figure 3.9. (A) SEM image of a glass microsphere attached to the apex of an AFM cantilever. (B) Light microscope image of CGAs produced using a 1 g L^{-1} SDS solution (Johnson *et al.*, 2009)

3.3.1.1 *Water purification and effluent treatment*

Subramaniam *et al.* (1990) were one of the first groups to investigate utilizing colloidal gas aphrons for clarifying industrial effluents. They applied CGAs generated from dilute solutions of anionic surfactants (Aerosol OT[TM], SDBS and LUX[TM] flakes) and a cationic surfactant (BDHA), to clarify palm oil mill effluent (POME), suspensions of microalgae and suspensions of three inorganic minerals (sand, alumina and calcium carbonate). In this study, the effect of various operating variables such as pH, temperature, air to solid ratio and solid concentration on the clarification efficiency were investigated. It was found that CGAs produced from ionic surfactants were most effective at pH values close to the respective pK values, but the pH of the CGA solution had no noticeable effect on aphron stability. The clarification rate increased with the efficiency of air utilization which was in turn, directly related to solids concentration. The density, size and nature of the solids had secondary effects.

Hashim *et al.* (1995) exploited CGAs in a flotation column to recover yeast from aqueous solutions. In order to produce CGAs, a cationic surfactant solution (2 g L^{-1}) of BHDC was stirred at a speed of 6000 rpm. Effects of pH, CGAs flow rate, superficial hydraulic loading rate (feed flow rate/cross sectional area of the column) and feed concentration were investigated. From the experimental observations it was concluded that CGA flow rate was a critical parameter in controlling the efficiency of the process, and high separation efficiency could be achieved at high CGA flow rates and relatively low residence time of the feed in the system. In addition, relatively low superficial hydraulic loading rate and low initial feed concentration were found to be effective in enhancing process performance. Finally, it was found that high separation efficiencies could be achieved in low feed phase pH.

Other research involving the clarification of baker's yeast suspension by CGAs prepared from BHDC was conducted by Hashim *et al.* (1998). Several operating parameters including CGA flow rate, air flow rate and the yeast concentration were investigated and at the optimum conditions (initial yeast concentration of 6 g L^{-1} and the corresponding air flow rate of 0.8 cm^3 s^{-1}), up to 95 % separation efficiency was achieved. They also determined the mechanism of particle-bubble attachment which was monolayer adsorption of yeast cells on the CGAs.

Hashim and Gupta (1998) used CGAs generated from SDS in a flotation column to separate fine fibres from a lean slurry of cellulosic pulp from paper mill effluent. The separation efficiency was measured as a function of column height, as slurry samples were collected at different points along the 0.35 m high column. Based on the results, the efficiency of the process initially increased along with height and 70 % efficiency was reached within the first 0.3 m. After this, there was no further increase. It was concluded that this technique can be applied to the recovery of fine cellulosic pulp from paper mill waste-water.

Basu and Malpani (2001) employed colloidal gas aphrons in a flotation column to remove methyl orange and methylene blue dye from water. The influence of operating variables including: surfactant type and concentration; CGA diameter and gas holdup; CGA flow rate; residence time; pH; and salt concentration were investigated through the measurements of percent dye removal. For this purpose, two different types of surfactant (HTAB and SDBS) at three different concentrations (350, 500, 700 ppm) under various stirring speeds were examined. For the range of experimental parameters studied, a maximum of 95-98 % of both methyl orange and methylene blue was removed. Process recovery was directly affected by the charge of surfactant as, when the surfactant had the similar charge to the dye, 40 % of dye was removed from the water. However, the oppositely charged dye and surfactant resulted in 98 % removal of dye. Based on the experimental observations, the removal of methyl orange was higher in alkaline conditions when HTAB was applied for the generation of CGAs. The percent removal of methylene blue was higher at acidic conditions when CGAs were generated from SDBS. The removal of methyl orange and methylene blue improved with increasing CGA flow rate and gas holdup and decreasing CGA diameter. Also, the percent removal of dyes increased with increasing CGA residence time in the flotation column.

In the study performed by Mansur *et al.* (2006), the flotation of fine particles of magnesium hydroxide (2.3-9 μm) and polystyrene (24-300 μm) in aqueous suspensions using CGAs was conducted. Three different type of surfactant (SDBS, HTAB and Tween 20) were used to generate CGAs, and the effect of surfactant type and concentration, and particle size on removal efficiency was investigated. Experimental results indicated that CGAs made from ionic surfactants (HTAB, SDBS) were more efficient at removing fine particles than those generated from the non-ionic surfactant (Tween 20). The optimum surfactant concentration was determined to be equal to the

critical micelle concentration for which high removal efficiency (more than 50 % of magnesium hydroxide and 97 % of polystyrene) was obtained. In addition, removal efficiency of magnesium hydroxide particles improved with increasing particle size, and the removal efficiency of polystyrene reached a maximum for the range of 24-140 μm.

3.4.1.3   Soil remediation

Comparative experiments of soil washing using CGA suspensions and conventional surfactant solutions were carried out by Roy *et al.* (1992a). In order to investigate the performance of CGA and conventional surfactant flushing systems, soil contaminated with 2,4-dichlorophenoxy acetic acid (2,4-D) was used. No significant difference was found in the performance of the two soil washing processes for 2,4-D which is highly water soluble. However, it was observed that the conventional method had higher surfactant consumption per gram of 2,4-D recovered from the soil compared to the CGA system. Furthermore, at low flow rates lower pressure drops across the soil column were observed in the pumping of CGAs, which is a considerable benefit of CGAs over surfactant solutions.

Roy *et al.* in three other separate works (Roy *et al.*, 1994, 1995a, & 1995b), utilized CGAs for soil flushing. In the first study (Roy *et al.*, 1994), the removal of hazardous oily waste from soil using an in-situ flushing technique was investigated and the performance of CGA suspensions with conventional surfactant solutions and water under different flow modes (*viz.* down-flow, up-flow and horizontal flow) on the removal efficiency was compared. Based on the experimental results, CGA suspensions generated from SDS had a greater recovery of oily waste (56 %) than conventional surfactant solutions (47 %) or water flood (43 %) in the down-flow (gravity-stable) mode. CGA suspensions also had a higher recovery than other methods in the removing the major chemicals in the waste (hexachlorobenzene, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, l,l,l-trichloroethane and tetrachloroethene). They also investigated the effect of surfactant concentration on the removal techniques. Increasing the surfactant concentration did not improve the removal efficiency of either CGA suspensions or conventional surfactant solutions. In the second study (Roy *et al.*, 1995b), the potential for CGA suspensions and conventional surfactant solutions to flush naphthalene from a contaminated soil matrix was studied. Experiments were performed to determine the relative suitability of anionic (SDS), cationic (HTAB) and non-ionic (Tergitol) surfactants in removing naphthalene from the soil. From the batch experiments, it was

found that the non-ionic surfactant was most effective at removing naphthalene from soil. In both surfactant solutions and CGA suspensions, increasing the surfactant concentration enhanced the removal rate of naphthalene from the soil. Experimental observations indicated that CGA suspensions were less efficient in naphthalene flushing compared to surfactant solution, which could be due to channeling and pore clogging in the soil matrix. In the last study (Roy *et al.*, 1995a), CGAs were used for soil flushing of residual transmission fluid. CGA suspensions generated from SDS were applied to flush residual levels of a light non-aqueous phase liquid (LNAPL) from a Superfund site (USA) soil. The efficiency of CGA suspensions was compared to a conventional anionic surfactant solution in both down-flow (gravity stable) and up-flow (gravity unstable) modes. For automatic transmission fluid (ATF) removal, CGA suspensions were found to be more effective than other techniques at any concentration under both down-flow and up-flow conditions. The mechanism of the removal of ATF by CGAs was proposed to be displacement, solubilisation and dispersion of ATF and electric repulsion at the surface of the soil particles. However, displacement seemed to be the only mechanism that was responsible for removal of ATF by a water flood. Increasing the SDS concentration from the CMC level to 30 mM did not increase the removal rate for either CGA suspensions or conventional surfactant solutions.

Kommalapati *et al.* (1998) investigated soil flushing using CGAs generated from natural surfactant solutions and compared the performance to conventional surfactant solutions. Natural surfactants produced from the fruit pericarps of *Sapindus mukorossi* (known as Ritha or soapnut) were used to generate CGAs in order to remove hydrophobic organic compounds (HOCs) from soil. Soil flushing experiments were conducted in glass columns 10 cm in height and 5.75 cm in diameter with stainless steel top and bottom plates, and the flushing solvents were pumped in to the top of the column at a flow rate of 2.5 mL min^{-1}. It was found that the recovery of chlorinated hydrocarbon, hexachlorobenzene (HCB) using CGA suspensions was higher than that for a water flood. However, natural surfactants were more effective in the form of conventional solutions than CGA suspensions at similar concentration in recovering HCB. Furthermore, the recovery of HCB remarkably increased by increasing natural surfactant concentration which was due to increase in the solubility of HCB.

Remediation of sandy soils contaminated with diesel oil using a surfactant solution, regular foams and colloidal gas aphrons was studied by Couto *et al.* (2009). SDS was used in all tests, and soils

prepared with different particle sizes (0.04–0.12 cm) and synthetically contaminated with different diesel oil contents (40-80 g kg^{-1}) were treated in the experiments. The effect of process parameters including surfactant solution flow rate, average soil particle size, initial oil concentration and surfactant concentration in injection fluid on the remediation efficiency was investigated through an experimental design. They proposed a mathematical model to determine the oil removal rate-constant and oil content remaining in the soil after remediation and also to estimate the percentage of oil removed. Under optimum conditions an oil removal efficiency of 96 % for aphrons, 88 % for regular foams and 35 % for surfactant solutions was achieved. Using regular foams and aphrons, high removal efficiencies were achieved using relatively small amounts of surfactant and also, removal efficiency increased by increasing initial oil concentration and rotation speed in regular foams and aphrons respectively. The experimental set-up used in the soil remediation tests is shown in Figure 3.10.
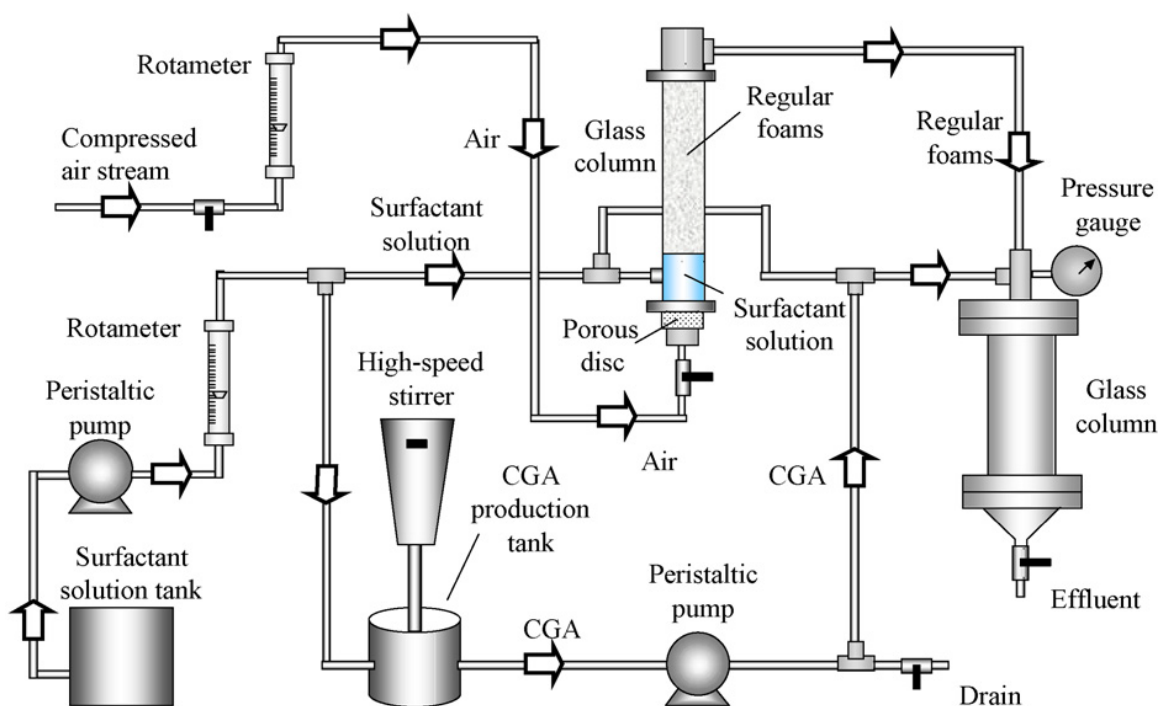
Figure 3.10. Experimental set-up used in the soil remediation experiments (Couto *et al.*, 2009)

Boonamnuayvitaya *et al.* (2009) used CGAs prepared from two commercial biodegradable and non-toxic surfactants (BioSolve and BioNonex) to remove pyrene from soil. They utilized pumice as a model of a natural soil that is free of organic material. In order to determine pyrene loading at different concentrations in soil, pumice and natural soil were pretreated by soaking in pyrene

solution. The stability of CGAs generated from different concentrations of BioNonex was studied and it was found that this increased for higher concentrations of surfactant. Preliminary experiments indicated that at the same concentration, the removal efficiency of BioNonex solution was higher than BioSolve solution. The removal of pyrene using BioNonex CGAs was performed in a packed column of pumice operated in continuous up-flow mode. It was found that the BioNonex CGA suspension was better in removal of pyrene (78 % removal) than BioNonex solution (68 % removal) and water (11 % removal). The maximum rate of removal achieved by 7 % BioNonex CGA was 120 mg h^{-1}. However, this amount decreased to 40 mg h^{-1} within 2 h.

3.4.1.4 *Drilling fluids*

The application of colloidal gas aphrons as drilling fluids was first described by Brookey (1998). The novel technique was used to drill horizontal and high angle wells through the damage-prone reservoirs in West and North Texas (USA), respectively. The CGA solutions were stabilized in a drilling fluid by using a high yield stress, shear thinning (HYSST) polymer which increases the strength of the bubble film and helps them to resist both compression and expansion. The experimental results exhibited good drilling conditions and no instances of invasion or damage formation were seen.

Since then, CGA-based drilling fluids have been successfully used in the petroleum industry to drill through high-angle and horizontal well construction of highly depleted reservoirs or low pressure zones using conventional equipment (Brookey, 1998; Gentzis *et al.*, 2009; Gokavarapu *et al.*, 2012; Gregoire *et al.*, 2005; Growcock *et al.*, 2007; Growcock *et al.*, 2003; Growcock *et al.*, 2004a; Ivan *et al.*, 2001; Ivan *et al.*, 2002b; Kinchen *et al.*, 2001; MacPhail *et al.*, 2008; Ramirez *et al.*, 2002; Rea *et al.*, 2003; Schaneman *et al.*, 2003; White *et al.*, 2003). Rea *et al.* (2003) stated that "No other fluids technology in the industry enables these types of operations. Since, standard wellsite fluid mixing equipment is all that is required to employ the technology and it is highly compatible with normal wellsite operations". The use of CGA based drilling fluids minimize formation damage by blocking pores of the rock with microbubbles, and reduce the filtration loss (Bjorndalen *et al.*, 2014). The high stability and delay in coalescence of CGAs help them to remain as discrete aphrons while entering into a depleted or lower pressure region. However, they can agglomerate to form a stable internal seal called a "micro-environment" (Rea *et al.*, 2003) as shown in Figure 3.11.
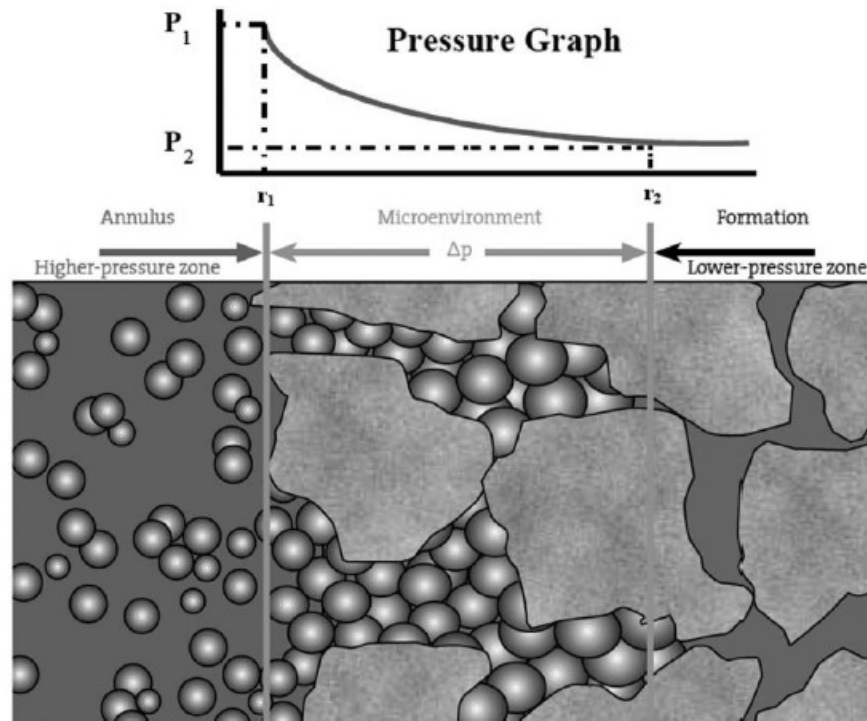
Figure 3.11. Microenvironment and sealing effect of gas aphrons (Nareh'ei *et al.*, 2012)

The mechanism of aphron-based drilling fluids, as described in the literature, is: "when aphrons penetrate the depleted zone, the difference between internal and external pressure causes them to expand, favoring the aggregation of bubbles which results in a micro-environment of bubbles that seal off the depleted formation. This phenomenon generates enough energy to prevent the invasion of fluids, or filtrate, into the depleted zone. Moreover, there is no formation of filter cake which reduces the possibility of drilling equipment becoming stuck in the well and also mitigates corrosion problems" (Brookey & House, 2002; Cardoso, 2010).

These CGA-based drilling fluids also bring several advantages to the well drilling industry, such as: high carrying capacity; low loss in circulation; reducing drilling time; reducing the amount of fluid placed in the formation; improving well productivity (oil recovery); and improving cement jobs after drilling (Brookey, 1998; Growcock *et al.*, 2006; Ivan *et al.*, 2002b; Ramirez *et al.*, 2002; Rea *et al.*, 2003). Furthermore, because there is no oil in the structure of CGAs and they have a water based formulation, this technique can be considered an environmental friendly technology (Ramirez *et al.*, 2002).

Ivan *et al.* in two different studies (Ivan *et al.*, 2001& 2002b), used aphron-based drilling fluids for drilling depleted reservoirs in different areas with the purpose of controlling downhole mud loss and formation damage. In the first study (Ivan *et al.*, 2001), the formulation, operational procedure, and field applications of aphron-based drilling fluids were investigated. Based on the observations obtained from application of aphron system in drilling of highly fractured sand in California, more than a 50 % and 10 % reduction in the mud loss and drilling time respectively, were achieved. In addition, the well could be drilled to the targeted total depth (TD) which was impossible earlier due to the circulation problems. In the second study, aphron-based drilling fluids were also used for drilling different ranges of fields and applications such as drilling low-pressure/low-fracture gradient sections, drilling fractured and high permeable sections, reservoir drill-in applications, and drilling normal and low-pressure sections (high density applications) (Ivan *et al.*, 2002b). According to the observations obtained from case studies, many drilling problems were solved and the drilling fluid losses were minimized or prevented in some cases. By using CGA-based drilling fluids, they achieved many benefits such as reducing drilling time from 33 days to 13 days, savings of one to two casing strings per well, eliminating under balanced drilling equipment, thus increasing the cost efficiency of the operation and improving well recovery.

In the other study also carried out by Ivan *et al.* (2002a), the chemical and physical characteristics of aphron-based drilling fluids were investigated. These characteristics included: stability, mechanism, formulation, rheology, and fluid loss.

Kinchen *et al.* (2001) tried to provide a case study to use aphron-based drilling fluids in a dolomite formation reservoir in New Mexico. The main purpose of this study was to minimize damage to the upper reservoirs. They tried to compare different drilling fluids in 16 wells. Conventional water-based fluids, drilling blind or dry, air/mist and aphron-based fluid were four different methods used in drilling wells. Air drilling gave the lowest fluid loss, followed by aphron-based drilling. However, from the production and operation point of view, the aphron-based drilling technique was more consistent with a high production, without any problems in drilling and casing. Also by using aphron based-drilling fluids, minimum corrosion and no safety issues due to H_2S were found.

Ramirez *et al.* (2002) performed a study on the field application of CGA-based drilling fluids in drilling very low pressure zone. They obtained very good results including: no circulation problem; reduction in drilling time; subsequent reduction in costs; improved well cleaning; eliminating the use of casing string; and improving the quality of well cementation.

The application of aphron-based drilling fluids in drilling of three depleted wells in Poza Rica field in Eastern Mexico was investigated by Rea *et al.* (2003). The main objective of this study was to avoid invasion and provide a safe and stable situation to continue drilling wells. They believed that aphron-based drilling could provide a safe working environment due to the micro-environment sealing creating a solid-free bridging of depleted sands while minimizing the invasion. The results showed that aphron-based drilling fluid resulted in a significantly lower environmental risk compared to both other fluids and operational techniques previously employed. Furthermore, from an economic point of view, it was proved that this technology was more efficient than the centrifuged diesel employed previously, with the average cost reduction of 44 % per workover.

White *et al.* (2003) developed aphron-based drilling technology to drill depleted high permeable sand reservoirs in the North Sea which tended to lose circulation. The primary objective of this study was to balance drilling conditions to minimize invasion and control losses. As aphron-based systems do not need any more equipment than conventional ones, they used the conventional fluid mixing equipment to form micro bubbles. The experimental observations successfully met the objectives of the study and no drilling fluid loss or fractures were observed during and after drilling.

Growcock and coworkers tried to develop aphron-based fluid technology and investigated the latest advances in this field (Growcock *et al.,* 2003, 2004a, 2004b, 2006 & 2007). The first study (Growcock *et al.*, 2003), described the application of water-based and oil-based aphrons in the drilling of permeable zones such as water-wet sands, laminated sand, and shale sequences. Successful mud loss control, better filtration and sealing improvement resulted from their study. In the other studies, they mostly discussed the design, properties, and characteristics of aphron-based drilling fluids and provided a technical basis for the successful drilling operation using colloidal gas aphrons (Growcock *et al.,* 2004a, 2004b, 2006 & 2007).

The applications of aphron fluid technology in three different completion and workover situations were studied by MacPhail *et al.* (2008). They exploited aphron-based fluids: (1) as a kill fluid to

prevent losses after conducting several well servicing operations in a dual string sour gas well; (2) to complete drilling of depleted dolomite limestone gas reservoir; (3) to provide a pressure support for preventing fluid leak-off under high pressure differentials. The results obtained from both drilling and re-entry of different formations proved the ability of aphron-based drilling fluids in improving well operations and reducing risk in complex situations (*e.g.* under dead well and static fluid conditions), and also in preventing fluid loss and increasing circulation efficiency.

In 2009, Gentzis *et al.* (2009) attempted to utilize aphron-based drilling fluids in coalbed methane drilling, and to evaluate the effect on the coal permeability and the efficiency in terms of filtration. Laboratory tests conducted using large diameter cores indicated poor performance compared to previous works, and failure of the aphron-based system. The authors believed that could be due to the test conditions. The low test pressure and mud formulation were the two issues that they claimed to be inappropriate test conditions, which were the causes of failure in compressing CGAs sufficiently and reduction on the viscosifier, respectively.

There are many other studies on preparation, characterization, and optimization of CGA-based drilling fluids which can give a good understanding of structure and important properties of aphron-based system (Arabloo & Pordel Shahri, 2014; Arabloo *et al.*, 2012a; Arabloo *et al.*, 2012b; Belkin *et al.*, 2005; Bjorndalen *et al.*, 2014; Bjorndalen & Kuru, 2008; Ivan *et al.*, 2002a; Nareh'ei *et al.*, 2012; Shivhare & Kuru, 2010; Xiangfei *et al.*, 2013). Composition and physical properties of CGAs such as density, viscosity, size distribution, gel strength, yield point and half-life were described in some of these studies (Belkin *et al.*, 2005; Ivan *et al.*, 2002a; Xiangfei *et al.*, 2013). Furthermore, CGA-based fluids made from different surfactants including SDBS (Bjorndalen *et al.*, 2014; Bjorndalen & Kuru, 2008), SDS (Nareh'ei *et al.*, 2012) and a plant-based surfactant, Saponin, (Arabloo *et al.*, 2012a) and xanthan gum as a polymer were characterized while produced in different methods including spinning disk (Arabloo *et al.*, 2012a; Nareh'ei *et al.*, 2012) and homogenizer (Bjorndalen *et al.*, 2014; Bjorndalen & Kuru, 2008).

3.4.1.5 *Summary of best practices*

Protein recovery and biological separation: According to several studies on protein recovery, CGAs generated from anionic surfactants had the best results in enrichment and recovery of proteins. However, CGAs from cationic and nonionic surfactants also showed good results in some

cases. Therefore, according to Fuda & Jauregi (2006), although electrostatic interactions mainly controlled the protein separation using ionic CGA, the selectivity of the separation was finally determined by conformational features. Furthermore, the stability of colloidal gas aphrons was affected by salt and surfactant concentration and pH. Surfactant concentration and volume of aphrons are the controlling factors in proteins partitioning.

Mineral processing and hydrometallurgy: The experimental observations showed the potential of CGAs in mineral processing and hydrometallurgy. The CGA-based systems exhibited higher recovery and lower process time compared to conventional systems for separation of fine particles and metal ions from aqueous solutions. Since the electrostatic interactions are the main driving forces in separation of fine particles using CGA flotation system, the best results obtained when CGAs generated from a surfactant oppositely charged from the desired particles. The best protocol for using CGAs in these separations requires a detailed understanding of the surface of the particles and their interaction with the surfactants. Future studies should investigate further the incorporation of collectors into the system, in order to facilitate a more selective recovery of fine (mineral) particles as in conventional flotation

Water purification and effluent treatment: Most of the studies in water purification by CGAs were in agreement that the CGA flow rate was the main factor in controlling separation efficiency, and high separation efficiency could be achieved at high CGA flow rates. Other effective parameters in the separation ability of CGAs were initial feed concentration and size of particles, pH, residence time, column size, and surfactant charge and concentration. CGAs generated using a surfactant with a charge opposite to that of the target particles showed the best results.

Soil remediation: In most of the studies in which CGA dispersion was used as a soil flushing medium to remove waste and chemicals, CGA dispersions were performed better than conventional surfactant solutions both in terms of recovery and surfactant consumption. However in some cases, due to other mechanisms, CGA dispersions were not as effective as surfactant solution. In general, choosing adequate type and concentration of surfactant with regard to soil matrix and contaminant structure was one of the key factors in successful soil flushing process. Although in some cases conventional surfactant solutions exhibited better results than CGAs, the best reagent/soil matrix in separation using CGA solutions were found to be as follows: SDS for

oily waste; Tergitol for naphthalene; SDS for LNAPL and ATF; SDS for sandy soil containing diesel oil; and biononex for pyrene.

Drilling fluids: Referring to the majority of research carried out on CGA-based drilling fluids, it can be concluded that they have been successfully applied in drilling technology and were able to reduce mud loss, drilling time, formation damage and invasion. Also, significant reductions in operational cost, corrosion, and safety issues were reported in some of the articles. In addition, almost all authors suggested aphron-based drilling systems for drilling of depleted and low pressure reservoirs. In these studies, anionic, cationic, and non-ionic surfactants and polymers were used as aphron generator and stabilizer (viscosifier) respectively.

3.4.2 Applications of colloidal liquid aphrons

Colloidal liquid aphrons have several applications including: predispersed solvent extraction (PDSE) (Hahm *et al.*, 2003; Hong *et al.*, 2001; Kim *et al.*, 2004b; Lee *et al.*, 2000; Luo *et al.*, 2013; Lye & Stuckey, 2000; Matsushita *et al.*, 1992; Michelsen *et al.*, 1986; Save *et al.*, 1994; Sebba, 1985b; Zhang *et al.*, 1996); immobilization of enzymes (Lamb & Stuckey, 1999; Lamb & Stuckey, 2000a; Lye *et al.*, 1996); soil and water remediation (Vidrine *et al.*, 2000; Yan *et al.*, 2011), and mass transfer (Srivastava *et al.*, 2000).

3.4.2.1 *Predispersed solvent extraction*

The first study on the potential application of CLAs in predispersed solvent extraction process was conducted by Michelsen *et al.* (1986). The aim of this research was to investigate the feasibility of applying a predispersed solvent extraction/flotation process to remove dissolved hazardous organics from the wastewater. For this purpose, the colloidal liquid aphrons were formulated and characterized in order to evaluate their performance in the extraction/flotation process. CLAs were generated from different type of surfactants and characterized in terms of stability, flotation recovery, solvent recovery, and size (Table 3.6). Furthermore, based on the initial experimental results, the predispersed solvent extraction method was 5 to 10 times more effective than conventional method in removing organics from waste-water.

Table 3.6. CLAs formulation, characteristics and performance in flotation (adapted from Michelsen *et al.*, 1986)

Water phase surfactant	Oil phase surfactant	CLA stability	Flotation clarity	Solvent recovery (mL)	CLA size (µm)
SDBS	DPC	good	fair	0.55	12-20
SDBS	Armeen C	good	fair	0.5	~10
Arquad 12-50	Tergitol 15-S-3	Slightly unstable	good	0.45	~20
Dodecyl pyridinium Chloride (DPC)	Oleic acid	slightly unstable	good	0.6	~20

Matsushita *et al.* (1992) were pioneers in using CGAs and CLAs for predispersed solvent extraction of dilute products. They investigated the effect of several solvents, varying from non-polar to slightly polar, and a variety of ionic and non-ionic surfactants, on CLA stability, size, and phase volume ratio (PVR). Furthermore, the influence of surfactant type, stirring time and speed on the generation of CGAs was also examined. Based on the experimental results, very stable CLAs were produced using non-polar solvents with a PVR as high as 20 (Table 3.7). However, as the solvent became more polar both the stability and the PVR decreased until stable CLAs could not be formed. The effect of the hydrophilic/lipophilic balance (HLB) number on CLA generation with slightly polar solvents was also investigated. It was found that CLAs could be made using quite polar solvents (*e.g.* pentanol) with their stability enhanced by increasing the HLB number of the non-ionic surfactant.

Table 3.7. Preparation of CLA from different solvents (adapted from Matsushita *et al.*, 1992)

Solvent	Solubility in water (wt %)	CLA Stability	CLA size (Sauter mean diameter, μm)	PVR
n-Decane	52 ppb	Very stable	14.0	20
n-Octane	$6.6 * 10^{-7}$	Very stable	10.8	20
Iso-Octane	-	Very stable	9.6	20
n-Hexane	0.00123	Very stable	9.6	20
Decalin	<0.02	Very stable	13.1	20
Kerosene	-	Very stable	11.1	20
p-Xylene	0.0156	Stable	29.8	20
Toluene	0.0515	Stable	30.8	20
Benzene	0.1791	Stable	7.2	20
Decan-l-ol	Insoluble	Stable	25.1	10
Octan-l-ol	0.0538	Stable	27.9	5
n-Pentanol	2.19	Unstable	-	-

Hahm *et al.* (2003) studied the predispersed solvent extraction of copper from water using CLAs. They applied colloidal liquid aphrons made of trioctylmetylammonium chloride (Aliquat 336) diluted with kerosene to remove copper ion using a complexing agent such as EDTA (Ethylenediaminetetraacteic acid) by the predispersed solvent extraction method. The effect of the type of water-soluble surfactants, phase volume ratio (PVR), and concentration of anionic SDBS on PDSE was investigated. Furthermore, the effect of SDBS on back extraction in PDSE was also studied. Under experimental conditions, the amount of copper transferred to the Aliquat 336 core was approximately similar in both PDSE using anionic SDBS and conventional solvent extraction. To optimize CLAs-based process, stability of CLAs containing a quaternary ammonium salt Aliquat 336 diluted with kerosene in the continuous phase was investigated by measuring the volume released to the surface. To destabilize CLAs, H^+ and OH^- were added. Results demonstrated that the stability of CLAs decreased with increasing concentration of OH^- and H^+.

The removal of an organic dye (Solvent Yellow 1) from water using predispersed solvent extraction was studied by Lee *et al.* (2000) and the results from predispersed solvent extraction method were compared to conventional solvent extraction operated under batch conditions.

Colloidal liquid aphrons prepared from kerosene were used as the predispersed organic solvent, and in the generation of CLAs, Tergitol 15-S-3 and SDBS were used as oil-soluble and water-soluble surfactants, respectively. It was found that higher extraction efficiency with CLAs could be achieved with a shorter contact time than that of a single-staged conventional extraction process. Experimental results indicated that colloidal liquid aphrons with their extremely large specific surface area could decrease processing time and energy costs. The authors also determined the recovery of combining CLAs with CGA flotation using different surfactants including SDBS, HTAB, and Brij 35. The results demonstrated that the recovery of CLAs depends on the surface charges of both CLAs and CGAs and also on the surface areas provided by CGAs.

Hong *et al.* (2001) applied CLAs to the predispersed solvent extraction of lactic acid and compared the equilibrium distribution of lactic acid with CLAs, and with solvent alone. SDBS and HTAB were used as water-soluble surfactant to produce CLAs. Results indicated that, although the contact time of the PDSE process with CLAs was short, there was little difference in equilibrium distribution between PDSE process with CLAs and with solvent alone. The toxicity of extractants and diluents on *Lactobacillus rhamnosus* was also determined for in situ extraction and it was found that long chain alcohols such as 1-octanol and 1-decanol were less toxic diluents. CLAs therefore reduced the toxicity of solvents on *Lactobacillus rhamnosus*. It can be concluded from this work that predispersed solvent extraction by CLAs has the advantage of both a rapid mass transfer rate and the toxicity reduction of extraction solvents.

In three separate studies carried out by Kim *et al.* (2002; 2004a & 2004b), colloidal liquid aphrons were applied to extract succinic acid from aqueous solution using PDSE technique. In these studies, AOT, 1-octanol, SDBS and Tergitol 15-s-3 were used for generating of CLAs as extractant, solvent, water soluble surfactant and oil soluble surfactant respectively. Experimental observations indicated that although no mechanical mixer was used in PDSE, there was no significant difference in the extractability by PDSE compared to conventional mixer-settler solvent extraction. The effect of pH and salt addition on the extraction of succinic acid and the stability of CLAs were investigated. It was found that pH had significant influence on the loading value (concentration of succinic acid in organic phase/ initial concentration of amine in organic phase) of succinic acid in PDSE by CLAs, as by increasing pH of the aqueous phase the loading values also increased. In addition, the stability of CLAs increased with increasing pH values in aqueous

phase and a decrease of TOA concentration in the organic phase. According to results obtained from salt addition tests, the extractability and the stability of CLAs decreased in the presence of sodium chloride.

The predispersed solvent extraction of chromium (Ш) from aqueous waste solution using HEHPEHE as extractant and its mixture, including an acidic extractant (D2EHPA), alkaline extractant (TOA) and neutral extractant (TBP) were studied recently by Luo *et al.* (2013). During the PDSE experiments CLAs were generated using HEHPEHE, kerosene, SDBS and Tween 20 as an extractant, a solvent, a surfactant in aqueous phase and a surfactant in oil phase respectively. The effects of main operating parameters, such as initial chromium (Ш) concentration, volume of CGAs, HEHPEHE volume fraction, PVR, mass fraction of SDBS, HTAB and Tween-20 and initial pH of aqueous waste solution were studied in order to investigate the extraction efficiency of PDSE and to determine optimum process conditions. It was found that by using HEHPEHE in PDSE of chromium (III) from aqueous waste solution, high extraction selectivity can be achieved. Furthermore, under the optimum conditions more than 99.9 % of chromium (III) could be extracted using this method.

Extraction of a microbial secondary metabolite, erythromycin, using both CLAs (prepared from 1 % (w/v) softanol 120 in decanol and 0.5 % (w/v) SDS in water) and a surfactant containing two-phase (aqueous-organic surfactants) systems, was studied by Lye & Stuckey (2000). It was found that the equilibrium partitioning of erythromycin was significantly influenced by the extraction pH and indicated a remarkable difference between the pH values lower and higher than pKa of the molecule. In order to investigate the influence of surfactants used for CLA generation on erythromycin partitioning, experiments were performed in surfactant bearing, two-phase systems. Experimental results indicated that neither the non-ionic surfactant (softanol) nor anionic surfactant (SDS) had any effect on the erythromycin equilibrium partition coefficients at pH 10. For extraction at pH 7, however, the recovery of the organic phase was found to decrease with increasing SDS concentration with the softanol having no effect on the equilibrium conditions. The electrostatic interaction between individual erythromycin and SDS molecules under stripping conditions was found to be responsible for the SDS results.

3.4.2.2 Enzyme immobilization

Lye *et al.* (1996) utilized colloidal liquid aphrons to immobilize *Candida cylindracea lipase*. They determined that successful immobilization of lipase by liquid aphrons was primarily due to electrostatic interactions between the surface charges on the protein and those of SDS at low pH values (pH < isoelectric point). The second important interaction playing a role in immobilization was hydrophobicity. The activity of both CLA-immobilized and free lipase was also measured for the hydrolysis of pnitrophenyl caprylate and pnitrophenyl acetate at different substrate concentrations and various continuous phase pH values. Based on the results, they were not very sensitive to pH changes and a broader optimum pH range in both cases was found for CLA immobilized lipase and also CLA immobilized lipase did not display a normal Michaelis-Menten dependence on substrate concentration, due to mass transfer limitations.

Lamb & Stuckey (1999) reported the application of colloidal liquid aphrons in the immobilization of six different enzymes varying in molecular weight and isoelectric point. All enzymes were found to be immobilized to different extents, with as much as 70 % of β-galactosidase and 90 % of α-amylase effectively being immobilized over a wide range of pH values (4-10). The results indicated that in most cases, pH had an insignificant influence on the degree of immobilization. The mechanism of immobilization appeared to be related to molecular weight, hydrophobicity and adiabatic compressibility of the enzyme. In addition, the activity of the enzymes improved after immobilization; on the other hand, SDS used in the CLAs production was found to be the major parameter influencing loss of activity of the immobilized enzymes. However, SDS also appeared to increase activity by changing protein conformation. Lamb & Stuckey (2000a) again utilized CLAs in the immobilization of enzymes. Colloidal liquid aphrons were generated from anionic (SDS, AOT 80), cationic (DTAB) and non-ionic (Brij 78, SA 20, S120, Atlas G 1300) surfactants and β-galactosidase was the enzyme used in the experiments. It was found that bulk phase pH and ionic strength had no effect on enzyme retention, indicating β-galactosidase immobilization was primarily due to hydrophobic interactions. However, immobilization could be improved to almost 100 % by varying the charge of the surfactants used in the preparation of the CLAs and the polarity of the internal solvent core. This indicated that electrostatic interactions also affect enzyme immobilization. Experimental observations showed a shift in the optimum pH of the enzyme

during immobilization, while the immobilized enzyme indicated a broader range, and a maximal activity at higher pH.

3.4.2.3   Water remediation

The remediation of dense non-aqueous phase liquid (DNAPL) contaminated aquifers using colloidal liquid aphrons was studied by Yan *et al.* (2011). The influences of electrolyte (AlCl$_3$) concentrations and temperature on the demulsification of CLA dispersion and the volume fraction of the dispersed oil phase (n-octane) were investigated. A series of batch tests were conducted to determine the recovery efficiency of DNAPL from sand pack under different concentrations, flow rates of CLAs and surfactant (Tergitol 15-S-9) flushing solutions. Based on the experimental observations it was suggested that CLAs could effectively destabilized by contact with multivalent ions carrying charges opposite to those of the surfactant generating the CLAs and they could be completely destabilized within a short period of time by a low concentration (0.05 M) of Al^{3+} in the continuous phase. As high as 94 % of the DNAPL removal was achieved under the conditions of 1 pore volume (PV) for CLAs, 4 PV and 1.5 mL min^{-1} for Tergitol solution.

3.4.2.4   Summary of best practices

Predispersed solvent extraction: It can be concluded from several studies on PDSE that the type of surfactant and solvent plays an important role in PDSE process directly or by affecting stability and size of aphrons. In addition, higher extraction efficiency, shorter processing time, and lower toxicity compared to conventional techniques can be achieved by using PDSE technique. Furthermore, pH and salt concentration are the other controlling factors in PDSE process.

Enzyme immobilization: There are two general conclusions that can be derived from studies on enzyme immobilization. First, electrostatic and hydrophobic interactions are the two most important mechanisms responsible for immobilization process. Second, pH and ionic strength do not have a significant effect on the immobilization of enzymes and proteins.

3.5   SCALE UP AND INDUSTRIAL APPLICATIONS

Most of the studies on aphron-based processes have been carried out on small scale and batch systems, with optimum conditions being determined based on these conditions. However, there

are a few studies on the scale up of separation processes using column flotation or continuous flotation (Jauregi & Dermiki; Spigno *et al.*, 2010), enzyme immobilization (Lye *et al.*, 1996), and in field applications in drilling technology (Gokavarapu *et al.*, 2012; Gregoire *et al.*, 2005; Ivan *et al.*, 2002b; Kinchen *et al.*, 2001; MacPhail *et al.*, 2008; Ramirez *et al.*, 2002; Rea *et al.*, 2003; White *et al.*, 2003). Therefore, there is an essential need for more studies into the application of aphrons at industrial scale, and continuous processes.

A feasibility study of industrial application of aphrons of CGA system and two other conventional separation systems, solvent extraction and supercritical carbon dioxide extraction (SCDE), was carried out by Jauregi & Dermiki (Dermiki *et al.*, 2009; Jauregi & Dermiki, 2010). They evaluated both capital and operational cost and it was found that in terms of capital costs, the CGA system was more expensive which may be due to the high cost of the diafiltration system for the removal of surfactant. However, in terms of operational costs, solvent extraction was the most expensive due to the high price of raw materials and the CGA separation system had the lowest operational cost. Although surfactants are expensive, due to low concentration consumption in producing CGAs, the operational cost remains low. Furthermore, comparing utility costs including electricity costs, SCDE had the highest cost and the CGA system was the second most expensive. Finally, from the waste disposal point of view, CGA system had the lowest cost. Overall, the authors suggested that if the surfactant removal was not required, the CGA separation process could be more cost effective than others. Furthermore, this process is more environmental friendly than solvent extraction method and also uses less hazardous equipment than SCDE.

3.6 TECHNICAL LIMITATIONS AND FUTURE RESEARCH SCOPES

Surfactants are the basic part of aphron's structure; however, they are expensive and can be often toxic which limits the applications of aphrons. Aphron technology can be a good alternative for some conventional techniques such as solvent extraction due to the reduction in the surfactant consumption, but the problem with surfactants still exist (Jauregi & Dermiki, 2010). Researchers have suggested some solutions to overcome these problems:

- Removal (recycling) of surfactant after separation process by use of a membrane/ filtration

- Using less toxic non-ionic surfactants instead of ionic surfactant

- Using biosurfactants as an alternative for synthetic surfactant. Biosurfactants are biodegradable, nontoxic, and can be produced from inexpensive waste sources (Boonamnuayvitaya *et al.*, 2009; Jauregi & Dermiki, 2010; Singh *et al.*, 2007).

Nevertheless, these alternative solutions have also some limitations. For example, removal/recycling the surfactants increases operational costs which is not attractive from an economical point of view. Also, using non-ionic surfactants is not always possible especially in the processes that electrostatic interactions are the main driving force during the separation process. Therefore, the alternative methods need further investigations in order to develop the aphron technology and overcome the existing limitations.

3.7   CONCLUSIONS

Aphrons are interesting systems which possess many beneficial properties including: high stability; small size and high interfacial area; hydrophobic inner shell; charged outer surface; and ability to flow and be pumped through pipes. These properties make them of interest in several separation processes. Aphrons can be produced from anionic, cationic and non-ionic surfactant, the choice of which depends on their applications, and they can be stored for a period of time without any significant change in their properties.

Colloidal gas aphrons can be prepared in several ways and their characteristics depend on various parameters such as the generation method, surfactant type and concentration, additives such as salts, enzymes, polymers and solvents, stirring time and pH of continuous phase. CGAs have potential applications in biological separation, mineral processing, cleaning water and soil, among others. The main mechanisms involved in these processes are ionic interactions, bubble entrained floc flotation, phase separation between the gaseous and liquid phase of CGAs and introduction of the contaminant into one of these phases and closer contact between remediation fluid and contaminant as a result of the high interfacial area of the CGA suspension (Hashim *et al.*, 2012).

Colloidal liquid aphrons can be generated by drop-wise addition of organic phase into the aqueous phase. The main characteristics of CLAs are stability and phase volume ratio which are affected by surfactant type and concentration, pH, additives and solvent type and concentration. The main applications of CLAs are predispersed solvent extraction, enzyme immobilization and soil and water purification.

This chapter covered a wide range of processes that have investigated the use of aphrons, both gas and liquid. The knowledge from protein separation may be transferable to other field such as mineral processing, and *vice versa*, hence the wide scope of this chapter. Knowledge transfer across research and industrial fields is paramount to aphrons becoming accepted as viable systems.

One aspect of note is that there is still no definite proof for the structure of aphrons as first proposed. Rather, the structure is still inferred, and the theory has not been disproven. It is hoped that in the near future someone will settle this once and for all. Nevertheless, whatever the structure, it can be seen that the properties of the aphrons are useful in a number of fields, often outperforming conventional processes. They are very interesting systems and warrant significant research in the future.

This thesis will continue with investigations into potential application of colloidal liquid aphrons to extract metal ions from aqueous systems commonly formed as effluent in the mining industry. The aim is at reducing the environmental impact of the mining operations, and the potential to generate the aphrons once the metal extraction has been completed. The focus of this thesis is on a copper-nickel system that is common to Canadian operations, including the Sudbury area of Ontario.

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CHAPTER 4.   COPPER ION REMOVAL FROM DILUTE SOLUTIONS USING COLLOIDAL LIQUID APHRONS

4.1   ABSTRACT

In this chapter, the extraction of copper (II) from dilute aqueous solution by predispersed solvent extraction (PDSE) using colloidal liquid aphrons (CLAs) will be described. The CLAs were made of LIX 984N as an extractant and an anionic, cationic, and nonionic surfactant. It was observed that the CLAs were in the micrometer size range, and that their size was controlled by the phase volume ratio. The phase volume ratio and extractant concentration in CLAs structure were the most effective parameters in this extraction process. CLAs were able to remove copper ions in less than one minute, and they remained stable for more than two months. The effect of surfactant type and concentration was also investigated, with the anionic surfactant found to produce the best results.

4.2   INTRODUCTION

Industrial effluents discharged from the mining and metallurgical plants are considered to be a major environmental challenge. These effluents often contain dissolved heavy metal ions, usually at low concentrations and low pH. The release of heavy metal bearing effluents into the environment, whether intentional or otherwise, can lead to serious problems for the local environment because heavy metals, unlike organic contaminant, are not biodegradable and tend to be toxic or carcinogenic (Fu & Wang, 2011). Therefore, strict environmental regulations and increasing global demand for heavy metals have led researchers to study heavy metal removal techniques. A diverse range of physicochemical techniques have been proposed for removing heavy metals from wastewater including: solvent extraction (Alguacil & Navarro, 2002; Dukov & Guy, 1982; Fouad, 2009; Navarro & Alguacil, 1999; Sridhar *et al.*, 2009; Xie & Dreisinger, 2010; Yun *et al.*, 1993); chemical precipitation (Alvarez *et al.*, 2007; Chen *et al.*, 2009; Fu *et al.*, 2007; Ghosh *et al.*, 2011); electrochemical treatment (Casqueira *et al.*, 2006; Heidmann & Calmano, 2008; Khelifa *et al.*, 2005; Merzouk *et al.*, 2009; Ölmez, 2009; Shafaei *et al.*, 2010); ion exchange and adsorption (Argun, 2008; Berber-Mendoza *et al.*, 2006; Dąbrowski *et al.*, 2004; Inglezakis *et*

al., 2007; Rodríguez-Iznaga *et al.*, 2002; Ye et al., 2011); membrane filtration (Guha et al., 1994; Kumar & Sastre, 1999; Raghuraman *et al.*, 1994; Valenzuela *et al.*, 1997); and biosorption (Nazari *et al.*, 2014; Nazari *et al.*, 2015; Xu & Liu, 2008).

Amongst the various techniques, solvent extraction appears to be the most attractive, not only for its simplicity and versatility (Bullock & King, 1975; Doungdeethaveeratana & Sohn, 1998; Flett *et al.*, 1973; Ritcey & Ashbrook, 1984), but also for its ability to treat a wide range of concentrations and its selectivity (Sengupta *et al.*, 2009). It is also termed liquid-liquid extraction and is based on the transfer of a solute substance (metal ions) from one liquid phase (aqueous phase) into another liquid phase (organic phase), according to its solubility. However, solvent extraction is most effective for treating relatively high concentrations (> 500 mg/L) (Kentish & Stevens, 2001) and requires a large distribution ratio in the treatment of dilute streams, which causes an increase in the organic phase volume to an unacceptable value, both from environmental and economic considerations (Kislik, 2012).

Colloidal solvent extraction using colloidal liquid aphrons (CLAs), or predispersed solvent extraction (PDSE), is a modified solvent extraction technique which was first proposed by Sebba (1985). The technique was proposed in order to overcome major disadvantages of conventional solvent extraction methods such as: need for mixing-settling stage; high solvent/aqueous ratio; and need for high initial metal concentration.

In PDSE, organic phase including the extractant are predispersed into micrometer sized globules termed colloidal liquid aphrons, which are believed to consist of an oil core encapsulated by a thin soapy (aqueous) shell as defined by Sebba (1987). This soapy shell makes the CLAs hydrophilic which allows them to disperse easily in the feed phase. The unique structure of CLAs makes them highly stable systems and their small size provides large interfacial area available for mass transfer. They show a significant resistance to coagulation and can be stored for long periods of time without any noticeable coalescence, and can also be transported through pumping without destroying the structure (Lee *et al.*, 2002; Sebba, 1987). These properties make CLAs of interest for separation processes such as removal of metals (Hahm *et al.*, 2003; Luo *et al.*, 2013); extraction of antibiotics (Lye & Stuckey, 2000) and organic pollutants (Hong *et al.*, 2001; Kim *et al.*, 2004b); oil recovery (Sebba, 1985, 1987); and water remediation (Yan *et al.*, 2011).

This chapter details the PDSE of copper from dilute solutions and investigate the effect of various experimental parameters on the extraction behavior as well as basic characteristics of CLAs.

4.3   MATERIALS AND METHODS

4.3.1   Materials

Copper (II) solutions were prepared by dissolving anhydrous cupric sulfate ($CuSO_4$) (Fisher scientific, India) in reverse osmosis purified water. For the CLA dispersion formulation, the oil phase comprised of kerosene (Sigma-Aldrich, USA), LIX 984N (BASF, Germany), and the nonionic surfactant Tergitol 15-S-3 (Talas, USA) as the diluent, extractant and oil soluble surfactant, respectively. LIX 984N reagent is a 1:1 volume blend of LIX 860N (5-nonyl salicylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone oxime) with the specific gravity of 0.935 – 0.955 in 25 ˚C and the flash point greater than 76 ˚C.

The anionic sodium n-dodecyl sulfate (SDS) (99 %, Avocado, UK), cationic hexadecyl trimethylammonium bromide (CTAB) (98 %, Sigma, India) and non-ionic polyethylene glycol sorbitan monostearate (TWEEN 60) (Sigma, USA) were also used as water soluble surfactants in the formation of the aqueous phase. 1 M sulfuric acid (Fisher Scientific, Canada) and 1 M sodium hydroxide (Fisher Scientific, Canada) were used to modify pH and 4 % nitric acid (Sigma-Aldrich, USA) was used to dilute samples before copper concentration analysis. All aqueous phases were prepared from reverse osmosis purified water at ambient temperature.

4.3.2   Preparation of CLAs

The CLA dispersion was prepared by the slow drop-wise addition of the oil (organic) phase containing LIX 984N, kerosene, and oil soluble surfactant into a foaming aqueous solution containing a water soluble surfactant. The aqueous phase was placed in beaker and mixed at a rate of 800 rpm for 10 minutes to make initial foams, followed by the gradual addition of the organic phase at a flow rate of 2 mL/min to the mixing aqueous phase, until the desired phase volume ratio was reached (PVR = Vorg/Vaq). The resulting CLA dispersions were viscous and had a creamy white appearance, showing no phase separation over a period of days. The schematic view of the CLA generation process is shown in Figure 4.1.
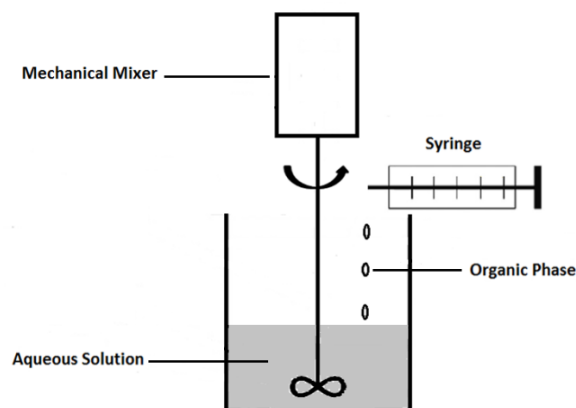
Figure 4.1. CLAs generation process

4.3.3   Size measurement and microscopic analysis

The size distribution of each CLA dispersion was determined using a particle size analyzer LA 920, (Horiba, Japan) using a refractive index of 1.44. Microscopic observations were obtained using light microscopy (Leitz Laborlux 12 Pol, Germany). CLA dispersions were generated at three different phase volume ratios, and then diluted with water (with the volumetric ratio of 1:9), in order to reduce the turbidity of dispersions and have a clear distribution. Other parameters including the initial extractant concentration, anionic surfactant concentration, stirring time and speed, pH, and temperature were kept constant.

4.3.4   Extraction process

Copper extraction experiments were conducted in 50 mL centrifuge tubes, 6.5 g (equal to 10 mL at a PVR of 4) of CLAs were added to 10 mL of Cu (II) solution. The mixture was mixed for 30 seconds followed by phase separation in a centrifuge (5 min, 4400 rpm). After centrifuging, the raffinate was removed and diluted with 4 % nitric acid in order to analyze the remaining copper concentration with inductively coupled plasma emission spectroscopy (ICP-OES, Thermo Scientific 6000 series). Ultimately, the copper extraction was calculated using Equation 4.1:

$$\text{Cu extraction \%} = \frac{(C_0 - C)}{C_0} \times 100 \qquad \qquad \text{Equation 4.1}$$

where C_0 is the initial concentration of copper (ppm) and C is the final concentration of copper (ppm) in the raffinate, as measured by ICP-OES. All the experiments were repeated a minimum of 4 times to ensure repeatability, and errors calculated at the 95 % confidence level.

4.3.5   Phase separation

Phase separation experiments were performed in a column with a diameter of 5.7 cm and a height of 35 cm (Figure 4.2). 150 mL of Cu solution was placed in column followed by gradual addition of 150 mL of CLAs to column with the rate of 7.5 mL/min. After addition of CLAs, phase separation process started and samples were taken over different time intervals. These experiments were carried out under two different conditions: introducing air using a glass frit for bubble generation at the bottom of column (Air flow rate: 40 cm^3/min); or without air, the same as the conventional solvent extraction process.
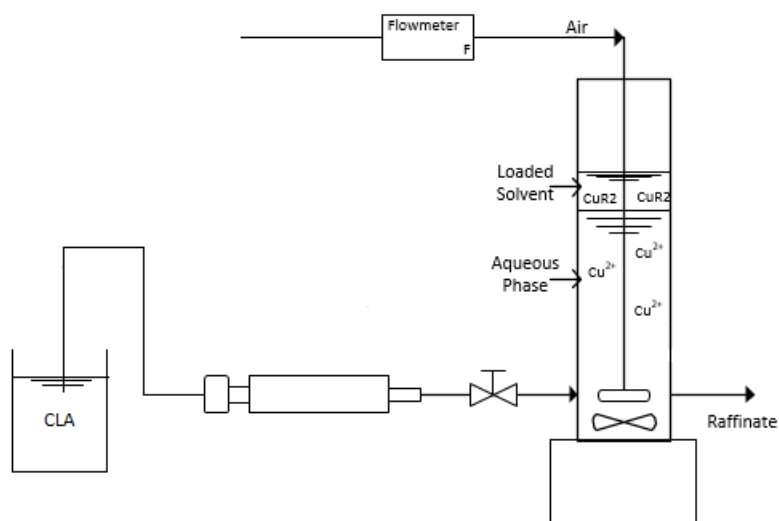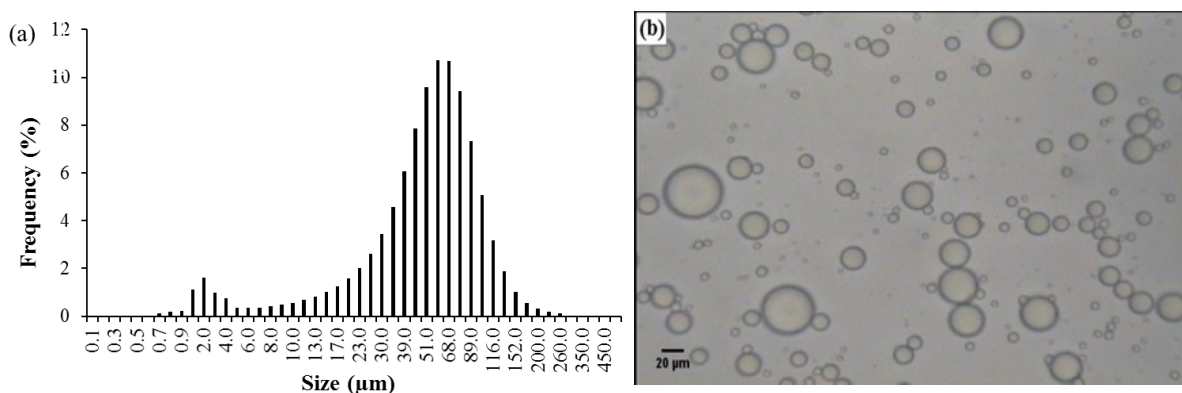

Figure 4.2. Phase separation process

4.4   RESULTS AND DISCUSSION

4.4.1   Size and structure of CLAs

CLA dispersions were prepared using 0.5 % (w/v) LIX, 0.24 % (w/v) SDS, and 0.1 % (v/v) Tergitol at three different phase volume ratios, 1, 4, and 10. Figure 4.3, Figure 4.4, and Figure 4.5 show the size distribution and optical micrographs of CLA dispersions at PVR 1, 4, and 10, respectively.

Figure 4.3. (a) Size distribution of CLAs; (b) optical micrograph of CLAs. PVR 1.
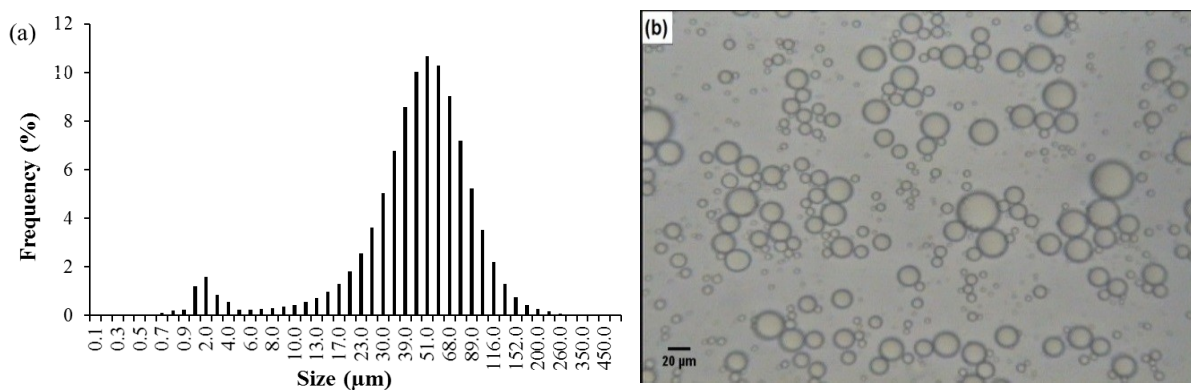
Figure 4.4. (a) Size distribution of CLAs; (b) optical micrograph of CLAs. PVR 4.
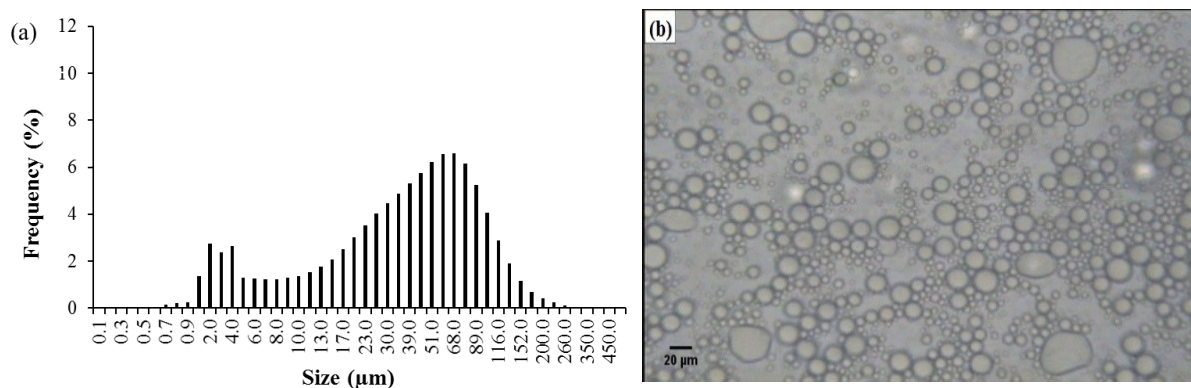
Figure 4.5. (a) Size distribution of CLAs; (b) optical micrograph of CLAs. PVR 10.

According to the size distribution graphs, two peaks were observed for each CLA dispersion while the minor peak indicates frequency (volume based) of small size aphrons (less than 10 µm) and the major peak represents the frequency of larger aphrons. Comparing the peaks at different PVRs, the minor peak for PVR 10 was significantly bigger and the major peak was smaller compared to PVR 1 and 4, which indicates the higher population of smaller size droplets in higher PVR value. This trend can also be observed in the optical micrographs.

The mean and median diameter of CLAs measured by particle size analyzer is presented in Table 4.1. Based on these values, the size of CLAs decreases with an increase in PVR which is in agreement with previous observations (Sebba, 1987; Yan *et al.*, 2011).

Table 4.1. Mean and median diameter of CLAs at different PVRs

PVR	1	4	10
Mean (µm)	54.69	50.54	45.09
Median (µm)	51.76	47.02	37.51

4.4.2 Copper extraction

4.4.2.1 *Effect of extractant concentration and PVR*

Extractant concentration and phase volume ratio are two key factors in generating CLAs. In order to investigate the extraction of copper ions using CLAs, first these two factors should be determined. Figure 4.6, Figure 4.7, and Figure 4.8 show the copper removal percentage by CLAs

generated at different phase volume ratios using different concentrations of LIX 984N as an extractant.
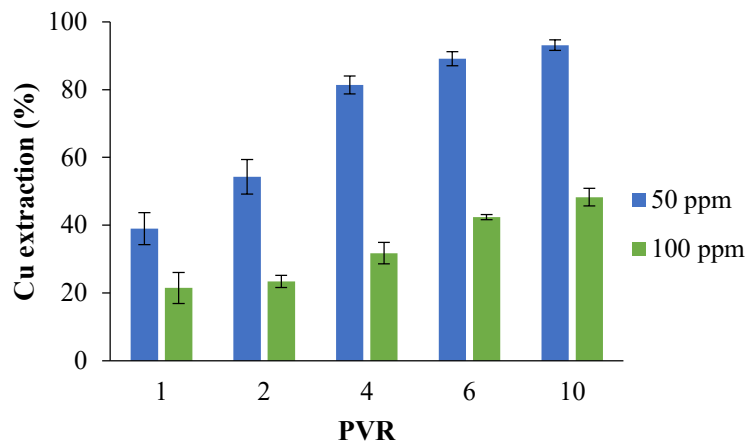
Figure 4.6. Copper extraction with: initial LIX 984N concentration= 0.1 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.
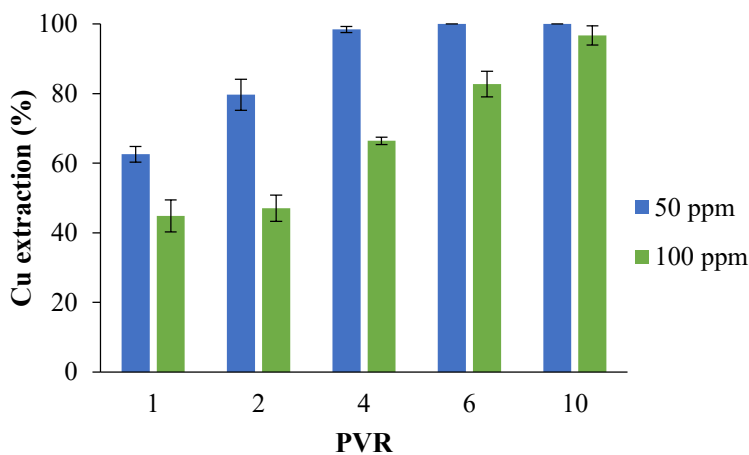
Figure 4.7. Copper extraction with: initial LIX 984N concentration= 0.2 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.
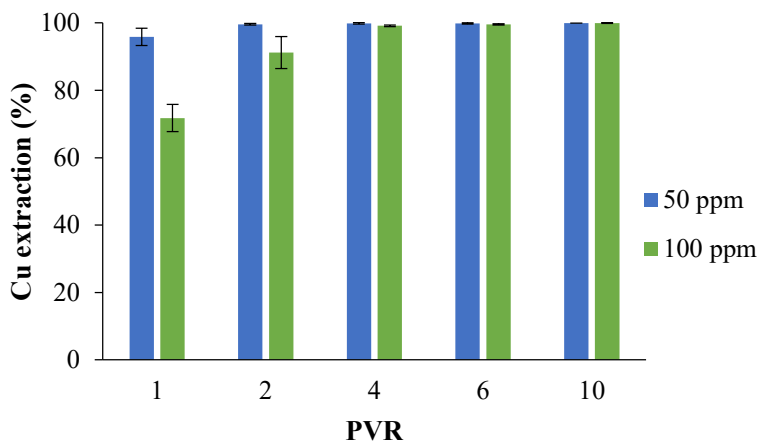
Figure 4.8. Copper extraction with: initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.

The experimental results indicated that both higher extractant concentration and higher PVR resulted in higher copper ion removal.

The difference between the copper removal percentage at different copper concentrations at low PVR or low LIX984N concentrations is due to extractant loading capacity, which is limited by the number of ions that can be exchanged with copper ions in solution. At 50 ppm, the maximum stoichiometric ratios were found to be 10.7, 6.5 and 4 for LIX concentrations of 0.1 % 0.2 % and 0.5 %, respectively. At 100 ppm, the maximum stoichiometric ratios were increased slightly to 11, 11.1 and 5.9 at 0.1 % 0.2 % and 0.5 % of LIX concentrations, respectively.

The main mechanism involved in extraction of copper ions using CLA is ion exchange between LIX 984N and copper bearing aqueous solution, as expressed by Equation 4.2:

$$Cu^{2+}_{(aq)} + 2\ HR_{(org)} \Longleftrightarrow CuR_{2\ (org)} + 2\ H^+ \hspace{2cm} \text{Equation 4.2}$$

where R represents the active component of the extractant.

Therefore, CLAs are able to remove almost 100 % of the copper from aqueous solutions as long as the extractant used in CLA formation has sufficient loading capacity. The initial LIX 984N concentration of 0.5 % (w/v), and PVR 4 were selected for the next series of experiments.

4.4.2.2 *Effect of surfactant type and concentration*

SDS, Tween 60, and CTAB were used as anionic, non-ionic, and cationic surfactants, respectively, to investigate the effect of water soluble surfactant with regard to its electrostatic charge. All of the surfactants were examined at four different concentrations which were chosen according to their critical micelle concentration (CMC). The CMC values for SDS, TWEEN 60, and CTAB are 0.24 % (w/v) (Cifuentes *et al.*, 1997; Seret *et al.*, 1987; Turro & Yekta, 1978), 0.0027 % (w/v) (Ćirin *et al.*, 2012; Hait & Moulik, 2001), and 0.036 % (w/v) (Cifuentes *et al.*, 1997; Tedeschi *et al.*, 2003) respectively. Figure 4.9, Figure 4.10, and Figure 4.11 present the copper extraction percentage for different concentrations of SDS, TWEEN 60, and CTAB, respectively.
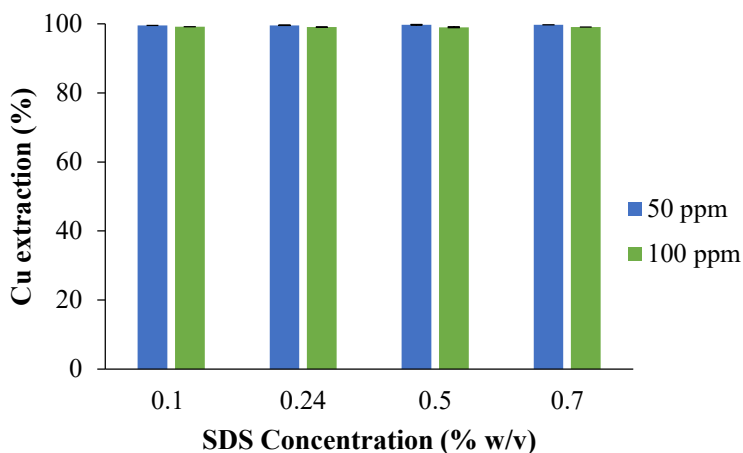
Figure 4.9. The effect of SDS concentration on the copper extraction: initial LIX 984N concentration= 0.5 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.
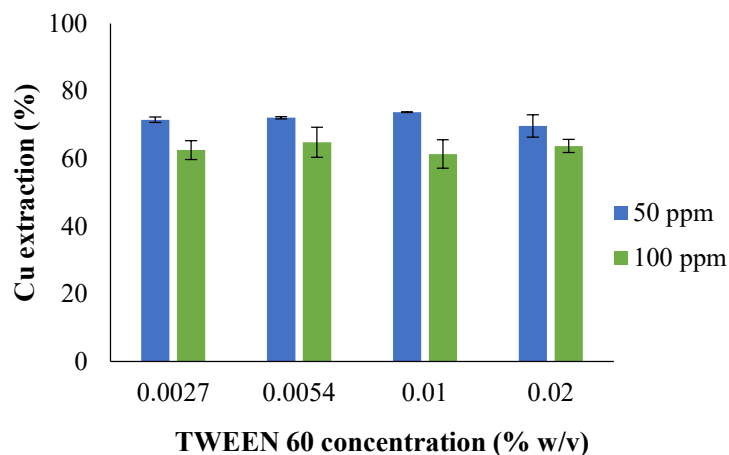
Figure 4.10. The effect of TWEEN 60 concentration on the copper extraction: initial LIX 984N concentration= 0.5 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.
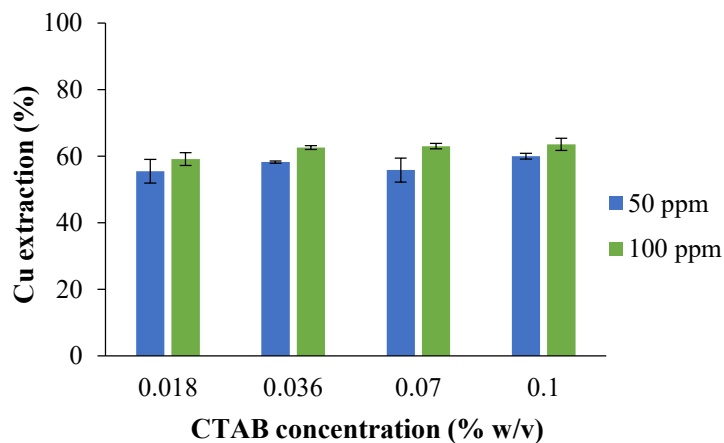
Figure 4.11. The effect of CTAB concentration on the copper extraction: initial LIX 984N concentration= 0.5 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.

No significant difference between copper ion extraction with respect to surfactant concentrations was found. However, changing the type of water soluble surfactant from anionic (SDS) to non-ionic (TWEEN 60), and then to cationic (CTAB) decreased the copper removal percentage significantly.

These results suggest that the extraction process is affected by electrostatic interactions between positively charged copper ions and the water soluble surfactant at the surface of CLAs. While negatively charged CLAs were able to extract almost 100 % of copper, the positively charged CLAs could only extract approximately 63 % of copper. Taking into account that both sets of

experiments were performed under the same conditions, and the only difference between them being the charge of surfactant, electrostatic interactions (attractive and repulsive forces respectively) were responsible for this notable difference. In the case of non-ionic surfactants, the results lay between the ones for anionic and cationic surfactants, due to the absence of electrostatic interaction (neither attractive nor repulsive).

4.4.2.3 Effect of pH

The influence of pH on the extraction of copper ions using CLAs was investigated in two different ways. First, the initial pH of copper was varied from 1.5 to 5.5 and after mixing with CLAs and extraction, the corresponding equilibrium pH was measured. In this pH range, copper mostly exists in the form of Cu^{2+} (see speciation diagram of copper in Appendix). However, increasing the pH to above 5.5 results in the hydrolysis of Cu^{2+} ions and, subsequently, the formation of $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)^-_3$, and $Cu(OH)_{2-4}$ (Doyle & Liu, 2003). The results are shown in Table 4.1.

Table 4.2. Copper extraction related to initial pH changes and corresponding equilibrium pH values

Initial pH	Equilibrium pH	Cu extraction (Average %)
1.5	1.43	30.86
2.0	1.94	76.80
2.5	2.32	98.63
3.0	2.5	99.20
3.5	2.62	99.42
4.0	2.63	99.64
4.5	2.66	99.50
5.0	2.67	99.47
5.5	2.68	99.47

By varying the initial pH in the range of 1.5-3, the equilibrium pH also changed accordingly. However, at an initial pH of 3 and greater, the extraction reached up to 99 %, and the equilibrium pH changed only slightly. These observations show the close relationship between the equilibrium pH and the extraction of copper using CLAs. Therefore, in the second approach, the pH of the final solution, including the equal volume of CLAs and copper solution with natural pH, was varied from 1.2 to 5.5 (without changing the initial copper solution pH). This was followed by phase

separation (centrifuging) and calculating the copper extraction. The results are shown in Figure 4.12.
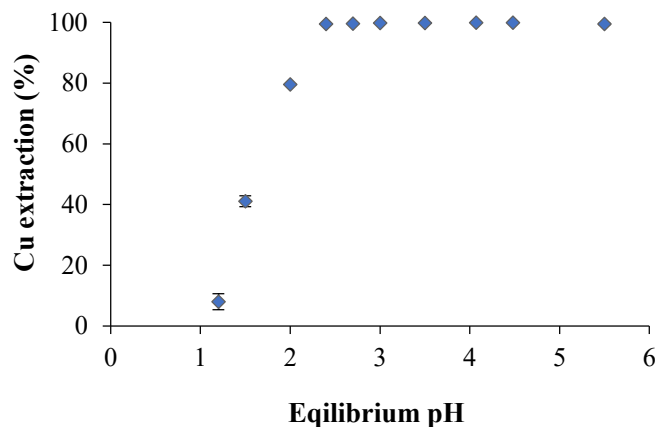
Figure 4.12. The effect of equilibrium pH on the copper extraction: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); and Tergitol concentration= 0.1 % (v/v).

The results from the second approach also indicated the same trend, that being lower extraction at equilibrium pH values lower than 2.5, followed by more than 99 % extraction at higher equilibrium pH. According to the results obtained from both approaches, the copper removal was noticeably lower at pH values below 2 compared to higher pH. This lower copper removal percentage is due to the higher concentration of hydrogen ions in the solution. As mentioned earlier, the major contributing mechanism appears to be ion exchange between acidic extractant LIX 984N and the copper loading aqueous solution (Equation 4.2). If the pH is too low, the equilibrium state shifts to the left resulting in a significant reduction in extraction efficiency.

4.4.2.4   Effect of contact time

The influence of the contact time on copper extraction was studied by contacting equal volumes of copper solution and CLA dispersion for different periods of time (from 0 min to 90 min). The results are shown in Figure 4.13, where it can be seen that there is an almost instantaneous removal of all the copper (100 ppm initial).
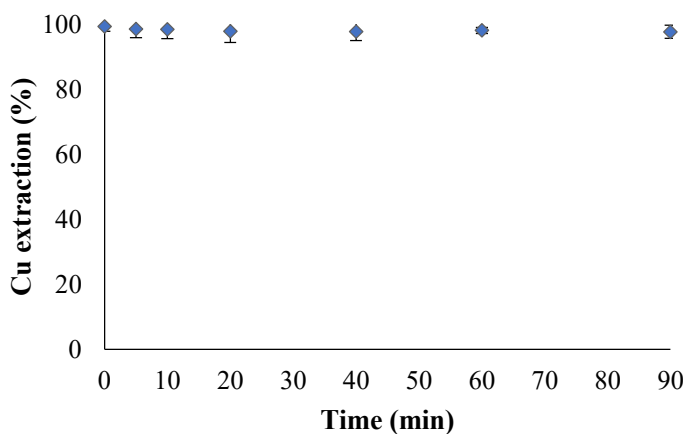
Figure 4.13. The effect of contact time on the copper extraction: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration: 0.1 % (v/v); and initial pH of copper solution= 4.

The same experiment was carried out for the solution with the initial copper concentration of 500 ppm in which the copper removal percentage under the same conditions (0.5 % (w/v) LIX 984N and 0.24 % (w/v) SDS) was approximately 45 % (Figure 4.14). This shows the rapid recovery of the maximum amount of copper by the CLAs.
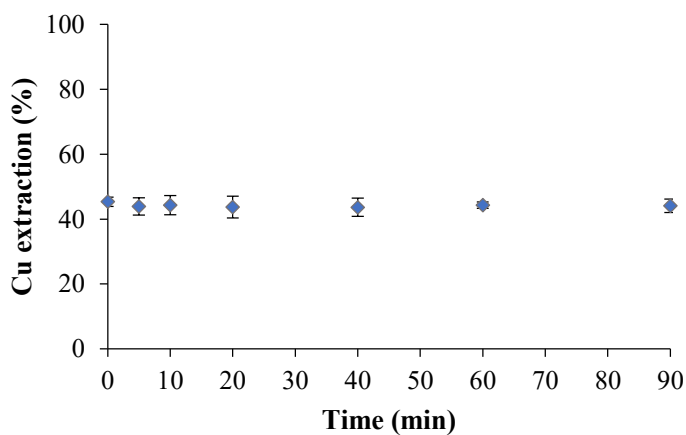
Figure 4.14. The effect of contact time on the copper extraction: initial copper concentration= 500 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.

It can be understood from the results that copper equilibrium was reached during the first seconds and the extraction process was very quick. The influence of contact time on the extraction percentage of copper is negligible regardless of initial copper concentration. Furthermore, it can be concluded that in predispersed solvent extraction of copper, mixing time is minimized. This fast extraction is one of the important advantages of PDSE method that almost eliminates mixing stage, which was one of the time and energy consuming stages in conventional solvent extraction.

4.4.2.5 Effect of aging

In previous experiments, CLA dispersions were prepared fresh to avoid any time-based changes in their structure or properties.

According to the published literature, colloidal liquid aphrons are stable for a long period of time and can be stored in sealed bottles for a long period of time, even years, without visible deterioration (Matsushita et al., 1992; Sebba, 1987). Visual observations during the experiments showed no visible change in the volume of CLA dispersion over a period of two months. In addition, in order to study the effect of storage time on the extraction ability of CLAs, the extraction process was carried out by using CLA dispersions which were stored in sealed bottles in room temperature for various periods of time, from a few hours to a maximum of 60 days. Figure 4.15 shows copper extraction percentage using aged CLAs.
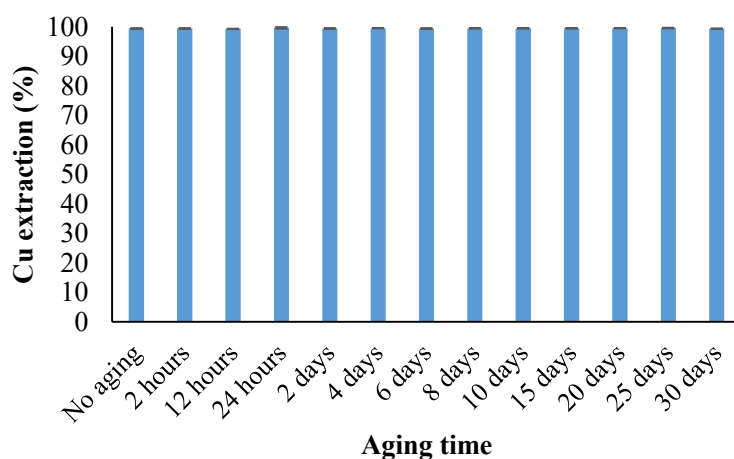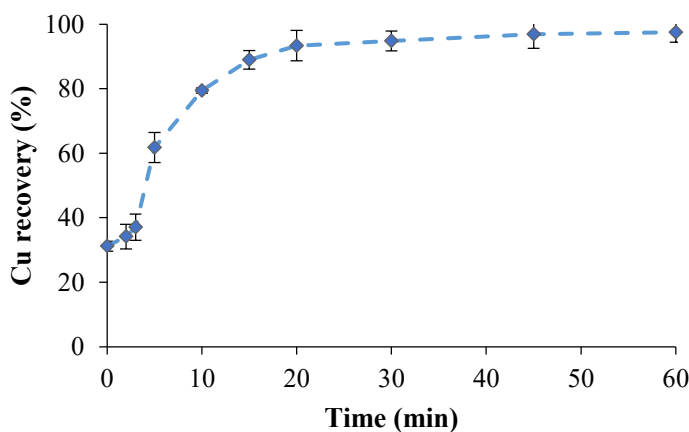

Figure 4.15. The effect of Aging of CLAs on the copper extraction: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4.

No significant change in copper removal over time was observed, confirming that CLA dispersions are stable and can be stored for at least two months without any change in their properties. Furthermore, there are no special considerations for storing such dispersions and they can be stored easily in any sealed vessel at room temperature.

4.4.3   Phase separation experiments

The purpose of these experiments was to separate copper-loaded CLAs from aqueous solutions in a column without centrifuging. The optimal conditions determined from previous experiments (initial LIX 984N concentration: 0.5 % (w/v), SDS concentration: 0.24 % (w/v), Tergitol concentration: 0.1 % (v/v), initial pH of copper solution: 4, and initial copper concentration: 100 ppm) were used for these experiments. Samples were removed at specified times from the column at a height of 2 cm and diluted with 4 % nitric acid, followed by copper concentration analysis with ICP-OES.

During the first set of experiments, no air was added to the system and the copper loaded CLAs moved to the top of column very slowly. The time-based extraction percentages are shown in Figure 4.16.

Figure 4.16. Phase separation in the column: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and initial pH of copper solution= 4. No air added.

The phase separation process was slow and at least 20 minutes was required to remove 90 % of copper from the solution. In order to attempt to increase the rate of phase separation, air was added to the system to investigate the potential of a flotation technique in the phase separation process. Figure 4.17 shows the copper extraction results taken from the flotation column.
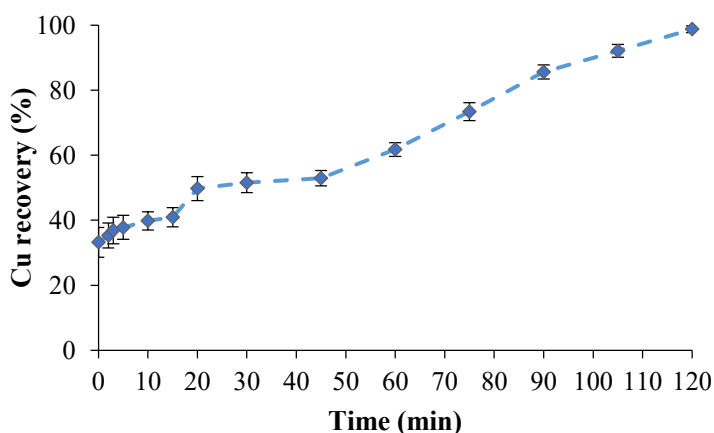
Figure 4.17. Phase separation in the column: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); initial pH of copper solution= 4; and air flow rate= 40 cm³/min.

It can be seen from the results that the phase separation process is even slower when air is added. The main reasons for this behavior are the small size of colloidal liquid aphrons and existence of surfactant in the CLAs structure. The former led to the slow rise of CLAs and the latter resulted in formation of foam by addition of air, which is not desirable. In order to overcome these problems and to have bigger CLA aggregates which rise faster, a flocculant was added to the system. Different types of non-ionic and ionic (both negative and positive) flocculants at different concentrations were tested and the positively charged FO 4115sh flocculant (manufactured by SNF-INC, USA) was determined to offer the best results. 50 ppm of the flocculant was added after addition of CLA dispersion to the copper aqueous solution, and the solution was conditioned for one minute prior the sampling. The results are shown in Figure 4.18 and Figure 4.19.
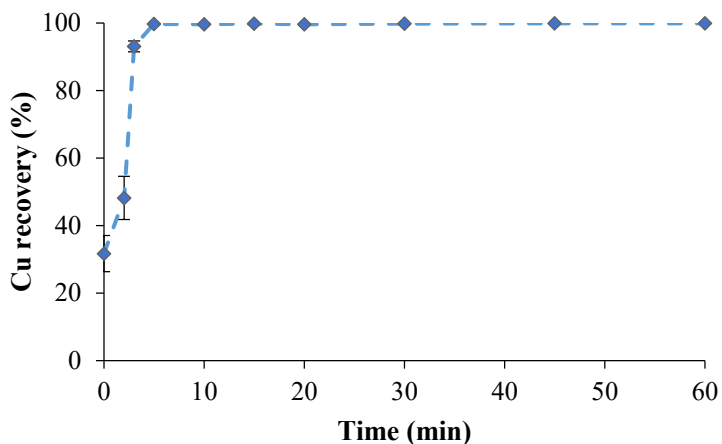
Figure 4.18. Phase separation in the column: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); initial pH of copper solution= 4; and flocculant concentration= 50 ppm. No air added.
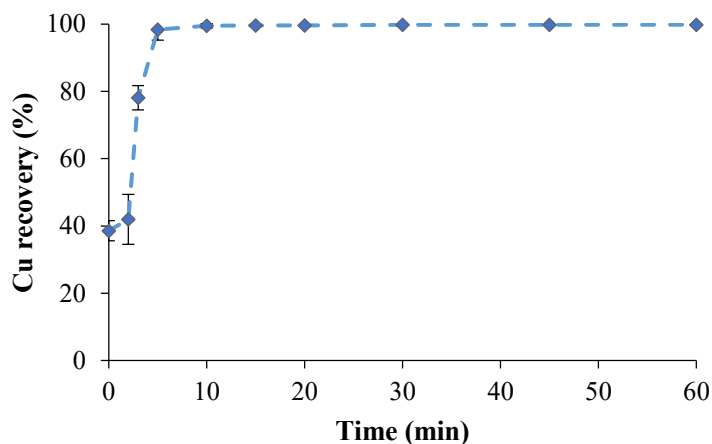

Figure 4.19. Phase separation in the column: initial copper concentration= 100 ppm; initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); initial pH of copper solution= 4; flocculant concentration= 50 ppm; and air flow rate= 40 cm^3 /min.

The addition of the flocculant resulted in rapid phase separation both with and without air addition. In both cases, more than 98 % of copper was removed from the solution after 5 minutes. Therefore, the addition of a flocculant makes the phase separation in column as an alternative method for centrifuging, which would be not favorable for an industrial scale application.

4.4.4 Regeneration and recycling of CLAs

The regeneration of CLAs was investigated by making new CLAs using recycled organic phase from old CLAs. For his purpose, after making a CLA dispersion under optimum conditions, the dispersion was destabilized by diluting with the equal volume of water, decreasing pH to 2.5-3, and centrifuging at 4200 rpm for 5 minutes. After a complete phase separation between the aqueous and organic phase, the organic phase was removed and used as organic feed to make a new CLA dispersion. The new CLAs have the same properties as the old one, including viscosity, creamy appearance, and stability. Figure 4.20 shows the size distribution of freshly made CLAs and regenerated CLAs after one week. The freshly made CLAs were generated in the following conditions: initial LIX 984N concentration= 0.5 % (w/v); SDS concentration= 0.24 % (w/v); Tergitol concentration= 0.1 % (v/v); and PVR= 4. The regenerated CLAs contained: recycled organic phase from old CLAs, SDS concentration= 0.24 % (w/v); and PVR= 4.
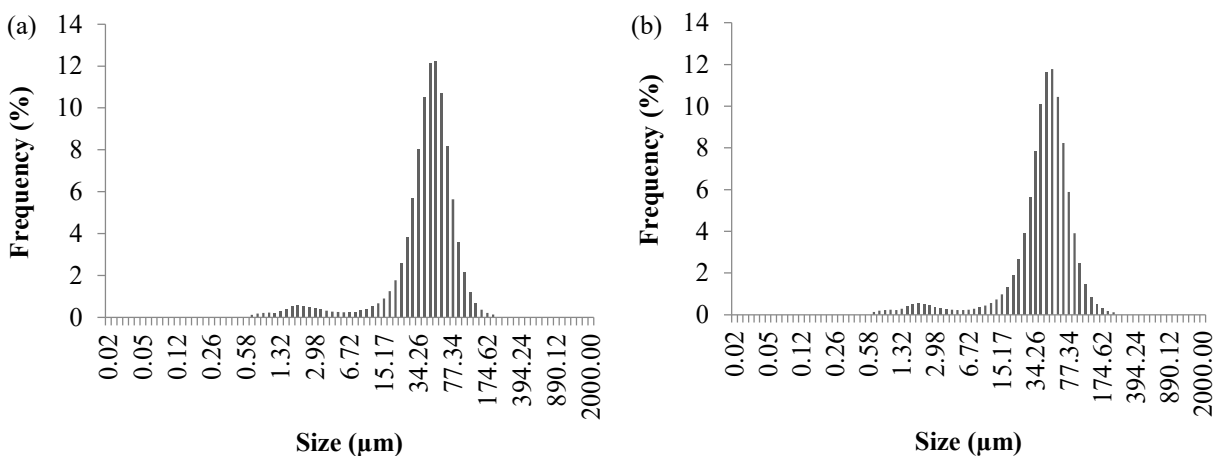
Figure 4.20. Size distribution of (a): freshly made CLAs and (b): regenerated CLAs after one week.

These graphs show very similar size distribution between freshly made CLAs and regenerated ones. While the mean and median of the freshly made CLAs are 44.95 µm and 42.55 µm respectively, the mean and median of regenerated CLAs are 45.77 µm and 42.92 µm, respectively, which again shows the very similar size distribution of two CLA dispersions.

4.5   CONCLUSIONS

In this chapter, the effect of experimental conditions on the predispersed solvent extraction of copper ions, using colloidal liquid aphrons, from dilute solutions was investigated. According to the experimental results, the CLAs were able to remove more than 99 % of the copper from dilute solutions under the following conditions: initial LIX concentration of 0.5 % (w/v); PVR of 4; initial copper solution pH of 3-5.5; water soluble surfactant being SDS; contact time being less than 1 min; CLAs storage time at least 2 months. The following experimental parameters were found to be most important: phase volume ratio; initial extractant concentration; water soluble surfactant charge; and pH. The other parameters including: surfactant concentration, contact time, and aging were found to be less important.

Based on the experimental observations, electrostatic interactions and ion exchange are believed to be the two major contributing mechanisms in the predispersed solvent extraction of copper. The former causes the initial contact between charged CLAs surface and copper ions by physical attraction, and the latter leads to completely extract the copper ions from solution by means of LIX 984N molecules. Finally, it can be concluded that predispersed solvent extraction can be successfully used for extracting copper ions from dilute solutions. The next chapter investigates the use of PDSE on another important metal in Canadian mineral processing that is often found in ores with copper, namely nickel. In addition, the recyclability of the CLAs is explored.

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CHAPTER 5. AN INVESTIGATION INTO PREDISPERSED SOLVENT EXTRACTION OF NICKEL (II) IONS FROM DILUTE AQUEOUS SOLUTIONS

5.1 ABSTRACT

In the previous chapter predispersed solvent extraction of copper was studied. This chapter details an investigation into the extraction of nickel ions from dilute aqueous solutions using colloidal liquid aphrons. The effect of four experimental parameters (extractant concentration, phase volume ratio (PVR), water soluble surfactant concentration and equilibrium pH) on the extraction process at three different nickel concentrations was studied. Response surface method was used to determine the significance of various experimental parameters. The most significant factors were shown to be different for the various metal ion concentrations tested, which may have implications for industrial practice. The equilibrium pH of 5 was found to be optimum point for all concentrations studied. The recyclability of organic phase also shown by reusing the stripped organic phase in a new extraction process. Reusing recycled organic phase in PDSE resulted in more than 99 % of extraction efficiency, thus indicating the potential benefit of a CLA-based extraction process.

5.2 INTRODUCTION

Nickel is one of the most important base metals and is a key component in industrial and consumer products such as in stainless steel, coinage, cars, mobile phones, rechargeable batteries, and kitchen appliances (Anyadike, 2002). There are more than 130 million tons of nickel resources in the world and more than 15 countries in the world produce nickel. Among these countries, Canada is a major producer and exporter of nickel and nickel products, being in the top five nickel producers in the world. Despite the general decreasing trend in metal prices in recent years, nickel prices increased by 12 % in 2014 which shows the increasing demand of nickel (*Mineral commodity summaries 2015*, 2015). This demand leads producers to consider the production of nickel from low grade ores and other secondary sources such as process wastewaters. In addition, the removal of nickel ions from process wastewater is also of environmental concern. Nickel is a

known human carcinogen and it may cause serious lung and kidney problems, pulmonary fibrosis, gastrointestinal distress, and skin dermatitis if it exceeds the critical level (Borba *et al.*, 2006; Fu & Wang, 2011).

Pressure acid leaching followed by solvent extraction (SX) is one method of processing nickel from laterite ores and has received more attention in the recent years due to the depletion of nickel sulfide ore resources (Agatzini-Leonardou *et al.*, 2009; Bacon & Mihaylov, 2002; Cheng, 2000; Cheng *et al.*, 2010). Solvent extraction is a well-established technique in removal of metal ions in hydrometallurgical processes; however, it is only economically feasible when the concentration of metal ions is high (>500 ppm) (Kentish & Stevens, 2001; Sengupta *et al.*, 2009). Therefore, solvent extraction may not be an effective technique to remove metals from dilute aqueous solutions.

Predispersed solvent extraction (PDSE) is a modified solvent extraction technique which uses the same principles as SX. In solvent extraction the metal bearing water is contacted with an organic water insoluble metal extractant and the metal ions transfer into the organic phase. In PDSE the organic phase including the extractant are predispersed into micrometer sized globules termed colloidal liquid aphrons (CLAs) in order to increase the interfacial area of organic phase, which results in lower extractant consumption and a faster extraction process.

Colloidal liquid aphrons, as proposed by Sebba (1987), are small droplets which consist of an oil core encapsulated by a thin soapy (aqueous) shell. This soapy shell (which contains a water soluble surfactant), makes the CLA's surface hydrophilic thus allowing them to disperse easily in the feed phase while the oil core carries the organic extractant and oil soluble surfactant. A mixture of non-ionic and ionic surfactants make CLAs stable by forming three distinct interfaces. They can be stored for long periods of time without any noticeable change in their properties (Matsushita *et al.*, 1992; Sebba, 1987) and also can be transported through pumping without destroying the structure. In addition, the small size of CLAs provides large interfacial area available for mass transfer (Lee *et al.*, 2002; Sebba, 1987).

Using CLAs in a PDSE process was first proposed by Sebba (1985). Further research comparing PDSE with conventional SX was performed by Michelsen *et al.* (1986), who reported that the effectiveness of PDSE for the removal of an organic compound (o- dichlorobenzene) from water was 5 to 10 times greater than conventional SX using the same quantity of the solvent, and that there was a considerable drop in solvent to feed ratio (1:500) (Michelsen *et al.*, 1986). Wallis *et*

al. (1986) also reported 20 % higher ethanol extraction with CLAs in PDSE compared to conventional SX.

Although PDSE represented significant potential in extraction of organic pollutants (Birajdar *et al.*, 2015; Hong *et al.*, 2001; Kim *et al.*, 2004a; Kim *et al.*, 2004b; Kim *et al.*, 2002; Lee *et al.*, 2000; Lye & Stuckey, 2000; Molaei & Waters, 2015; Zhang *et al.*, 1996), it is not a well-established method in the removal of metal ions. There is only a few research on PDSE of copper (Hahm *et al.*, 2003) and chromium (Luo *et al.*, 2013). In the previous chapter, predispersed solvent extraction was successfully used in extraction of copper (II) ions from dilute solutions with more than 99% of copper recovery and effect of different experimental parameters were investigated as well as CLAs structure and alternative phase separation technique. In case of nickel, there is no evidence in literature regarding the application of PDSE in extraction of nickel ions. Hence, the main goal of this chapter is to investigate the potential application of PDSE technique in extraction of nickel (II) ions from dilute aqueous solutions and to study the effects of four process parameters: initial water soluble surfactant concentration, initial extractant concentration, phase volume ratio, and equilibrium pH on the predispersed solvent extraction of nickel from dilute solutions. These four factors were chosen based on the preliminary screening experiment. Response surface methods and central composite design were used to study the effect of parameter and to determine the optimum experimental condition. The stripping and recyclability of the organic phase was also examined in the current chapter.

5.3   MATERIALS AND METHODS

5.3.1   Materials

Nickel (II) solutions were prepared by dissolving Nickelous Sulfate ($NiSO_4.6H_2O$) (Anachemia, USA) in reverse-osmosis purified water. For the CLA dispersion formulation, the organic phase consisted of LIX 984N (BASF, Germany) as nickel extractant and kerosene (Sigma-Aldrich, USA) and Tergitol 15-S-3 (Talas, USA) as a LIX diluent, and oil soluble surfactant, respectively.

The aqueous phase was comprised of anionic sodium n-dodecyl sulfate (SDS) (99 %, Avocado, UK), as water soluble surfactant. Sulfuric acid (Fisher Scientific, Canada) and sodium hydroxide (Fisher Scientific, Canada) were used to modify pH; and 4 % nitric acid (Sigma-Aldrich, USA)

was used to dilute samples before nickel concentration analysis. All aqueous phases were prepared using reverse osmosis purified water at ambient temperature.

5.3.2 Preparation of CLAs

The CLA dispersions were prepared by the slow drop-wise addition of the organic phase containing LIX 984N, kerosene, and Tergitol 15-S-3 (oil soluble surfactant) into a foaming aqueous solution containing the SDS (water soluble surfactant). While different concentrations of LIX 984 N and SDS were examined during the experiments, the concentration of Tergitol 15-S-3 was kept constant at 0.1 % (v/v). Further details about CLAs preparation is given in Section 4.3.2.

The CLA dispersions were prepared fresh every day and kept for maximum of 24 hours. However, as noted in Chapter 4, CLAs can be stored for at least 2 months without any change in their extraction ability.

5.3.3 CLA size analysis

The size distribution of CLA dispersions made with different SDS concentrations was determined using a particle size analyzer, LA 920 (Horiba, Japan), at a refractive index of 1.44. CLA dispersions were generated with four different SDS concentration, and then diluted with water at 1:9 volumetric ratio, in order to reduce the turbidity of dispersions and have a clear distribution. Other experimental parameters such as the initial extractant concentration, PVR, and Oil soluble surfactant concentration were kept constant at 0.5 % (w/v), 4, and 0.1 % (v/v), respectively.

5.3.4 Extraction process

Nickel extraction experiments were conducted in 100 ml beakers, 15 ml of CLA dispersion was added to 15 ml of Ni (II) solution. The mixture was stirred while the pH adjusted to the desired value. Once the pH was adjusted and equilibrium was reached, the solution was transferred to a centrifuge tube and centrifuged for 5 min at 4200 rpm to ensure a rapid phase separation. Following the phase separation, the raffinate was removed and diluted with 4 % nitric acid prior to analysis of the remaining nickel concentration by inductively coupled plasma emission spectroscopy (ICP-OES, Thermo Scientific 6000 series). The nickel extraction was calculated using Equation 5.1.

$$\text{Ni extraction \%} = \frac{(C_0 - C)}{C_0} \times 100 \qquad\qquad \text{Equation 5.1}$$

where C_0 is the initial concentration of nickel (ppm) and C is the final concentration of nickel (ppm) in the raffinate, as measured by ICP-OES.

Once the raffinate was removed and analyzed to calculate the extraction efficiency, the metal loaded organic phase was filtered and prepared for stripping stage and the concentration of loaded nickel in the organic phase was calculated through mass balancing.

5.3.5 Stripping and recycling

Once the optimum conditions for the nickel extraction were determined, the nickel loaded organic phase from the extraction process with 100 ppm initial nickel concentration was removed and subjected to stripping experiments. The nickel loaded organic phase was mixed with sulfuric acid concentrations at different concentrations (25, 50, 100, 150 g/L) and two different acid to organic volumetric ratios (1:1 and 1:2) for 10 minutes at 300 rpm. After the stripping, the acid phase was removed, diluted and analyzed by ICP-OES.

The recycling experiments were performed using the stripped organic phase (under the optimum stripping conditions). New CLA dispersions using recycled organic phase were generated and the extraction process was carried out in the same procedure as outlined in Section 5.3.4.

5.3.6 Experimental design methodology

In this chapter, central composite design (CCD) was used to design the experiments and response surface method (RSM) was used to analyze the relationship between the factors and the response and to find optimum conditions for the response with a minimum number of experiments. Using these methods also helps to determine the most significant parameters and their interactions (Kökkılıç *et al.*, 2015; Montgomery, 2012; Zhou *et al.*, 2015).

For CCD, four factors, *i.e.* extractant concentration (Ex. Con.), phase volume ratio (PVR), SDS concentration (S. Con.), and equilibrium pH (Eq. pH), were chosen at the five levels ($\pm\beta$, ± 1, 0), and extraction percentage are selected as response. From literature (Box & Hunter, 1957; Montgomery, 2012), the required number of test for the CCD was calculated as being 31. In order

to have more reliable results each test was replicated two times and the average responses were calculated. The coded and corresponding actual values of the variables are shown in Table 5.1.

Table 5.1. Independent variables and their levels (all to 2 d. p.)

Variable	Symbol	Coded variable Level				
		Lowest $-\beta$ (-2)	Low -1	Center 0	High +1	Highest $+\beta$ (+2)
Extractant concentration (% w/v)	x_1	0.10	0.30	0.50	0.80	1.00
Phase volume ratio	x_2	1.00	3.25	5.50	7.75	10.00
SDS concentration (% w/v)	x_3	0.10	0.25	0.40	0.55	0.70
Equilibrium pH	x_4	4.00	5.50	7.00	8.50	10.00

When the results were obtained, a second order regression model, which describes extraction percentage, was created. A typical second-order model can be expressed by Equation 5.2.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \qquad \text{Equation 5.2}$$

where y is the predicted response, x_i and x_j are the variables; β_0 is the constant coefficient; β_i and β_{ii} represent the linear effect and quadratic effect of the ith factor respectively; and β_{ij} represents the interaction effect, between the ith and jth variables; and ε represents the error in the system (Gunaraj & Murugan, 1999a, 1999b; Kökkılıç *et al.*, 2015; Kwak, 2005; Montgomery, 2012; Yi *et al.*, 2010).

The proposed model was then analyzed with the Fisher's statistical test for the analysis of variance (ANOVA) to obtain the coefficients and assess the quality of "goodness of fit". All statistical analyses were produced using "Minitab® 17 statistical software" and contour plots were drawn using "MATLAB R2015b academic use".

5.4 RESULTS AND DISCUSSION

5.4.1 Statistical model for nickel extraction

The designed experiments were performed in a randomized order, and the results (responses) were calculated. Table 5.2 shows the coded and actual levels of variables and the responses.

Table 5.2. Coded, actual level and results

Run	Coded Level of factors				Actual level of factors				Response (Extraction, %)		
	x_1	x_2	x_3	x_4	Ex. Con.	PVR	S. Con.	Eq. pH	20 ppm	100 ppm	300 ppm
1	-1	1	1	1	0.3	7.75	0.55	8.5	89.21	73.45	75.90
2	-1	-1	-1	-1	0.3	3.25	0.25	5.5	96.09	83.23	29.91
3	1	1	1	1	0.8	7.75	0.55	8.5	92.29	84.65	82.21
4	2	0	0	0	1.0	5.50	0.40	7.0	99.87	98.56	96.07
5	1	-1	1	1	0.8	3.25	0.55	8.5	57.52	67.42	71.09
6	0	0	-2	0	0.5	5.50	0.10	7.0	57.613	89.11	81.25
7	-1	-1	1	-1	0.3	3.25	0.55	5.5	99.73	91.64	28.18
8	0	2	0	0	0.5	10.00	0.40	7.0	78.47	74.29	65.19
9	0	-2	0	0	0.5	1.00	0.40	7.0	73.79	56.18	32.24
10	-1	1	1	-1	0.3	7.75	0.55	5.5	99.96	88.21	42.73
11	0	0	0	0	0.5	5.50	0.40	7.0	91.13	74.58	50.74
12	0	0	0	0	0.5	5.50	0.40	7.0	95.08	79.93	47.51
13	-2	0	0	0	0.1	5.50	0.40	7.0	92.12	58.46	24.08
14	0	0	0	0	0.5	5.50	0.40	7.0	89.34	84.97	53.57
15	0	0	2	0	0.5	5.50	0.70	7.0	82.25	84.43	65.90
16	0	0	0	0	0.5	5.50	0.40	7.0	98.99	77.35	56.80
17	1	1	1	-1	0.8	7.75	0.55	5.5	99.97	99.99	93.84
18	1	1	-1	-1	0.8	7.75	0.25	5.5	97.54	91.12	72.67
19	-1	-1	1	1	0.3	3.25	0.55	8.5	51.64	36.58	27.16
20	0	0	0	2	0.5	5.50	0.40	10.0	71.23	47.83	61.11
21	1	-1	1	-1	0.8	3.25	0.55	5.5	99.78	99.86	87.72
22	1	-1	-1	1	0.8	3.25	0.25	8.5	62.55	63.11	83.58
23	0	0	0	0	0.5	5.50	0.40	7.0	89.23	80.45	58.13
24	-1	1	-1	1	0.3	7.75	0.25	8.5	78.43	67.76	90.74
25	-1	-1	-1	1	0.3	3.25	0.25	8.5	41.88	39.77	74.99
26	1	-1	-1	-1	0.8	3.25	0.25	5.5	97.44	99.38	75.33
27	0	1	0	-2	0.5	5.50	0.40	4.0	99.60	93.75	25.31
28	0	0	0	0	0.5	5.50	0.40	7.0	90.31	77.56	61.90
29	1	1	-1	1	0.8	7.75	0.25	8.5	82.30	67.92	68.81
30	-1	1	-1	-1	0.3	7.75	0.25	5.5	95.60	70.87	30.25
31	0	0	0	0	0.5	5.50	0.40	7.0	82.75	74.65	58.78

Using the results in Table 5.2, the second order response functions representing extraction percentage at 20 ppm, 100 ppm, and 300 ppm nickel concentration, y_{20}, y_{100} and y_{300} respectively, were expressed as a function of extractant concentration (x_1), PVR (x_2), SDS concentration (x_3), and equilibrium pH (x_4). The coded model equation for nickel extraction at 20 ppm, 100 ppm and 300 ppm are presented in Equation 5.3, Equation 5.4, and Equation 5.5, respectively; which are the expanded versions of Equation 5.2.

$$y_{20} = 91.31 + 2.19\,x_1 + 5.86\,x_2 + 4.50x_3 - 12.15\,x_4 + 1.55\,x_1^2$$
$$- 3.56\,x_2^2 - 5.55\,x_3^2 - 1.05\,x_4^2 - 1.02\,x_1x_2 - 1.10\,x_1x_3$$
$$+ 1.63\,x_1x_4 + 1.21\,x_2x_3 + 8.19\,x_2x_4 + 0.64\,x_3x_4$$

Equation 5.3

$$y_{100} = 80.02 + 6.89\,x_1 + 4.59\,x_2 + 1.30\,x_3 - 12.52\,x_4 - 0.272\,x_1^2$$
$$- 3.22\,x_2^2 + 2.79\,x_3^2 - 1.84\,x_4^2 - 3.17\,x_1x_2 + 1.36\,x_1x_3$$
$$- 0.83\,x_1x_4 + 1.76\,x_2x_3 + 7.96\,x_2x_4 - 1.38\,x_3x_4$$

Equation 5.4

$$y_{300} = 58.20 + 14.58\,x_1 + 6.14\,x_2 - 2.26\,x_3 + 8.02\,x_4 + 0.99\,x_1^2$$
$$- 0.10\,x_2^2 + 5.49\,x_3^2 - 1.47\,x_4^2 - 5.21\,x_1x_2 + 5.32\,x_1x_3$$
$$- 10.40\,x_1x_4 + 5.65\,x_2x_3 + 3.38\,x_2x_4 - 6.97\,x_3x_4$$

Equation 5.5

In order to estimate the significance and accuracy of the developed models, ANOVA (Table 5.3) was used.

Table 5.3. Summarized ANOVA for regression models

Initial nickel concentration (ppm)	F- value	p-value	R^2 (%)	S	lack of fit
20	8.96	0.000	88.68	7.42	0.109
100	16.84	0.000	93.64	5.77	0.074
300	17.69	0.000	93.93	7.43	0.101

According to Table 3, the calculated F-values of the models are higher than the F value in the F-distribution table with 5 % significance level, ($F_{0.05}$ $_{(14,\ 16)}$ = 2.448) (Montgomery, 2012), the p-values are smaller than 0.05 and the p-values of the lack of fit are bigger than 0.05. The lack-of-fit is tested when the data contain replicates (*e.g.* at center point). Replicates represent "pure error" because only random variation can cause differences between the observed response values. To determine whether the model accurately fits the data the p-value of lack of fit is compared to the significant level (α=0.05). The P-value > α means that there is no evidence that the model does not fit the data.

The table also shows the R^2 values and the standard deviations (S). According to Montgomery (Montgomery, 2012), the models with $R^2 \geq 80\%$ are assumed as being good fit models. From the above, it can be concluded that the regression models are considered acceptable and good fits.

5.4.2 Effect of experimental variables

Table 5.4 represents the summarized Student's t- test which includes p-value and T-value of each experimental parameter and their square and interaction effects. The p-values indicate the significance of variables and interactions, having 95 % confidence level, all the variables and interactions with the p-value ≤ 0.05 are considered as significant (Montgomery, 2012). T-value is the result of Student's t-test and measures the size of the difference relative to the variation in data to identify the significance of the variables. The greater the magnitude of T-value, the greater significance.

Table 5.4. Summarized Student's t-test

Source	20 ppm		100 ppm		300 ppm	
	P-Value	T-value	P-Value	T-value	P-Value	T-value
x_1	0.160	1.47	0.000	7.11	0.000	10.50
x_2	0.002	3.75	0.004	3.37	0.002	3.75
x_3	0.033	2.34	0.097	1.76	0.297	-1.08
x_4	0.000	-7.81	0.000	-11.10	0.000	4.64
x_1^2	0.307	1.05	0.691	-0.41	0.286	1.10
x_2^2	0.023	-2.51	0.007	-3.08	0.614	-0.51
x_3^2	0.002	-3.63	0.072	1.92	0.001	3.97
x_4^2	0.416	-0.84	0.093	-1.79	0.151	-1.51
$x_1 x_2$	0.700	-0.39	0.143	-1.54	0.013	-2.78
$x_1 x_3$	0.456	-0.76	0.758	0.31	0.009	2.99
$x_1 x_4$	0.465	0.75	0.784	0.28	0.000	-5.47
$x_2 x_3$	0.578	0.57	0.114	1.67	0.014	2.76
$x_2 x_4$	0.001	4.33	0.000	4.8	0.172	1.43
$x_3 x_4$	0.674	0.43	0.623	-0.50	0.003	-3.57

It can be seen from Table 5.4 that the most significant factor at 20 ppm and 100 ppm is equilibrium pH (x_4) and at 300 ppm is extractant concentration (x_1), whereas the second significant factors are PVR (x_2), extractant concentration (x_1) and equilibrium pH (x_4) at 20 ppm, 100 ppm and 300 ppm respectively. In general, the water soluble surfactant concentration is not considered as very significant factor especially at 100 ppm and 300 ppm.

In order to obtain a better understanding of the system and to analyze the effect of variables in the experimental range, the contour plots of the fitted models were plotted and are presented in Figure 5.1, Figure 5.2 and Figure 5.3. The contour plots show the relationship between two

variables and responses while the other variables are at center (0) level (Ex. Con. (% w/v) 0.55, PVR 5.5, S. Con. (% w/v) 0.4, Eq. pH 7).
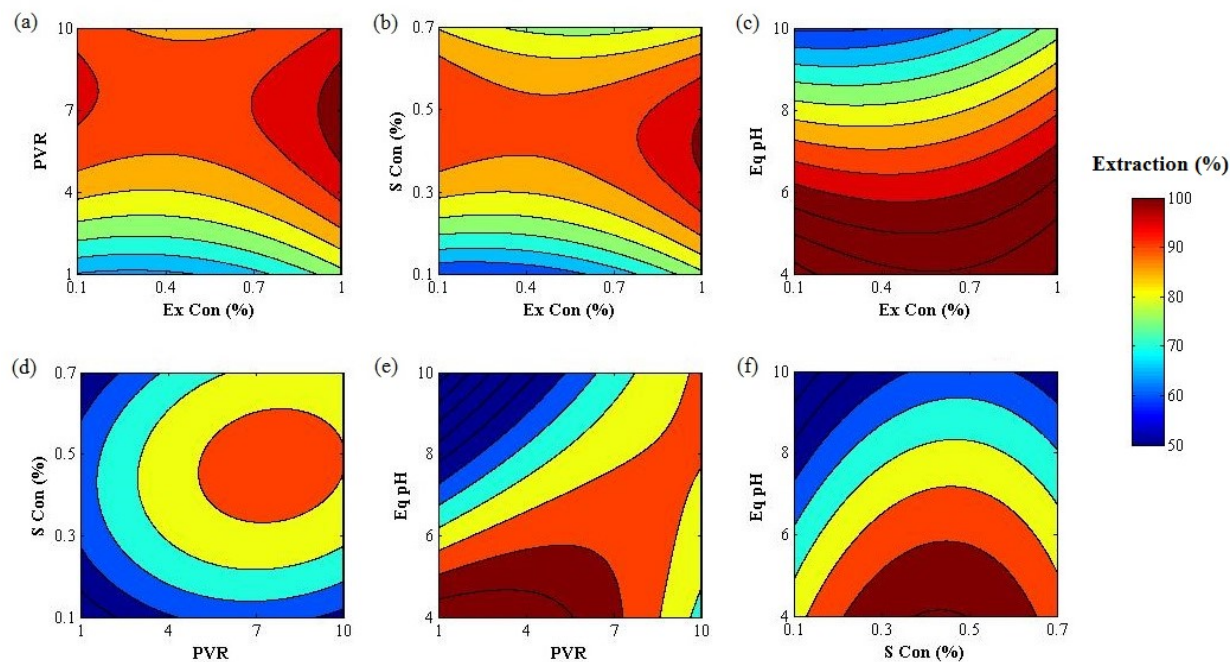
Figure 5.1. Contour plots of extraction at 20 ppm initial nickel concentration. Hold Values: Ex. Con. (% w/v) 0.55, PVR 5.5, S. Con. (% w/v) 0.4, Eq. pH 7. (a): effect of Ex. Con. & PVR; (b): effect of Ex. Con. & S. Con; (c): effect of Ex. Con. & Eq. pH; (d): effect of PVR & S. Con; (e): effect of PVR & Eq. PH; and (f): effect of S. Con. & Eq. pH.
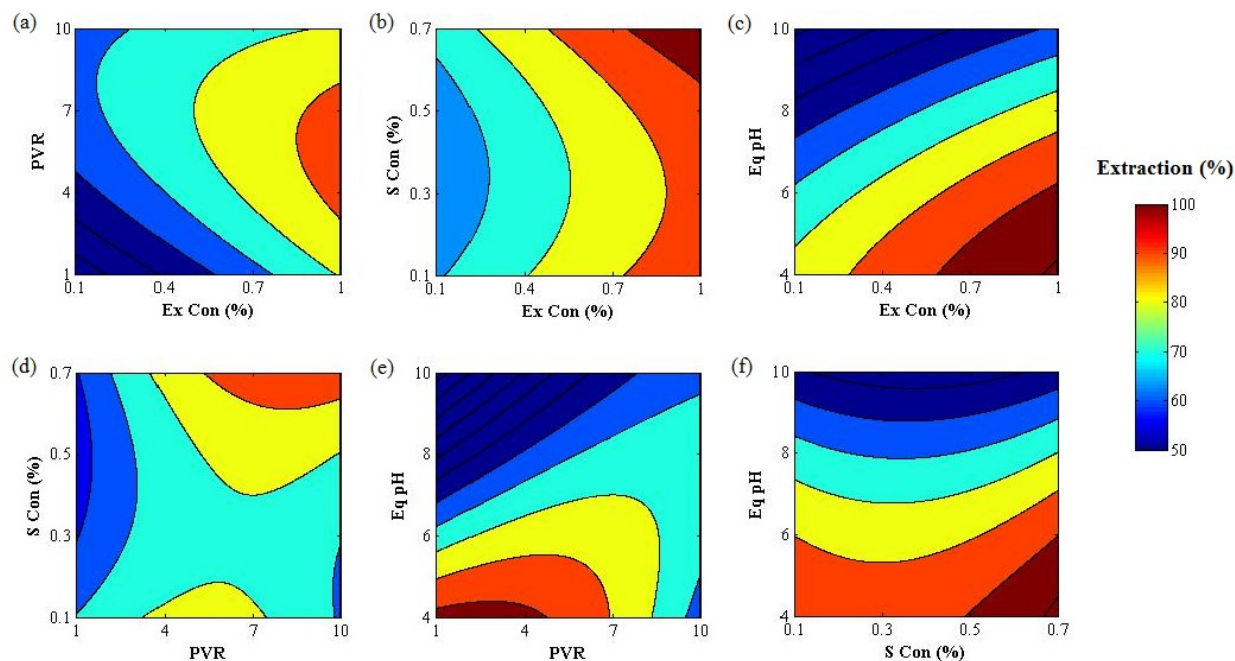
Figure 5.2. Contour plots of extraction at 100 ppm initial nickel concentration. Hold Values: Ex. Con. (% w/v) 0.55, PVR 5.5, S. Con. (% w/v) 0.4, Eq. pH 7. (a): effect of Ex. Con. & PVR; (b): effect of Ex. Con. & S. Con; (c): effect of Ex. Con. & Eq. pH; (d): effect of PVR & S. Con; (e): effect of PVR & Eq. PH; and (f): effect of S. Con. & Eq. pH.
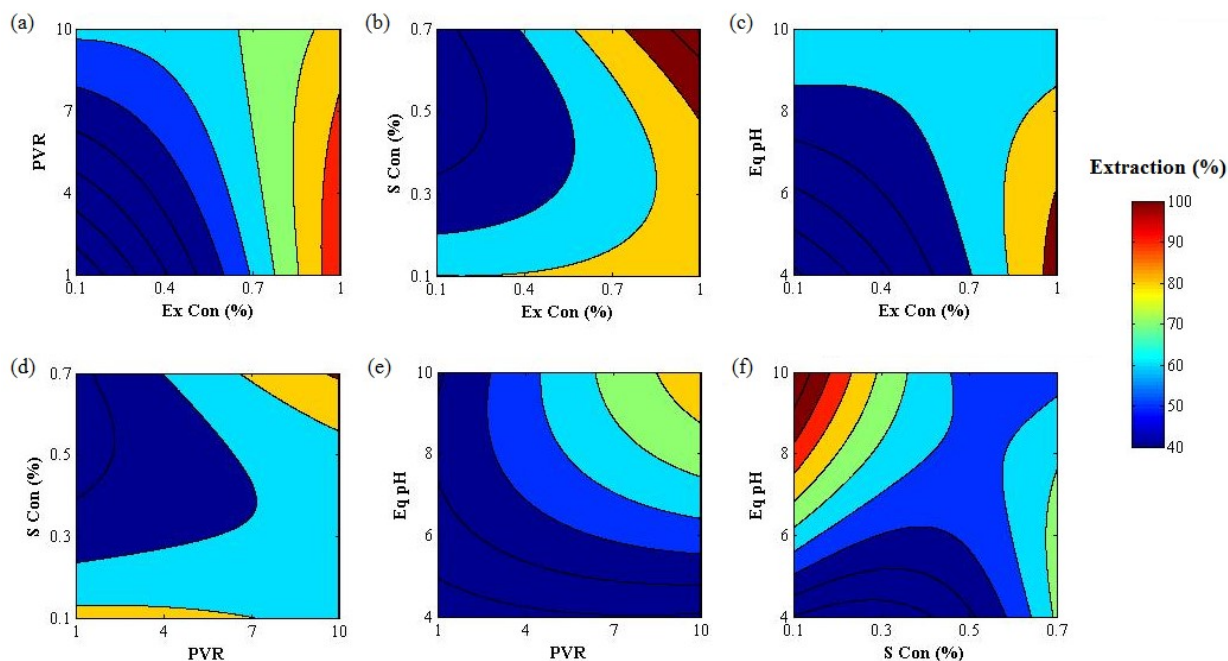
Figure 5.3. Contour plots of extraction at 300 ppm initial nickel concentration. Hold Values: Ex. Con. (% w/v) 0.55, PVR 5.5, S. Con. (% w/v) 0.4, Eq. pH 7. (a): effect of Ex. Con. & PVR; (b): effect of Ex. Con. & S. Con; (c): effect of Ex. Con. & Eq. pH; (d): effect of PVR & S. Con; (e): effect of PVR & Eq. PH; and (f): effect of S. Con. & Eq. pH.

5.4.2.1 Effect of equilibrium pH

Equilibrium pH is one of the dominant experimental parameters in the PDSE of nickel. As mentioned previously, it is the most significant factor for the 20 ppm and 100 ppm nickel extractions and the second most significant factor at 300 ppm. The importance of equilibrium pH was not only observed in the first order variable effect; it also has significant interactions with other factors. For example, at 20 and 100 ppm, the interaction of equilibrium pH with PVR is important, and at 300 ppm the interactions of equilibrium pH with extractant concentration and water soluble surfactant concentration are significant (see Table 5.4).

The contour plots also show how significantly equilibrium pH influences the extraction efficiency: looking at plots c, e & f in Figure 5.1, Figure 5.2 and Figure 5.3, the effect of equilibrium pH on the extraction percentage can be seen. Although low pH values are favored at all three concentrations, at 300 ppm the high pH values also show good results (Figure 5.3 (e& f)). The reason for this different behavior can be explained by the extraction mechanism for nickel using LIX 984N as an extractant. Because LIX 984N is a cation-exchanger chelating extractant, the extraction process progresses by ion exchange between positively charged nickel ions and H^+ ions existing in the extractant structure (Chauhan & Patel, 2014; Li *et al.*, 2011). Equation 5.6 shows the ion-exchange reaction between nickel ions and extractant.

$$Ni^{2+}{}_{(aq)} + HR_{2\,(org)} \longleftrightarrow NiR_{2(org)} + 2\,H^+{}_{(aq)} \qquad\qquad \text{Equation 5.6}$$

where R represents the active component of the extractant.

It can be seen from Equation 5.6 that Ni^{2+} and HR_2, which represent extractant (LIX 984N), are on the left hand side of equation and H^+ ions are on the right hand side of the two-way reaction.

At 300 ppm, when the concentration of extractant is high enough (Figure 5 (c)) to extract all the existing nickel ions, equilibrium is reached at lower pH values (4-6). However, if the extractant concentration was lower (0.55% in Figure 5 (e& f)) in order to have high extraction and to exchange all the nickel ions with hydrogen ions in the extractant, the pH should be increased. The pH increase lowers the concentration of H+ ions in the system, which moves the reaction to the right, resulting in more extraction of nickel ions.

5.4.2.2 Effect of extractant concentration

Extractant concentration is the most significant factor at 300 ppm, the second significant factor at 100 ppm, and insignificant at 20 ppm nickel concentration (see Table 5.4). This can be explained with regard to existing nickel ions in the system. At 20 ppm, due to a very low concentration of nickel, the smallest amount of extractant was able to extract all the nickel from solution (if the other factors chose to be in optimum range). This can be seen from Figure 5.1(a, b& c), where the maximum extraction can be observed in a wide range of extractant concentration. At 100 ppm, as Figure 5.2 (a, b& c) shows the extraction percentage increased by increasing the extractant concentration; however, the process is more pH dependent than extractant concentration dependent. At 300 ppm, due to high concentration of nickel ions larger amount of extractant is required to extract the ions; thus, extractant concentration plays very important role in this concentration. Figure 5.3 (a, b& c) shows the maximum extraction was reached in high extractant concentration range.

5.4.2.3 Effect of phase volume ratio

Phase volume ratio, which is the volumetric ratio of organic phase to aqueous phase in the CLAs structure, is an important characteristic of CLAs. The experimental results and data presented in Table 5.4 and contour plots in Figure 5.1, Figure 5.2 and Figure 5.3 show that the PVR is one of the important factors in all nickel concentrations, which has a positive effect on the nickel extraction. The main reason for this positive effect is that by increasing the PVR, the amount of organic phase increases and because the organic phase includes extractant, more extractant will enter the system, resulting in higher extraction.

5.4.2.4 Effect of water soluble surfactant concentration

The water soluble surfactant (SDS) concentration was the least significant factor at 100 and 300 ppm, and it was the third important factor at 20 ppm (Table 5.4). With regard to these results and previous observations on the PDSE of copper (Chapter 4) the SDS concentration can be considered as being the least effective parameter in this process. In PDSE process the ion-exchange reaction can be promoted by providing electrostatic interaction between charged CLAs and metal ions. While the small size of CLAs provides a high interfacial area and increases the ion exchange

probability, the charged surface of CLAs also increases the availability of ions to be extracted by extractant by attracting contour-ion metal ions. In order to make use of this electrostatic interaction between CLAs and metal ions, an anionic water soluble surfactant should be used in the formation of CLA dispersions. However, the concentration of this anionic surfactant does not have a significant influence on the extraction. This is because the main involving mechanism in PDSE of nickel is ion-exchange between extractant and metal ions and the existence of negatively charged surfactant on the surface of CLAs promotes this process by drawing the metal ions closer to the surface. The effect of surfactant type and concentration on the PDSE of copper was studied previously, and it was determined that using cationic or non-ionic surfactant decreases the extraction efficiency; however, changing the anionic surfactant concentration does not change the extraction efficiency noticeably.

Although the insignificant effect of anionic surfactant concentration on the extraction, the concentration of water soluble surfactant has an effect on the size and stability of CLAs (Beyer *et al.*, 1986; Matsushita *et al.*, 1992; Sebba, 1985). The effect of anionic surfactant (SDS) concentration on the CLA's size was investigated by analyzing the size distribution of CLAs dispersion in four different SDS concentrations. The results are presented in Figure 5.4 and Table 5.5
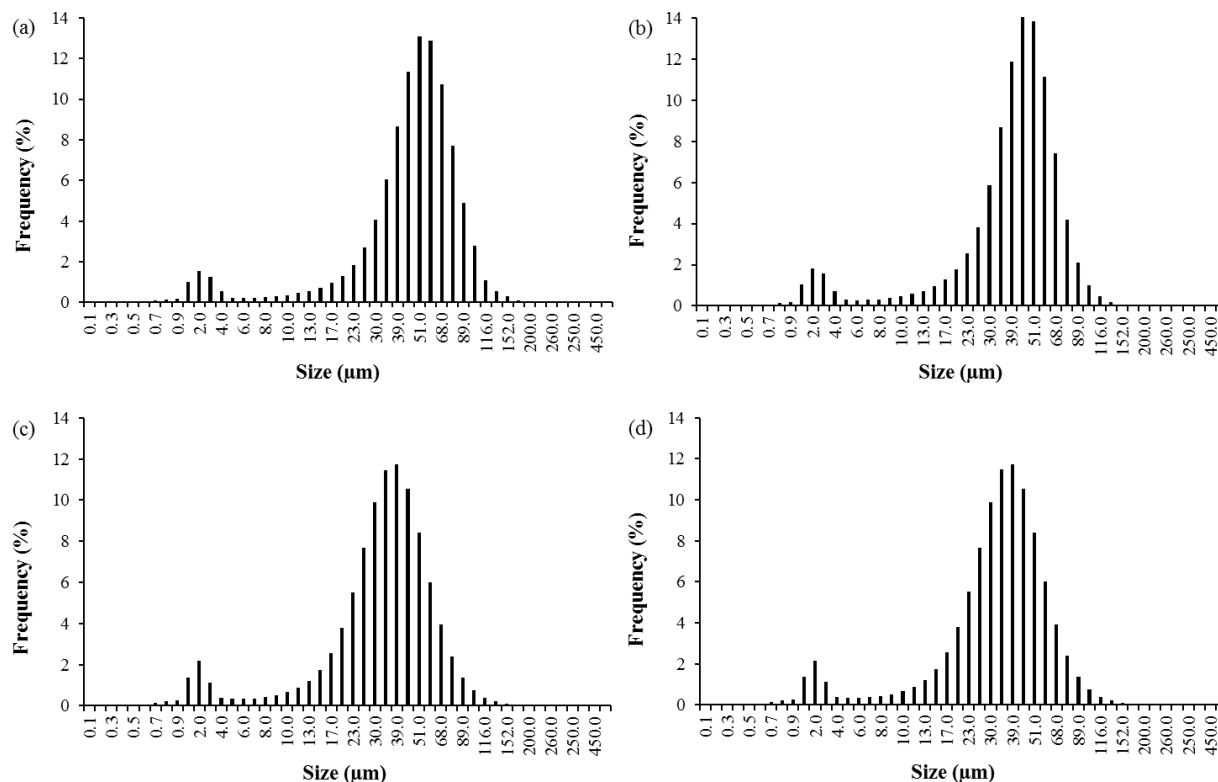
Figure 5.4. Size distribution of CLAs in different SDS concentration; (a): 0.1 % (w/v), (b): 0.3 % (w/v), (c): 0.5% (w/v) and (d): 0.7 % (w/v)

Table 5.5. Mean and median of CLAs generated with different SDS concentrations

Size	SDS Concentration (%)			
	0.1	0.3	0.5	0.7
Mean (µm)	48.89	41.18	34.40	28.18
Median (µm)	47.33	40.94	32.61	27.10

5.4.3 Optimization of process conditions

Although the contour plots can give overall idea about the effect of factors and show the regions with high extraction percentage, they may not indicate the optimum region. This is because these graphs were plotted in center points and if the optimum range was not located in the center level, the contour plots cannot show them precisely. More accurate information about the optimum regions can be obtained by drawing overlaid contour plots.

By plotting the individual contours areas with high response for each pair of factors at any desired hold values for each two other factors can be determined. By overlaying these individual plots, the final optimum conditions can be determined. Overlaid contours were plotted at 3 levels for each factor which were found to have high extraction by analyzing the contour plots.

Figure 5.5, Figure 5.6 and Figure 5.7 show the overlaid contours for ≥ 95 % extraction percentage at 20 and 100 ppm and ≥ 90 % extraction percentage at 300 ppm, respectively. In overlaid contours, the regions with maximum responses at different conditions were shown. The region that has more overlap (dark areas) can be considered as being the optimum region.
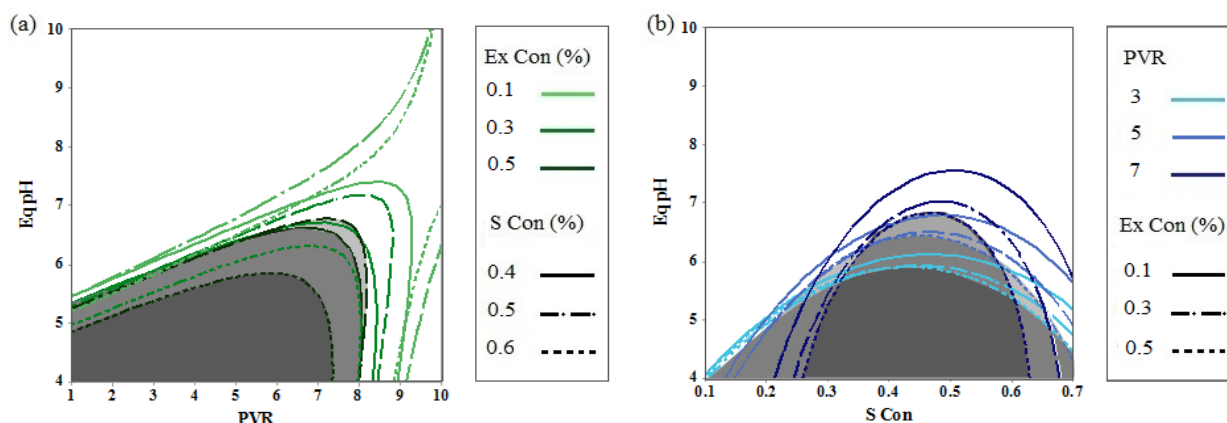

Figure 5.5. Overlaid plots of the significant factors at 20 ppm (the lines represent ≥ 95 % extraction)
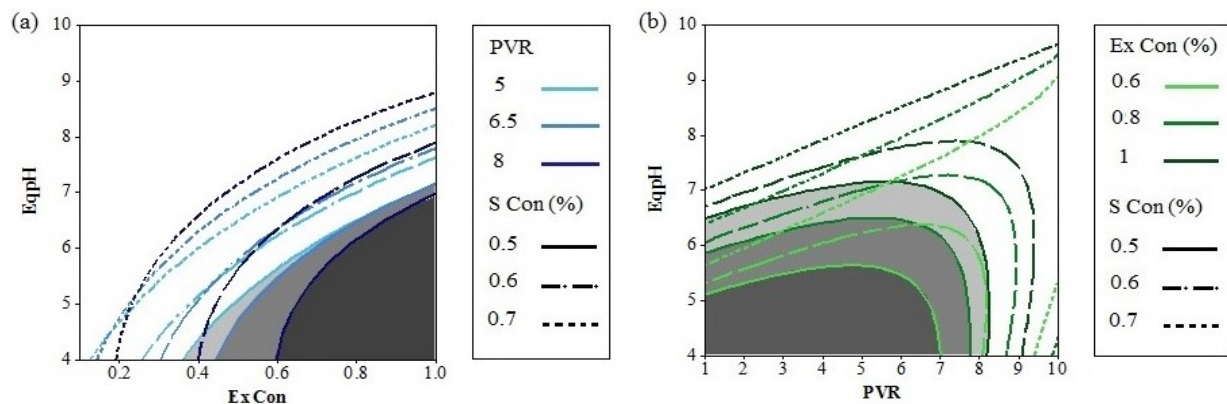

Figure 5.6. Overlaid plots of the significant factors at 100 ppm (the lines represent ≥ 95 % extraction)
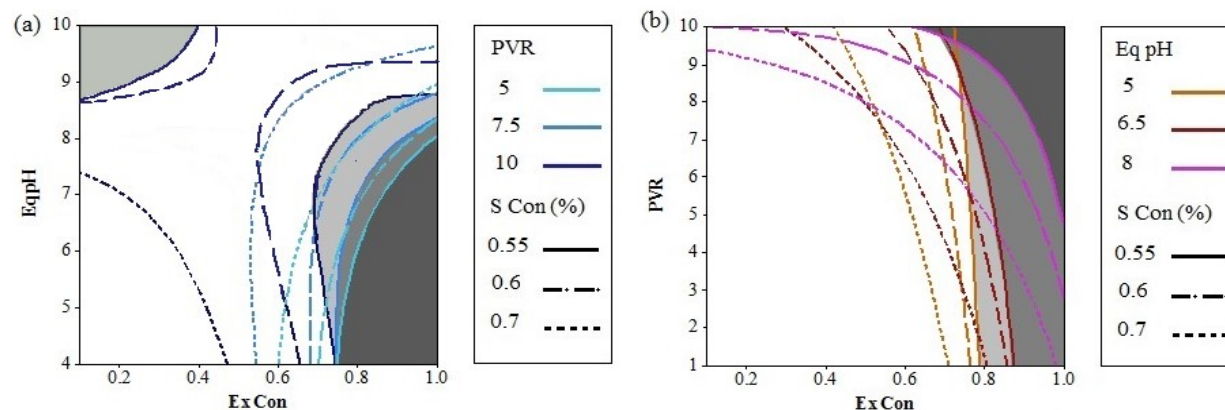
Figure 5.7. Overlaid plots of the significant factors at 300 ppm (the lines represent ≥ 90 % extraction)

Using these overlaid plots, the optimum range for each concentration was determined and presented in Table 5.6.

Table 5.6. Optimum ranges from overlaid contours

Initial Nickel Concentration	Variable range			
	Ex. Con. (% w/v)	PVR	S. Con. (% w/v)	Eq. pH
20 ppm	0.1-1	4-7	0.3-0.6	4-5.5
100 ppm	0.6-1	4-7	0.5-0.7	4-5.5
300 ppm	0.8-1	7-10	0.55-0.7	4-6

Once the optimum range for each variable was estimated, a number of points from optimum ranges and for random conditions close to optimum range were chosen to carry out the validation tests. The validation experiments were applied to confirm the validity of the models, and also to determine the final optimum points that could be present with a high degree of confidence. These tests were replicated two times to ensure the reproducibility of the data, and 95 % confidence interval level of each set of experiments was calculated. The selected points, average of experimental results, fitted results from proposed models and errors are presented in Table 5.7.

Table 5.7. Comparative data in for validation purpose

Test number	Initial nickel concentration	Conditions				Response (Extraction, %)		
		Ex. Con. (% w/v)	PVR	S. Con. (% w/v)	Eq. pH	Experimental mean	predicted *	Error
1	20	0.2	4	0.3	5	96.40	100.00	-3.60
2	20	0.2	4	0.4	5	97.38	100.00	-2.62
3	20	0.2	5	0.4	5	99.77	100.00	-0.23
4	20	0.2	5	0.4	8	79.41	79.00	0.41
5	100	0.6	4	0.5	5	98.18	100.00	-1.82
6	100	0.7	4	0.5	5	99.55	100.00	-0.45
7	100	0.4	4	0.5	5	92.00	92.11	-0.11
8	100	0.6	4	0.5	7	76.84	79.41	-2.57
9	100	0.7	4	0.3	5	98.68	100.00	-1.32
10	300	0.8	7	0.55	5	96.45	96.28	0.17
11	300	0.9	7	0.55	5	98.97	100.00	-1.03
12	300	0.7	7	0.55	5	87.41	82.31	5.10
13	300	0.8	7	0.55	7	85.09	89.47	-4.38

* The predicted values higher than 100 are considered as 100

Once the validation experiments were carried out, the experimental results were compared with the predicted responses calculated from models. Figure 5.8 shows the predicted and experimental data for the validation tests.
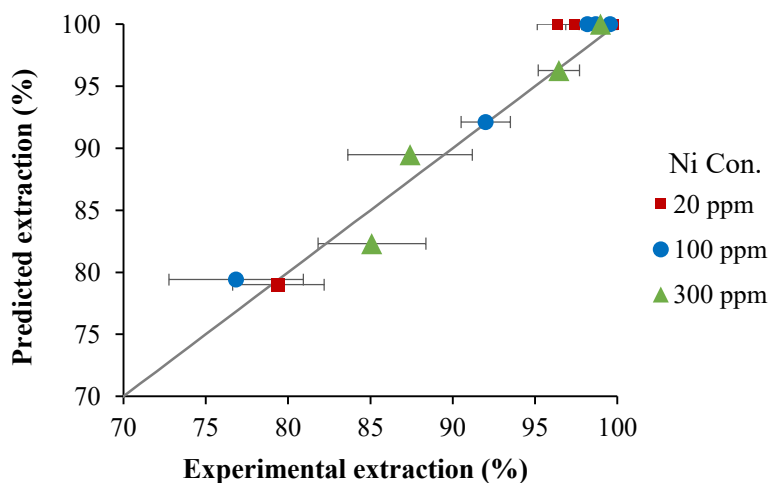
Figure 5.8. Predicted *vs.* experimental responses. The error bars represent 95 % confidence intervals of experimental data

The plotted points in Figure 5.8 represent the experimental response against the predicted ones. Considering the 95 % of confidence intervals of experimental data, the points were mostly along the linear x=y line which means that the predicted and experimental data are very close to each other. The R^2 value for these points was calculated to be 0.962, which compared to the models' R^2 is higher and shows the validity of the predicted responses.

The selection of optimum operating conditions could be different based on chemical consumption, environmental and instrumental limitations, and efficiency. During this study, the optimum points were selected based on the extraction efficiency in a laboratory setting. Therefore, test numbers 3, 6, and 11 from Table 5.7 were selected as the optimum points for 20 ppm, 100 ppm and 300 ppm nickel concentrations, respectively; due to the highest extraction percentages which were exhibited in these tests. However, all the other points which were tested in optimum ranges show high extraction efficiency (> 95 %).

The validation tests confirm the significance of equilibrium pH particularly at 20 ppm and 100 ppm. The changing in Eq. pH caused significant drops in extraction percentages in all three concentrations. For example, a decrease of more than 20 % was observed when the Eq. pH was changed from 5 to 8 and 7 at 20 ppm and 100 ppm, respectively (see Table 5.7 test numbers 3, 4 and 5, 8). Extractant concentration also is one of the important factors at 100 and 300 ppm, as it can be seen from test numbers 7 and 12. For instance, 0.1 % decrease in Ex. Con. at 300 ppm resulted in 9 % decrease in Extraction percentage (see Table 5.7 test numbers 10 and 12). The insignificant effect of SDS concentration at 100 ppm can be seen from test number 9, where decreasing S. Con. from 0.5 % to 0.3 % only decreases around 1 % of extraction percentage.

It can be concluded from the validation tests that the optimum ranges generated from models are reliable. The optimum points were chosen to achieve the maximum extraction efficiency with the minimum possible reagent consumption which is desirable both economically and environmentally. In addition, a number of tests with a lower amount of extractant, which is the most expensive reagent in the process, and different equilibrium pH, which is the less controllable factor in the process were performed to examine the flexibility of models and goodness of fit out of the optimum ranges, as well as confirming the optimum points.

5.4.4 Stripping

Tests on the stripping process were carried out with the aim of cleaning and purifying the organic phase, to be reused in the extraction process. For this purpose, after conducting the predispersed solvent extraction process under optimum conditions at 100 ppm initial nickel concentration, the metal loaded organic phase was removed and contacted with different concentration of sulfuric acid in two different acid to organic (A/O) ratios. Figure 5.9 presents the results of stripping experiments.
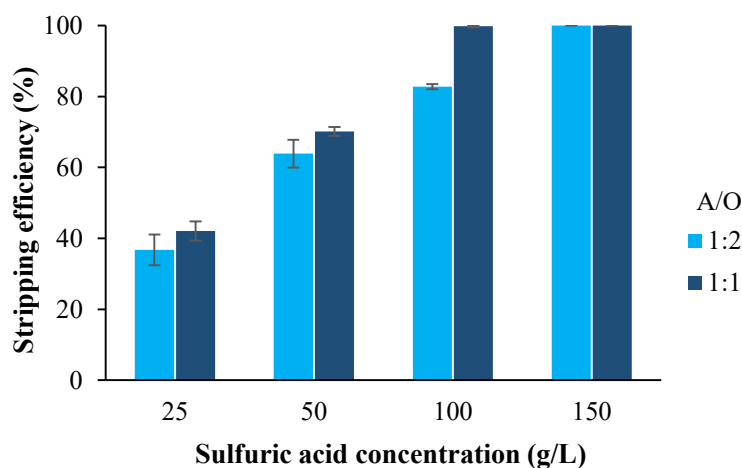
Figure 5.9. Stripping with different concentrations of sulfuric acid and different A/O ratios (error bars represent 95 % confidence intervals)

Figure 5.9 reveals that the maximum stripping efficiency (100 %) can be reached by using 100 g/L of sulfuric acid in the A/O ratio of 1:1 and 150 g/L of sulfuric acid in both A/O ratios. Since at the 150 g/L acid concentration the 100 % stripping can be obtained in both A/O ratios, the optimum stripping condition was selected to be 150 g/L sulfuric acid, and acid to organic ratio of 1:2 due to lower consumption of acid.

5.4.5 Recycling

Once the stripping process was conducted on the metal loaded organic phase and the organic phase became free of nickel ions, the recycled organic phase was used to make a new CLA dispersion and perform a new extraction process. In order to make the CLA dispersion, the recycled organic

phase was gradually added to 0.5 % SDS solution up to the point that PVR of 4 was reached. The prepared CLA dispersion was added to an equal volume of nickel solution at an initial nickel concentration of 100 ppm. The extraction process was carried out exactly the same as the one with freshly made CLAs. Once the equilibrium pH of mixing solution of CLAs and nickel solution reached 5, the raffinate was removed and filtered and analyzed using ICP-OES. The results for 5 replicates are presented in Table 5.8.

Table 5.8. Extraction results using recycled organic phase

Test number	Ex. Con. (% w/v)	PVR	S. Con. (% w/v)	Eq. pH	Extraction (%)
1	Recycled (0.7)	4	0.5	5	99.56
2	Recycled (0.7)	4	0.5	5	99.35
3	Recycled (0.7)	4	0.5	5	99.68
4	Recycled (0.7)	4	0.5	5	99.42
5	Recycled (0.7)	4	0.5	5	99.39

The results in Table 5.8 demonstrate the high extraction efficiency of recycled organic phase. No change in the extraction percentage of CLAs made from recycled organic phase (Table 5.8) was observed compared to freshly made CLAs (Table 5.7; Test number 6). This confirms that the organic phase can be recycled and reused without any reduction in its extraction efficiency. By successful recycling of organic phase, a full extraction- stripping process can be proposed as shown in Figure 5.10.
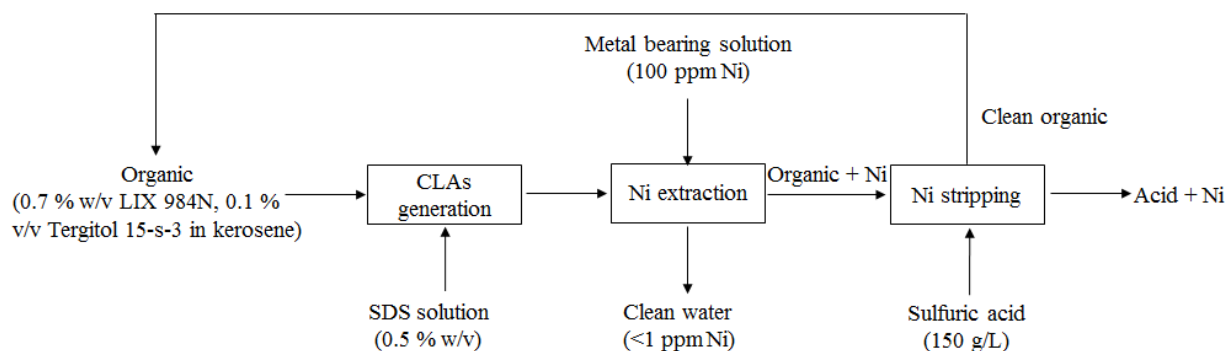
Figure 5.10. The proposed extraction, stripping processes flowsheet under the optimum conditions at 100 ppm nickel concentration

The recyclability of organic phase makes PDSE a potential separation method in heavy metal removal and wastewater treatment; it reduces the high operational cost of extractant and environmental impacts of organic contamination, which are considered to be major concerns of many treatment methods.

5.4.6 Comparison between predispersed solvent extraction and conventional solvent extraction

Solvent extraction (SX) tests in the absence of surfactants were conducted under the same conditions as predispersed solvent extraction tests. PDSE experiments were performed at optimum experimental conditions which were defined in Section 5.4.3. and for SX experiments, the volumes of organic phase were calculated based on the optimum PVR values. Other parameters such as nickel solution volume and concentration, extractant concentration and pH were kept the same as PDSE experiments. The results are shown in **Figure 5.11**.
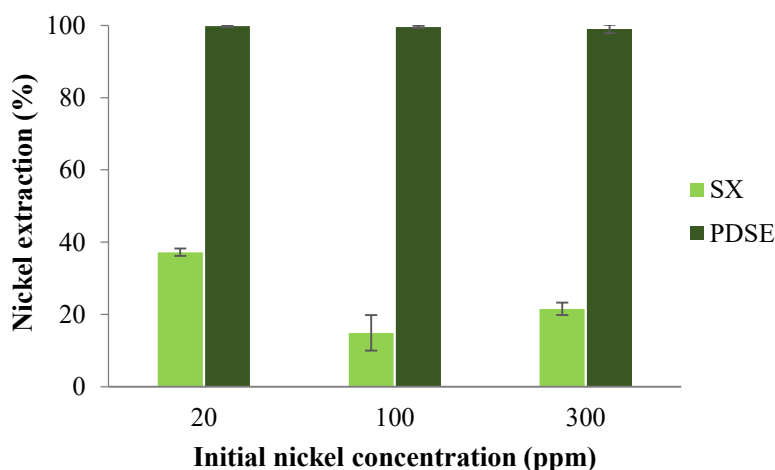
Figure 5.11. Nickel extraction using solvent extraction (SX) and predispersed solvent extraction (PDSE)

It can be seen from **Figure 5.11** that PDSE exhibits very higher extraction when compared to solvent extraction. Nickel extraction with PDSE was approximately 3, 7, and 5 times higher than conventional SX at 20 ppm, 100 ppm and 300 ppm nickel respectively. This significant difference between extraction efficiency of PDSE and SX could be due to the higher interfacial area which is

provided by micrometer sized CLAs in PDSE. Furthermore, using anionic surfactant in the CLAs' structure may be another reason for this remarkable improvement, due to establishing electrostatic interactions which facilitate the ion exchange reaction between extractant and nickel ions as it was explained in Section 5.4.2.1.

5.5   CONCLUSIONS

The predispersed solvent extraction of nickel ions from dilute solutions using colloidal liquid aphrons was investigated. Due to a need to comprehensive study of the effect of experimental parameters on the extraction process, a design of experiments technique was employed. Four experimental variables with five levels were investigated using response surface methodology. Extractant concentration, SDS concentration, PVR and equilibrium pH were the four parameters that were investigated.

It was found that for 20 ppm and 100 ppm initial nickel concentration, equilibrium pH was the most significant parameter. The most significant factor at 300 ppm was the extractant concentration which was also the second important factor at 100 ppm nickel concentration. PVR was found to be significant in all three concentrations and SDS concentration had significant effect only at 20 ppm. Optimum values for this process were determined using contour and overlaid plots and confirmed by validation tests. While different extractant concentration, PVR and SDS concentration is needed for optimum nickel extraction at different nickel concentrations, the optimum equilibrium pH was determined to be 5 for all three concentrations.

This optimum point was selected without any initial consideration or limitation, if there is any limitation in each of the parameters the new set of optimum point could be obtained using the proposed models; and after validation by real experiments, could be used as new optimum points.

Stripping experiments were carried out with the organic phase obtained from extraction tests with 100 ppm initial nickel concentration and the optimum stripping conditions were determined to be 150 g/L sulfuric acid and A/O ratio of 1:2. The stripped and nickel-free organic phase was subsequently used to generate a new CLA dispersion to apply in extraction process in order to examine the recyclability. The experimental results showed no difference between the extraction efficiency of CLAs made with recycled organic phase and freshly made CLAs.

Both this chapter and Chapter 4 have shown that copper and nickel can be extracted from dilute aqueous solutions of one cation using CLAs. The following chapter extended this to the selective recovery of each of these from a solution containing calcium as an undesired contaminant.

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CHAPTER 6. SELECTIVE REMOVAL OF COPPER AND NICKEL IONS FROM SYNTHETIC PROCESS WATER USING PREDISPERSED SOLVENT EXTRACTION

6.1 ABSTRACT

Predispersed solvent extraction of copper and nickel from single cation bearing solutions were investigated in Chapters 4 and 5, respectively. In this chapter predispersed solvent extraction and stripping of copper and nickel ions from synthetic process water containing calcium ions was investigated, and the effect of four experimental parameters on extraction efficiency was studied. The extraction process was performed in two stages. In the first stage, maximum copper extraction was targeted with nickel extraction minimized. During the second stage, nickel was extracted from the remaining copper free aqueous solution and optimum conditions for maximum nickel recovery were determined. In order to investigate the effect of experimental parameters including: extractant concentration, phase volume ratio, equilibrium pH and calcium concentration on the nickel extraction, response surface methodology (RSM) was used. It was found that equilibrium pH, extractant concentration and calcium concentration were the most significant factors on the nickel extraction. While the first two factors had a positive effect, the latter one negatively affected the response. In order to selectively extract copper, while keeping nickel extraction to a minimum, the following conditions were determined: extractant concentration of 0.2-0.3% (w/v), PVR of 2, equilibrium pH of 2.5 and calcium concentration can be varied from 50 to 350 ppm. The optimum conditions for maximum nickel concentration were also found for three level of calcium concentrations. The stripping experiments were also carried out and optimum acid concentrations of 10 g/L and 5 g/L were determined for stripping of copper and nickel respectively.

6.2 INTRODUCTION

In spite of various wastewater treatment techniques and strict environmental regulations, large volumes of industrial effluents which contain dissolved heavy metal ions are being discharge into environment every day. One of the primary source of this heavy metal bearing effluents are mining, and specifically mineral processing industry. For example, the wastewater of process plant in the

Sudbury region of Ontario, Canada, may contain around 10 ppm copper, 20 ppm nickel and up to 500 ppm calcium, before any treatment (Nazari *et al.*, 2015b). Whereas, according to Canada's waste discharge regulations, the authorized limits of copper and nickel in waste to be discharged to the environment are 0.5 ppm and 1 ppm, respectively (*Metal Mining Effluent Regulations*, 2016).

There are several methods utilized to remove heavy metals from wastewater streams such as solvent extraction (Kul & Oskay, 2015; Li *et al.*, 2011; Yun *et al.*, 1993), chemical precipitation (Chen *et al.*, 2009; Fu *et al.*, 2007; Ghosh *et al.*, 2011), ion-exchange and adsorption (Argun, 2008; Berber-Mendoza *et al.*, 2006; Dąbrowski *et al.*, 2004; Inglezakis *et al.*, 2007; Rodríguez-Iznaga *et al.*, 2002), membrane technologies (Guha *et al.*, 1994; Raghuraman *et al.*, 1994; Valenzuela *et al.*, 1997), electrochemical methods, coagulation, flocculation, flotation (Casqueira *et al.*, 2006; Heidmann & Calmano, 2008; Khelifa *et al.*, 2005; Merzouk *et al.*, 2009; Shafaei *et al.*, 2010), and biosorption (Nazari *et al.*, 2014, 2015a; Volesky & Holan, 1995; Xu & Liu, 2008). Among these techniques solvent extraction is one of the most established separation technologies for wastewater treatment (Fu & Wang, 2011). Solvent extraction, or liquid-liquid extraction, is a simple and versatile process which offers a highly selective and rapid separation. Although one of the major applications of solvent extraction is the selective separation of heavy metal ions from wastewater streams, it is not very effective and economically feasible for the treatment of wastewater with low concentrations of metals. This can be due to the low interactions between the organic phase (contains extracting agent) and metal ions in the aqueous phase. Predispersed solvent extraction (PDSE) is an alternative extraction technique which overcomes this problem by pre-dispersion of organic phase into small globules (called aphrons). These colloidal liquid aphrons (CLAs) are micro-meter sized surfactant stabilized multilayer droplets which provide high interfacial area resulting in higher and faster extraction compared to conventional solvent extraction technique.

PDSE showed many potential applications such as: extraction of antibiotics (Lye & Stuckey, 2000) and organic pollutants (Hong *et al.*, 2001; Kim *et al.*, 2004); separation of bio-based products (Birajdar *et al.*, 2015); removal of metals (Hahm *et al.*, 2003; Luo *et al.*, 2013); oil recovery (Sebba, 1985, 1987); and water remediation (Yan *et al.*, 2011). PDSE was first employed in 1980s by Sebba (1985), in order to extract organic solutes from water and further studies reveled the higher efficiency of PDSE compared to conventional solvent extraction (Michelsen *et al.*, 1986; Wallis

et al., 1986). Despite showing promise, the application of PDSE is not well-established and requires more research. In the previous chapters, this technique was employed to extract copper (Chapter 4) and nickel (Chapter 5) ions from dilute aqueous solutions containing one type of cation.

In this chapter, the selective extraction and stripping of copper and nickel ions from synthetized process water containing calcium ions using PDSE is detailed. For this purpose, the effects of four important process parameters: initial extractant concentration (Ex. Con.), phase volume ratio (PVR), equilibrium pH (Eq. pH), and calcium concentration (Ca Con.) on the PDSE of metal ions were studied, to optimize the process for maximum copper and nickel extraction. Response surface methods and central composite design were used as tools for designing and conducting the experiments, determining the significant parameters and optimizing the extraction percentages as response. Stripping experiments then performed in order to design a complete process. All statistical analyses were produced using "Minitab® 17 statistical software" and contour plots were drawn using "MATLAB R2015b academic use".

6.3   MATERIALS AND METHODS

6.3.1   Materials

The synthetic wastewater solutions were prepared according to the composition of a Sudbury nickel mine tailings pond. These solutions contain 10 ppm of copper (II), 20 ppm of nickel (II) and 20-500 ppm of calcium ions. In order to make these solutions. anhydrous cupric sulfate ($CuSO_4$) (Fisher scientific, India), nickelous sulfate ($NiSO_4.6H_2O$) (Anachemia, USA), and anhydrous calcium sulfate ($CaSO_4$) (Acros, USA) were dissolved in reverse osmosis purified water.

6.3.2   Preparation of CLAs

The CLA dispersion was prepared by the drop-wise addition of the organic phase containing LIX 984N, kerosene, and oil soluble surfactant (Tergitol 15-S-3) to a foaming aqueous solution containing 0.4 % (w/v) of water soluble surfactant (sodium n-dodecyl sulfate). Details of CLA formation can be found in Chapter 4, Section 4.3.2.

6.3.3 Predispersed solvent extraction process

An equal amount of prepared CLA dispersion and metal-containing solution were mixed, followed by pH adjustment while the mixture was being stirred. After the extraction process, the concentration of each metal in the raffinate was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the metal concentration in the loaded organic phase was calculated by mass balance. More details about the extraction process are available in Chapter 5, Section 5.3.4.

The extraction experiments were performed in two stages. In the first stage, the process was optimized for the maximum copper extraction and minimal nickel extraction. Once the copper ions were extracted during the first stage, the raffinate was processed via the second extraction stage which was optimized for the maximum nickel extraction and the organic phase obtained from each extraction stage was sent to subsequent stripping stage. The flowsheet of the whole process is presented in Figure 6.1.
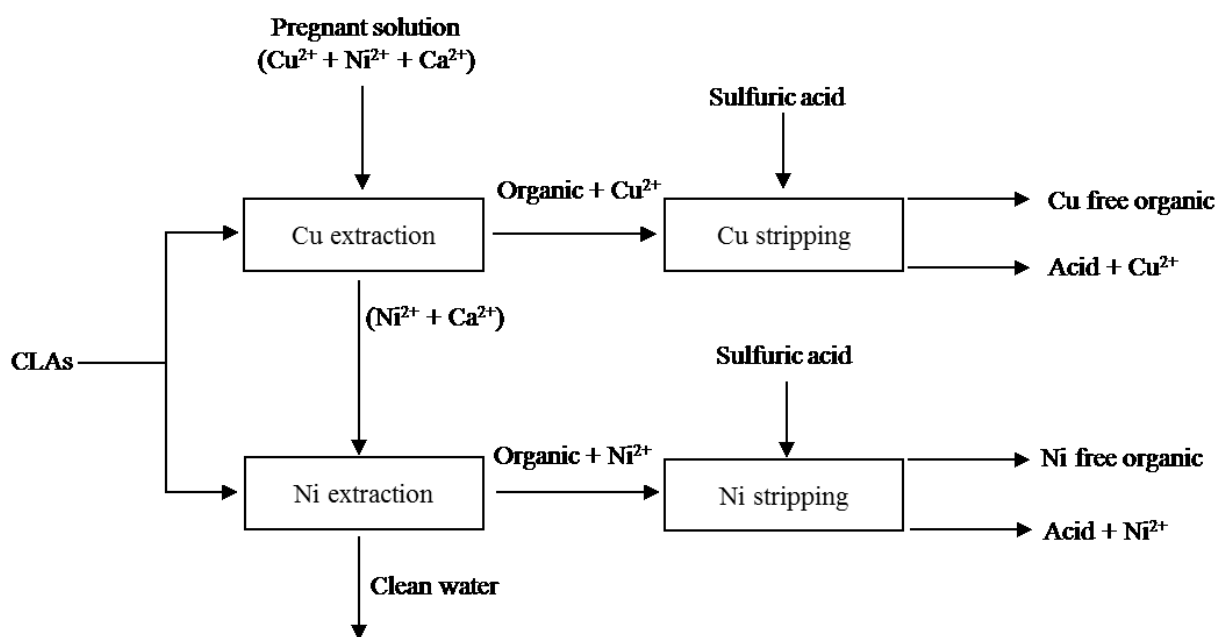

Figure 6.1. Flowsheet of the two stage extraction and stripping of copper and nickel ions

Once the optimum extraction conditions for copper and nickel extraction were determined, the extraction process under the optimum conditions was conducted in a column. These experiments aimed at investigating the selective PDSE at a larger scale and also to apply a potential industrial separation technique by eliminating the centrifugation process. For this purpose, a glass column with a diameter of 5.7 cm, a height of 35 cm, and a sampling point at 1.5 cm above the bottom of the column (Figure 6.2), was used. 150 mL of process water with equal volume of CLA dispersion were placed in the column and pH was adjusted to the optimum pH for each extraction stage. Once the pH was adjusted, phase separation process started and samples were taken over different time intervals. These experiments were carried out under two different conditions: without any flocculant; and with the addition of the cationic FO 4115 SH flocculant (SNF Inc., USA).
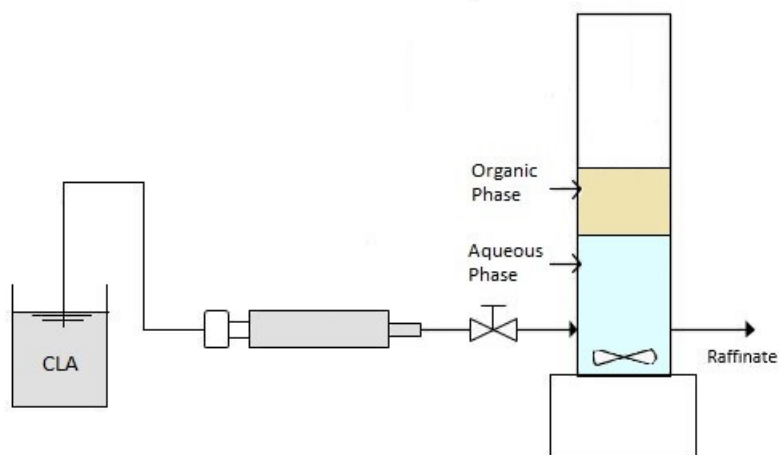
Figure 6.2. Extraction column

6.3.4   Stripping process

The stripping experiments were carried out using optimum conditions for extraction. Once the extraction processes were completed and the raffinates were removed to analyze the metals concentration, the organic phase was contacted with different concentration of sulfuric acid with 1:1 acid to organic (A/O) volumetric ratio to find the optimum acid concentration.

6.4   RESULTS AND DISCUSSION

6.4.1   Design of extraction experiments

The extraction experiments were designed using response surface methodology (RSM) and central composite design (CCD). The details about RSM and CCD can be found in Chapter 5, Section. 5.3.6. Four experimental parameters including extractant concentration (x_1), PVR (x_2), equilibrium pH (x_3) and calcium concentration (x_4) were selected to be the main factors. The coded and corresponding actual values of variables are shown in Table 6.1.

Table 6.1. Independent variables and their levels

Variable	Symbol	Coded variable Level				
		Lowest	Low	Center	High	Highest
Extractant concentration (% w/v)	x_1	0.05	0.20	0.30	0.40	0.55
Phase volume ratio	x_2	1	2	3	4	5
Equilibrium pH	x_3	1.5	3.0	4.5	6.0	7.5
Calcium concentration (ppm)	x_4	20	135	250	365	480

Once the experiments were performed in the predetermined random order, the responses were calculated and presented in Table 6.2.

Table 6.2. Coded, actual level and results

Run	Coded Level of factors				Actual level of factors				Response (Extraction, %)		
	x_1	x_2	x_3	x_4	Ex. Con.	PVR	Eq. pH	Ca Con.	Cu	Ni	Ca
1	1	1	1	-1	0.400	4	6.0	135	100.00	93.64	35.57
2	1	-1	1	1	0.400	2	6.0	365	100.00	68.29	36.99
3	1	1	-1	1	0.400	4	3.0	365	100.00	6.88	11.98
4	-1	1	1	-1	0.200	4	6.0	135	98.37	49.17	25.44
5	0	2	0	0	0.300	5	4.5	250	100.00	42.90	16.33
6	-1	-1	1	1	0.200	2	6.0	365	98.98	19.37	27.77
7	-1	-1	1	-1	0.200	2	6.0	135	99.83	28.60	43.56
8	2	0	0	0	0.550	3	4.5	250	99.73	38.46	27.48
9	0	0	0	0	0.300	3	4.5	250	99.78	28.73	17.07
10	0	-2	0	0	0.300	1	4.5	250	99.61	30.29	49.32
11	0	0	0	0	0.300	3	4.5	250	99.98	25.01	16.89
12	0	0	0	0	0.300	3	4.5	250	99.64	22.57	15.32
13	0	0	0	0	0.300	3	4.5	250	99.79	33.58	16.72
14	0	0	0	2	0.300	3	4.5	480	99.40	27.78	8.41
15	-1	1	-1	-1	0.200	4	3.0	135	100.00	10.54	24.81
16	-1	1	1	1	0.200	4	6.0	365	99.83	24.21	10.99
17	-1	-1	-1	1	0.200	2	3.0	365	99.89	5.097	11.50
18	0	0	-2	0	0.300	3	1.5	250	37.77	0.00	7.96
19	0	0	0	0	0.300	3	4.5	250	100.00	24.77	14.30
20	-2	0	0	0	0.050	3	4.5	250	99.98	5.93	14.08
21	0	0	2	0	0.300	3	7.5	250	100.00	62.12	31.27
22	1	1	1	1	0.400	4	6.0	365	99.99	70.04	5.13
23	1	-1	-1	-1	0.400	2	3.0	135	98.62	8.19	21.90
24	0	0	0	0	0.300	3	4.5	250	99.73	36.31	22.19
25	1	1	-1	-1	0.400	4	3.0	135	100.00	8.89	26.37
26	0	0	0	0	0.300	3	4.5	250	98.85	29.54	14.11
27	-1	-1	-1	-1	0.200	2	3.0	135	99.93	3.16	17.06
28	1	-1	1	-1	0.400	2	6.0	135	99.51	90.30	66.20
29	-1	1	-1	1	0.200	4	3.0	365	99.54	8.68	15.16
30	0	0	0	-2	0.300	3	4.5	20	99.45	69.69	56.66
31	1	-1	-1	1	0.400	2	3.0	365	100.00	6.14	8.60

From the data presented in Table 6.2, it can be observed that copper extraction percentage was near the maximum under almost all experimental conditions, except at the lowest level of equilibrium pH (1.5). Therefore, the response model was only defined for nickel extraction and further optimization stages were designed to have selective extraction of copper and nickel (i.e. minimal nickel extraction and maximum copper, followed by maximum copper extraction).

The second order response model for nickel extraction (y_{Ni}) was represented as a function of extractant concentration (x_1), PVR (x_2), equilibrium pH (x_3), and calcium concentration (x_4). The coded model equation is presented as Equation 6.1.

$$y_{Ni} = 27.63 + 12.31\ x_1 + 2.65\ x_2 + 20.57\ x_3 - 5.60\ x_4 - 2.09\ x_1^2$$
$$+ 1.21\ x_2^2 - 0.18\ x_3^2 + 4.82\ x_4^2 - 2.33\ x_1 x_2 + 15.49\ x_1 x_3 \qquad \text{Equation 6.1}$$
$$- 1.31\ x_1 x_4 + 1.13\ x_2 x_3 - 1.33\ x_2 x_4 - 4.85\ x_3 x_4$$

The summarized ANOVA table (Table 6.3) shows the important properties of the model. According to this data the p-value of the model is smaller than 0.05, the model's F-value is higher than the F value in the F-distribution table with 5 % significance level, ($F_{0.05}$ $_{(14,\ 16)}$ = 2.448), and the p-values of the lack of fit is bigger than 0.05. Therefore, the model is considered to be acceptable and shows a good fit. In addition, the R^2 value calculated for this model is 94.24 % which again confirms the accuracy and good fit of the model (Montgomery, 2012).

Table 6.3. Summarized ANOVA for regression model.

p- value	F-value	R^2 (%)	S	lack of fit
0.000	18.69	94.24	8.46	0.051

6.4.2   Analysis of variables for nickel extraction

In order to analyze the experimental variables and determine the significant factors, p and T values in Table 6.4 can be studied. The p-values in this table determine which factors and interactions are important in the proposed model; however, in order to figure out the magnitude of their importance and the sign of their effect on the response T-values should be used.

Table 6.4. Summarized Student's t-test for nickel extraction tests

	p-Value	T-value	Contribution (%)
x_1	0.00	6.11	14.32
x_2	0.15	1.51	0.97
x_3	0.00	11.73	54.56
x_4	0.01	-2.97	5.84
x_1^2	0.22	-1.26	1.08
x_2^2	0.46	0.76	0.11
x_3^2	0.91	-0.11	0.05
x_4^2	0.02	2.62	2.48
$x_1 x_2$	0.39	-0.88	0.28
$x_1 x_3$	0.00	5.86	12.36
$x_1 x_4$	0.63	-0.49	0.09
$x_2 x_3$	0.60	0.53	0.10
$x_2 x_4$	0.54	-0.62	0.14
$x_3 x_4$	0.04	-2.27	1.86

From the data in Table 6.4, it can be seen that the most significant factor in this process is equilibrium pH with the T-value of 11.73 greater than 50 % contribution, followed by extractant concentration (14.32 % contribution) and calcium concentration (5.84 % contribution). Although The first two significant factors (Eq. pH and Ex. Con.) had positive effect on the response, the last one (Ca Con.) had a negative effect on the response according to the negative sign of T-value.

The contour plots of the fitted model are displayed in Figure 6.3. The contour plots show the relationship between two variables and responses while the other variables are at the center (0) level (Extractant Concentration 0.3 % (w/v), PVR 3, Equilibrium pH 4.5, Calcium Concentration 250 ppm).
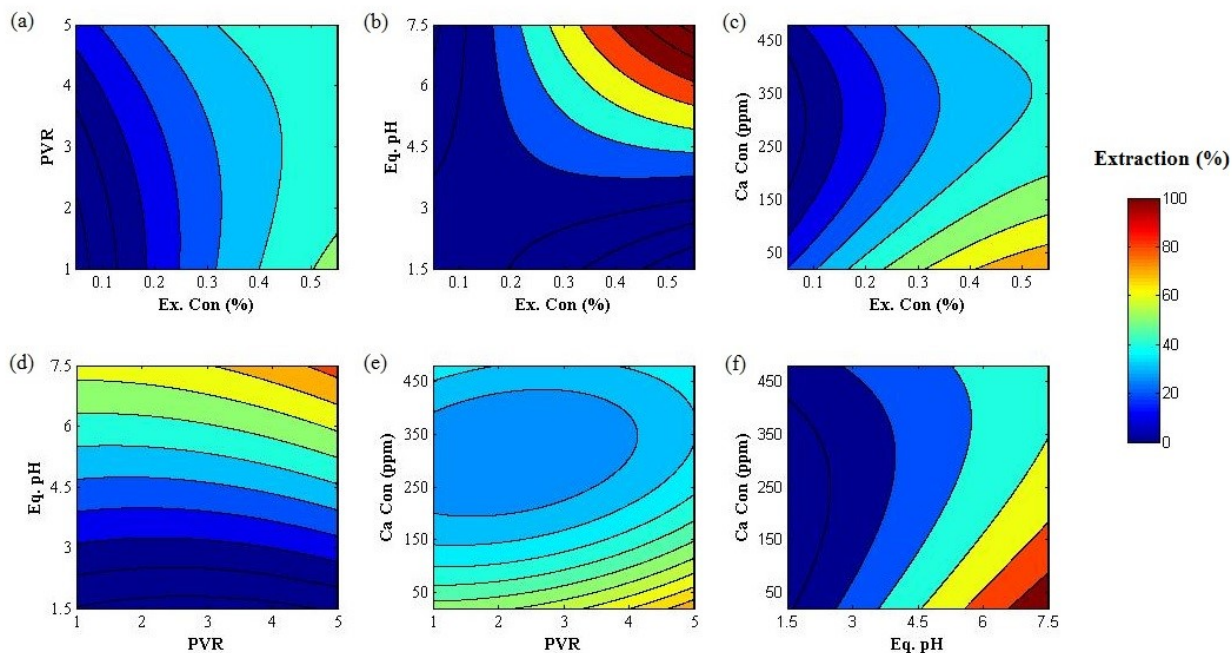
Figure 6.3. Contour plots of Ni extraction. Hold values Ex. Con. 0.3 % (w/v), PVR 3, Eq. pH 4.5, Ca Con. 250 ppm. (a): effect of Ex. Con. & PVR; (b): effect of Ex. Con. & Eq. pH; (c): effect of Ex. Con. & Ca Con; (d): effect of PVR & Eq. pH; (e): effect of PVR & Ca Con; and (f): effect of Eq. pH & Ca Con.

6.4.2.1 *Effect of extractant concentration*

Extractant concentration is one of the significant factors in the nickel extraction (with 14 % contribution) which has positive effect on the response (Table 6.4) meaning that the extraction of nickel ions increases by increasing the extractant concentration which can also be seen from Figure 6.3 (a, b& c). Part b of Figure 6.3 shows that if the PVR and calcium concentration were kept constant at 3 and 250 ppm, respectively; the best results could be obtained at > 0.4 % Ex. Con. and high pH values (> 6).

The reason for this significant effect of extractant concentration on the nickel extraction is the ion-exchange mechanism which is involved in this process. The exchange of nickel for the hydrogen in the extractant is considered to be the main mechanism of solvent extraction of nickel using LIX 984N as extractant (Chauhan & Patel, 2014; Li *et al.*, 2011). This reaction can be simply shown in Equation 6.2.

$$\text{Ni}^{2+}_{\ (aq)} + 2\text{HR}_{\ (org)} \xrightleftharpoons{\hspace{1.2cm}} \text{NiR}_{2\ (org)} + 2\ \text{H}^{+}_{\ (aq)} \hspace{2cm} \text{Equation 6.2}$$

The components of the ion-exchange reaction are $\text{Ni}^{2+}_{\ (aq)}$ which represents the dissolved nickel ions in water; $\text{HR}_{2\ (org)}$ representing extractant (LIX 984N); $\text{NiR}_{2\ (org)}$ which represents nickel-extractant complex after ion-exchange; and $\text{H}^{+}_{(aq)}$ which is related to the pH of the system. With increasing extractant concentration, $\text{HR}_{2\ (org)}$ increases; thus, in order to reach to equilibrium and consume more extractant, the reaction tends to drive to the right direction resulting in more nickel being exchanged.

6.4.2.2 *Effect of phase volume ratio*

The PVR is the only factor in the PDSE of nickel with no significant effect on the response. Furthermore, PVR has neither a square effect nor two-way interaction with any of other factors that confirms the non-significant effect of PVR. However, a slight positive effect of this parameter on the extraction of nickel can be observed Figure 6.3 (d& e). This little improvement as a result of increasing of PVR is due to increasing of volume of the organic phase which was entered to the system.

In Chapter 5, Section 5.4.2.3, the PVR was introduced as an important factor in PDSE of nickel; however, it was considered to be non-significant in the extraction of nickel in the current system. The main reason for this could be different ranges which have been selected for these two processes. In Chapter 5, PVR was varied from 1-10, however in this chapter PVR range was 1-5. The other reason can be the existing of other metal cations in the system which make it very pH dependent. The influence of pH is very dominant with more than 54 % of contribution; hence, other factors have less effect consequently.

6.4.2.3 *Effect of equilibrium pH*

Equilibrium pH is the most significant parameter in the PDSE of nickel ions from synthetic process water with 56 % of contribution (Table 6.4). As it can be seen from Figure 6.3 (b, d& f) the process is highly affected by Eq. pH and the best results could be achieved at relatively high Eq. pH values. As it was shown in Equation 6.2 that H^{+}, which represents the equilibrium pH of the solution, is one of the key components of ion-exchange, which is on the opposite side to Ni^{2+} in the two-way

reaction. Therefore, in order to drive the reaction to the right and consume more Ni^{2+}, the concentration of H^+ should be kept low (high pH). Under this condition, in order to reach equilibrium and produce more H^+ ions in the right side, more nickel ions are exchanged with hydrogen ions on the left side.

Since the equilibrium pH is the most significant factor, the interaction between this factor with other factors is also important. According to Table 6.4 the interaction of equilibrium pH with two other significant factors (Ex. Con. and Ca Con.) are both considered to be significant. Although the interaction of Eq. pH with Ex. Con. has a positive sign, indicating that they move in the same direction and have a positive effect on the response (which also can be seen from linear effects), its interaction with Ca Con. has a negative *T*-value which is due to the different linear effect of these parameters.

6.4.2.4   *Effect of calcium concentration*

Calcium concentration is another significant parameter in the PDSE process that negatively affects the response. From Figure 6.3 (c, e& f) it can be seen that a lower amount of calcium is favored by this process. The negative effect of calcium concentration on nickel extraction is because the calcium ions also exist as Ca^{2+} and they can be exchanged with hydrogen ions as Cu^{2+} and Ni^{2+} do. Since LIX 984N is more selective to extract copper ions, the concentration of calcium does not affect copper extraction significantly. However, this extractant is not very selective for nickel over calcium; thus, there is a competition between Ca^{2+} and Ni^{2+} ions to be exchanged by H^+ ions, more calcium ion in the environment resulted in lower chance of nickel extraction. This is why calcium concentration has negative effect on the nickel extraction.

In case of square effects, Ca Con. was the only factor that had significant square effect. The positive *T*-value in square effect of Ca Con. (Table 6.4) means that the negative effect of calcium concentration on response (linear effect of Ca Con) lasts up to certain point and after that point it levels off and the response does not decrease remarkably by further increasing the Ca Con.

6.4.3 Optimization of process conditions

6.4.3.1 First stage of extraction: copper extraction

In order to selectively extract the copper ions from synthetic process water containing nickel and calcium the model was optimized to remove minimum nickel while the copper extraction was at a maximum. For this purpose, the response optimizer of Minitab 17 was used and the following points were selected. Since the calcium concentration was an uncontrolled factor (because calcium exists in the process water as an impurity) and could not be fixed to an optimum value, the optimum conditions were defined for three levels of Ca Con. The validity of these optimum conditions was also confirmed by validation test in which each point was tested five times to ensure the reproducibility of results. Table 6.5 shows the optimum points and responses (experimental and predicted by model) for the first stage of extraction.

Table 6.5. Optimum points for maximum copper and minimum nickel recovery with experimental and predicted responses.

Test number	Conditions				Response (Extraction, %)				
	Ex. Con. (% w/v)	PVR	Eq. pH	Ca Con. (ppm)	Experimental mean			Predicted	Error
					Cu	Ni	Ca	Ni	
1	0.2	2	2.5	50	99.61	10.68	55.02	12.50	-1.82
2	0.2	2	2.5	200	99.32	3.61	33.02	3.00	0.61
3	0.3	2	2.5	350	99.25	2.95	23.56	4.30	-1.35

Table 6.5 shows that by using low concentrations of extractant (0.2 %- 0.3 %) and a low ratio of organic to aqueous (2) at acidic pH (2.5), the copper ions could be extracted with more than 99 % of efficiency. Under this condition, nickel extraction was relatively low, and depended on the initial calcium concentration (the calcium extraction varied from 23 % to 55 %).

6.4.3.2 Second stage of extraction: nickel extraction

Once the copper ions were extracted from synthetic process water solutions, the aqueous solution was subjected to the extraction process one more time. This time the model was optimized for maximum nickel extraction. In order to find the optimum range with maximum nickel extraction overlaid contours were plotted. Drawing overlaid plots is an accurate way to find optimum conditions because it makes it possible to see the effect of all four factors in one plot. Figure 6.4

displays the overlaid plots of factors. Each line represents >95 % of nickel extraction and the regions with maximum responses at different conditions are shown.
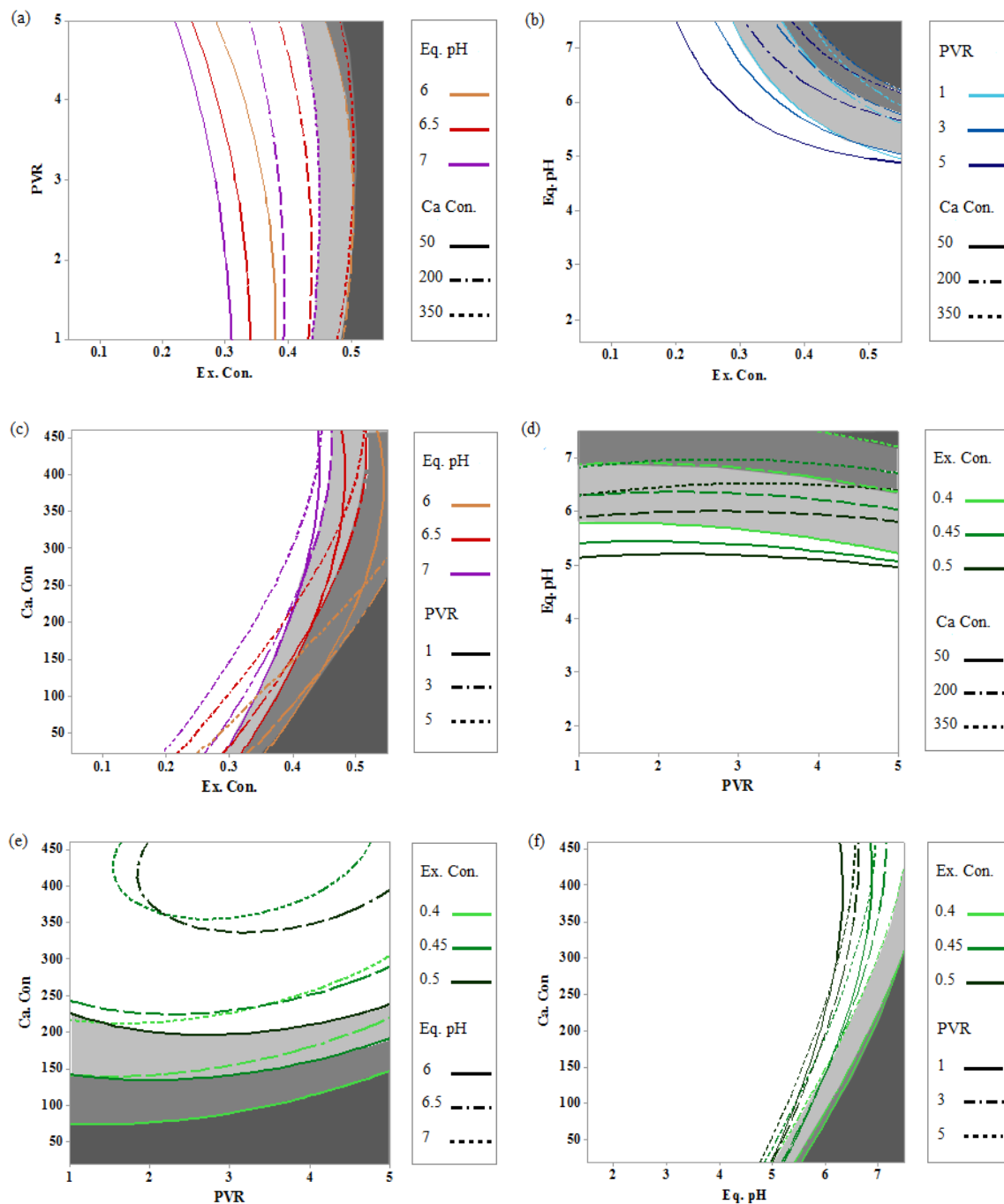
Figure 6.4. Overlaid plots for maximum nickel extraction (the lines represent ≥ 95 % extraction)

Using the overlaid contour plots, the following points (in Table 6.6) were found as optimum points for three different calcium concentrations. Validation tests also were carried out in order to validate the optimum points.

Table 6.6. Optimum points for maximum nickel recovery with experimental and predicted responses

Test number	Conditions				Response (Extraction, %)				
	Ex. Con. (% w/v)	PVR	Eq. pH	Ca Con. (ppm)	Experimental mean			Predicted *	Error
					Cu	Ni	Ca	Ni	
4	0.4	3	6	22	100.00	99.28	52.59	100.00	-0.72
5	0.4	3	6.5	133	100.00	95.11	52.85	99.06	-3.95
6	0.5	3	6.5	267	100.00	95.86	46.37	100.00	-4.14

* The predicted values higher than 100 are considered as 100

It can be seen from the data in Table 6.6 that with increasing calcium concentration either equilibrium pH or extractant concentration should be increased to maintain the high nickel extraction efficiency. This is due to the negative effect of calcium concentration on the extraction of nickel as explained previously. Thus, the positive effect of equilibrium pH or extractant concentration can compensate this negative effect.

Once the optimum extraction conditions for copper and nickel extraction were determined, the extraction process in a column under the optimum conditions was conducted. The column extraction experiments were also carried out in two stages. In the first stage, a synthetic aqueous solution (10 ppm Cu^{2+}, 20 ppm Ni^{2+} and 50 ppm Ca^{2+}) was subjected to extract copper in column under the optimum condition which was given in Table 6.5 (Ex con: 0.2 % (w/v), PVR: 2, and Equilibrium pH: 2.5).

Since the small size of CLAs decreases their rising velocity and may increase the phase separation time, a set of experiments were conducted with the addition of cationic flocculant (FO 4115 SH). The role of the cationic flocculant was to flocculate the negatively charged CLAs and thus increase their rise velocity. Figure 6.5 shows the copper recovery at different time intervals with and without the addition of the flocculant.
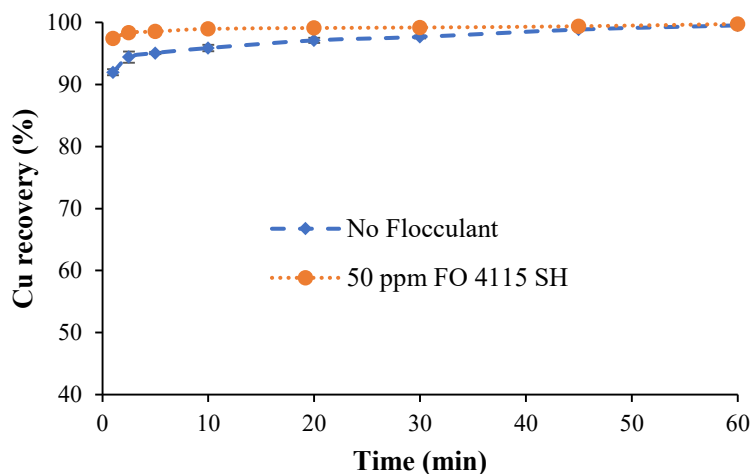
Figure 6.5. Copper recovery in the extraction column with and without addition of flocculant

It can be seen from Figure 6.5 that copper extraction and phase separation in column is a very fast process, resulting in more than 90 % of copper being recovered in the first minute either with or without the flocculant. The results also show that the phase separation was very fast even without the addition of flocculant which can be due to low PVR value (2) of the CLAs. This is due to the fact that the low PVR values resulted in larger and less stable CLAs, which tend to coalescence and become bigger, and larger CLAs can rise faster which improves phase separation (Matsushita *et al.*, 1992)

In the second stage the raffinate from the first stage was removed and filtered and was subjected to extract nickel using the optimum conditions detailed in Table 6.6 (Ex con: 0.4 % (w/v), PVR: 3 and Equilibrium pH: 6). Figure 6.6 shows the nickel recovery with and without the addition of flocculant.
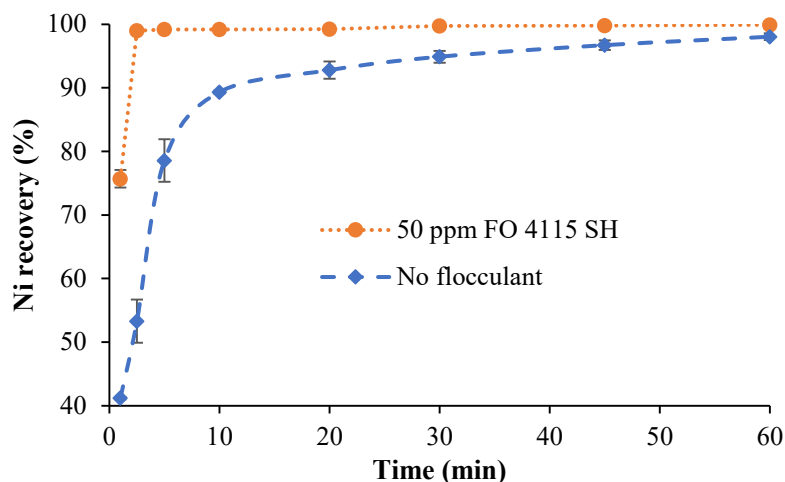
Figure 6.6. Nickel recovery in the extraction column with and without addition of flocculant

Figure 6.6 shows that without the addition of flocculant at least 10 minutes was required to reach 90 % nickel recovery, and maximum recovery was not obtained even after allowing 60 minutes. The reason for this slow phase separation is the high concentration of anionic surfactant (SDS) in the aqueous solution. The aqueous solution used for these experiments was the raffinate of copper extraction process and comprises dissolved SDS from the previous stage. Whereas, the addition of flocculant accelerated the phase separation process and increased the nickel recovery to more than 99 % in less than 3 minutes.

6.4.4 Stripping

The stripping experiments were performed on the metal loaded organic phase obtained from test number 2 and 5. Once the extraction process was completed, the organic phase was removed and contacted with different concentrations of sulfuric acid in a 1:1 acid to organic phase volume ratio and mixed for 10 minutes at 300 rpm. The acid phase was then removed, diluted and analyzed using ICP-EOS. The initial concentrations of metals in organic phase was calculated by mass balancing and compared to the stripped metal concentration in the acid phase. Figure 6.7 and Figure 6.8 display the stripping results for Cu-loaded (Table 6.5, Test # 2) and Ni-loaded (Table 6.6, Test # 5) organic phase respectively.
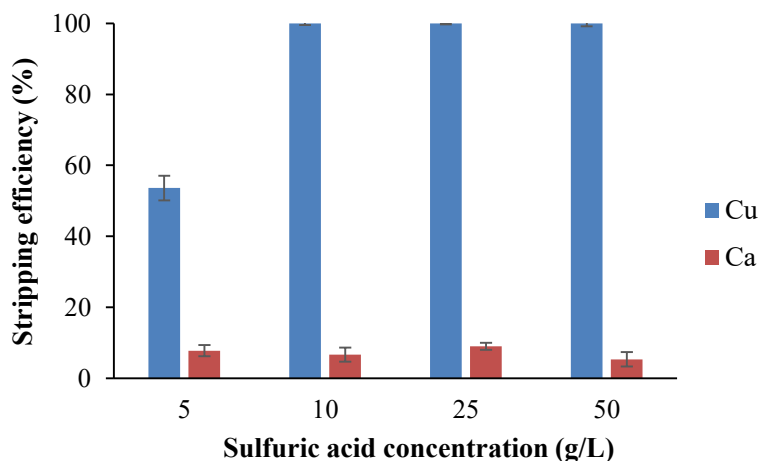
Figure 6.7. Stripping of copper loaded organic phase
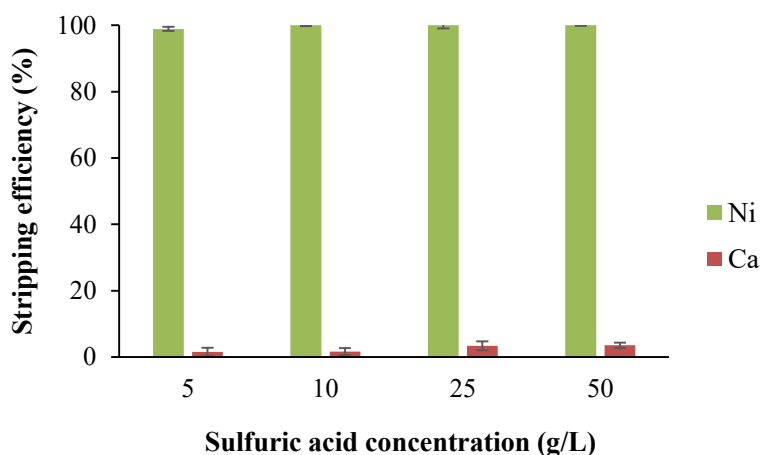
Figure 6.8. Stripping of nickel loaded organic phase

Figure 6.7 and Figure 6.8 indicate that although the initial concentration of copper in the solution was lower than initial concentration of nickel (10 ppm and 20 ppm, respectively), higher concentration of sulfuric acid was needed to strip Cu than Ni. In order to strip the copper loaded metal at least 10 g/L of sulfuric acid solution was required. However, 5 g/L sulfuric acid was able to strip nearly 99 % of the nickel from the organic phase. Since the stripping process is the opposite reaction of extraction, the stripping pH should be low enough to prevent extraction and drive the

reaction in the opposite side; thus, copper requires a lower pH (higher concentration of sulfuric acid) than Ni.

Furthermore, less than 10 % of calcium was stripped with these concentrations of sulfuric acid. Therefore, copper and nickel could be selectively extracted and stripped by selecting the optimum operating conditions appropriate for each metal.

6.5 CONCLUSIONS

Two stage PDSE of synthetic process water was successfully applied, which resulted in the selective extraction of copper and nickel ions. It was found that copper can be selectively extracted in the first stage of extraction using relatively low values of extractant concentration (0.2 %- 0.3 % (w/v), PVR (2), and equilibrium pH (2.5). in the second stage of PDSE, nickel was removed from the copper free solution under the optimum conditions. Since the concentration of calcium ions, which was one of the significant factors in this process, was not a controllable factor, the optimum conditions for each stage of extraction were determined at three levels of calcium concentrations. At low concentration of calcium, Ex. Con. of 0.4 %, PVR of 3 and Eq. pH of 6 are required to have >99 % of nickel extraction. By increasing the calcium concentration either Eq. pH or Ex. Con or both should be increased to have high nickel extraction. The optimum stripping conditions for both copper loaded and nickel loaded organic phase were also found, which were 10 g/L of sulfuric acid for copper and 5 g/L for nickel and 10 minutes mixing time at the speed of 300 rpm. Finally, the successful extraction experiments in column which eliminates centrifuging process offers the potential application of PDSE in industrial scales.

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CHAPTER 7.   CONCLUSIONS, CONTRIBUTIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1   CONCLUSIONS

This thesis focused on treating aqueous solutions containing low concentrations of heavy metals using colloidal liquid aphrons *via* the predispersed solvent extraction technique. This goal was achieved in two steps. In the first step, the individual extraction of copper and nickel from dilute aqueous solutions was investigated and the important experimental parameters were determined. During the second step, the selective extraction of copper and nickel from synthetic process wastewater was studied, and optimum conditions for extracting each metal action were determined. Furthermore, the characterization of colloidal liquid aphrons on the basis of size and stability was performed as well as stripping and recyclability studies. The following conclusions can be drawn from this research:

- Size distribution of CLAs using different experimental conditions were investigated and it was observed that CLAs were in the micrometer size range, and their size was affected by the phase volume ratio (PVR) and water soluble surfactant concentration. The larger PVR and higher concentration of anionic surfactant resulted in smaller size of CLAs. These observations were also confirmed by optical micrographs.

- CLAs can be stored for at least two months without any change in their physical properties and extraction ability.

- Using PDSE, more than 99 % of the copper was removed from dilute solution at acidic pH values (3.5-5.5). Less than one minute contact of time was required, and there was no additional mixing required, which is both time and energy consuming.

- The charge of the water soluble surfactant has a greater influence on the extraction ability of CLAs than its concentration. In order to extract positively charge metal ions, an anionic surfactant was required.

- Using a column for phase separation, copper recovery was slow and at least 20 minutes was required to remove 90 % of the copper from the solution. The addition of a cationic flocculant improved the recovery rate to 98 % in less than 5 minutes.

- PDSE showed promising results on nickel extraction with more than 99 % extraction possible under the optimum experimental conditions.

- PDSE experiments on three different initial concentrations of nickel showed that the impact of experimental parameters on the extraction rate varied with concentration. In lower initial nickel concentrations (20 ppm and 100 ppm), equilibrium pH was the most significant factor while in higher concentration (300 ppm), extractant concentration was the most significant factor. In addition, for 20 ppm metal ion concentration, the extractant concentration had an insignificant effect; however, at 100 ppm and 300 ppm, the concentration of anionic surfactant was the least significant factor on the nickel extraction.

- Ion exchange and electrostatic interactions are believed to be the two major contributing mechanisms in the predispersed solvent extraction of copper and nickel. The latter makes the initial contact between metal cations and negatively charged CLAs and the former completes the extraction by exchanging hydrogen ions in LIX984N structure for metal cations.

- The organic used in the generation of CLAs was shown to be recyclable. Preliminary experiments showed that the CLAs made with recycled organic have similar physical properties to the original one. Furthermore, the CLAs made from stripped and recycled organic, showed no difference on the extraction efficiency when compared to the freshly made CLAs.

- Selective PDSE of copper and nickel from synthetic process wastewater containing calcium was investigated, and it was found that copper can be selectively extracted at low pH using low concentrations of LIX 984N and a low PVR. Nickel then was extracted from the copper free solution at a higher pH using higher concentrations of LIX 984N.

- The extraction efficiency of nickel in ternary system (copper, nickel and calcium) is mostly affected by equilibrium pH, however extractant concentration and calcium concentration also had a significant effect on the nickel extraction.

- LIX 984N which has been used as extractant in PDSE processes was mostly selective on extraction of copper over nickel and calcium. Since the extractant did not exhibit significant selectivity for nickel over calcium, increasing calcium concentration negatively affected nickel extraction.

- Despite the lower initial concentration of copper in ternary system compared to nickel, the stripping of copper required higher concentration of sulfuric acid than nickel stripping which could be related to different extraction pH (equilibrium pH).

7.2   CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

As mentioned in Chapter 3, although there are various wastewater treatment techniques, each of these techniques has a number of limitation and drawbacks which restrict their applications in industry. These limitations can be varied from low selectivity and high capital or operational costs to low adaptability with existing equipment. The goal of this thesis was to examine the application of a not extensively-studied extraction technique to overcome the drawbacks of solvent extraction, whilst taking advantage of the simplicity and reliability of solvent extraction. PDSE exhibits a number of advantages over conventional solvent extraction that make it of interest. These advantages include: the ability to treat low concentrated wastewater; fast extraction; low energy consumption due to elimination of mixing stage; and low organic consumption. In addition, PDSE is able to keep the outstanding properties of solvent extraction such as high selectivity, simplicity and recyclability as well as good adaptability with existing or abandoned solvent extraction units. Therefore, the major contribution to knowledge of this work would be expanding PDSE as a wastewater treatment technique which can be applied in the situations for which solvent extraction is not effective.

7.3   FUTURE WORK

Although PDSE was first proposed in 1980s, it has not been comprehensively studied specially in case of metal recovery. This thesis detailed the PDSE of copper and nickel from dilute solutions.

However, there are specific aspects of this technique that require further investigation. These include:

- Fundamental investigation of CLA's structure and physicochemical properties. Such investigations should involve the generation of CLAs using different solvents and surfactants as well as various experimental conditions such as mixing rate, temperature and pressure.

- The application of PDSE in the selective removal of various metals such as base metals, heavy metals, and rare earth elements from different solutions such as chloride, ammoniacal and sulphate should be investigated. Also, wastewater samples from different industries should be subjected to a selective PDSE process.

- PDSE with a mixture of extractants in order to investigate any synergetic effects.

- Investigation into alternative phase separation techniques such as the application of colloidal gas aphrons.

- Scaling up and developing a continuous process.

APPENDIX

Effect of phase volume ratio, extractant and surfactant concentration on the predispersed solvent extraction of copper

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ABSTRACT

Solvent extraction is the one of the most common techniques for recovering metal ions from aqueous systems. However, solvent extraction is generally limited to relatively high concentrations and requires a high organic/aqueous ratio. Predispersed solvent extraction (PDSE) is a modified solvent extraction technique in which organic phase pre-comminute into colloidal liquid aphrons (CLAs). In this study, the extraction of copper by the PDSE technique was investigated. The main focus of this study was on the characterization and application of CLAs under different operational conditions, and to investigate the effects of different parameters on the extraction of copper from dilute streams. The effect of phase volume ratio (PVR), initial extractant concentration and initial copper concentration was studied and optimum conditions for copper removal using CLAs generated by LIX 984N as extractant, oil soluble and water soluble surfactants were proposed. Experimental observations indicated that PVR and initial LIX 984N concentrations had a significant effect on copper extraction.

Keywords: Predispersed solvent extraction, copper, colloidal liquid aphrons, wastewater treatment

INTRODUCTION

The effluents discharged from the mining and metallurgical industry contain a significant amount of heavy metals, which cause serious problems to the human health and environment (Akcil & Koldas, 2006). Heavy metal minerals are broken down slowly by weathering and exposure to rainfall and ground waters, and are usually insoluble in water (Dean, Bosqui, & Lanouette, 1972). Acid mine drainage (AMD) considered to be a significant environmental challenge in the mining industry, is formed during oxidation of sulfide minerals (Demopoulos, 1998; Feng, Aldrich, & Tan, 2000; Kuyucak, 2002; Tarkan & Finch, 2005; Younger, Banwart, & Hedin, 2002). Increasing commercial demand for metals, decreasing high grade resources and also ecologic problems caused by heavy metal bearing industrial effluents has impelled researchers to develop effective separation methods to extract heavy metals from dilute solutions.

Solvent extraction is the one of the favored techniques for metal recovery (including heavy metals) from aqueous systems due to its simplicity, speed, and versatility (Bullock & King, 1975; Doungdeethaveeratana & Sohn, 1998; Flett, Okuhara, & Spink, 1973; Ritcey & Ashbrook, 1979). It comprises removing specific metal ions from solution using an organic reagent. However, solvent extraction is generally limited to relatively high concentrations (> 500 mg/L) (Kentish & Stevens, 2001) and requires a large distribution ratio in the treatment of dilute streams, which causes an increase in the organic phase volume to an unacceptable value both from environmental and economic considerations (Kislik, 2012).

The requirement to treat large volume of dilute wastes cheaply had led researchers to develop a new method which was termed ''air-assisted solvent extraction'' (AASX) proposed by Finch and coworkers (Chen, Finch, Distin, & Gomez, 2003; Tarkan & Finch, 2005). The major goal is providing a high specific surface area with low organic/aqueous ratio while maintaining rapid phase separation. Although AASX technique was successful in overcoming some drawbacks of conventional solvent extraction, low recovery and high extraction time are two major disadvantages of this technique that limit its application in the industry (Li, Chen, & Hsiao, 2008; Tarkan & Finch, 2005; Tarkan, Gelinas, & Finch, 2006).

Predisposed solvent extraction (PDSE) is the other modified solvent extraction technique which was first proposed by Sebba (1985) in order to overcome major disadvantages of conventional solvent extraction (need for mixing-settling stage and high solvent/aqueous ratio). The effectiveness of the PDSE method was shown to be 5 to 10 times greater than conventional solvent extraction using the same quantity of the solvent and there was a considerable drop in solvent to feed ratio (1:500) (Zhang et al., 1996). In PDSE, liquid-liquid extraction is performed using a system called colloidal liquid aphrons (CLAs) which as defined by Sebba (1987) are micron-sized solvent droplets encapsulated by a thin soapy (aqueous) shell. Colloidal liquid aphrons have several beneficial properties, such as high stability and large interfacial area which make them of interest to separation processes (Lee et al., 2002)

PDSE has been applied to various applications such as removal of metals (Hahm et al., 2003; Save, Pangarkar, & Kumar, 1994; Sebba, 1985, 1987), and hydrophobic organic compounds (Lee, Hong, & Hwang, 2000), recovery of organic acid from fermentation process (Kim, Hong, & Hong, 2002), oil recovery (Sebba, 1985, 1987), and the recovery of proteins in bioprocess (Lye, Pavlou, Rosjidi, & Stuckey, 1996). PDSE has also potential application in wastewater treatment especially for dilute streams and for compounds those are less volatile than water.

The purpose of this study is to demonstrate the potential of PDSE for the extraction of copper ions from dilute aqueous solutions and to investigate the effect of the experimental parameters on the process efficiency. Furthermore, preliminary tests were carried out to investigate the structure of colloidal liquid aphrons.

EXPERIMENTAL

Materials

Copper (II) solutions were prepared by dissolving anhydrous cupric sulfate ($CuSO_4$) (Fisher scientific) in reverse osmosis purified water. For the CLA dispersion formulation, the solvent used was Kerosene (Sigma-Aldrich) containing n-paraffins (27.08 %), naphthenes (55.92 %), aromatics (16 %) and olefins (1 %) with a density of 821.3 kg/m^3. The copper extractant was LIX 984N (BASF, Germany) which was a 1:1 volume blend of LIX 860N-I (5-nonyl salicylaldoxime) and LIX 84N-I (2-hydroxy-5-nonylacetophenone oxime) in a high flash point hydrocarbon diluent. The anionic surfactant sodium n-dodecyl sulfate (SDS) 99 % (Avocado,UK) and nonionic surfactant Tergitol 15-S-3 (Talas, USA) were used as the water soluble and oil soluble surfactant respectively in the CLAs formation process. 1 M sulfuric acid (Fisher Scientific) was used to modify pH and all aqueous phases were prepared from reverse osmosis purified water.

CLAs Generation

The CLA dispersion was prepared by the slow drop-wise addition of the organic phase containing LIX 984N (0.1 %, 0.2 %, and 0.5 % (w/v) in kerosene) into a foaming aqueous solution containing anionic surfactant SDS (0.1 %, 0.24 %, 0.5 %, and 0.7 % (w/v) in water). The initial volume of the aqueous phase was typically 10 mL, and the organic phase was added gradually at a flow rate of 2 mL/min to the mixing

aqueous phase with the mixing rate of 800 rpm, until the desired phase volume ratio was reached (PVR = Vorg/Vaq). The resulting CLAs were very viscous, having a creamy white appearance, with stable CLAs formulation showing no phase separation over a period of days. The schematic view of CLAs generation process is shown in Figure 1.
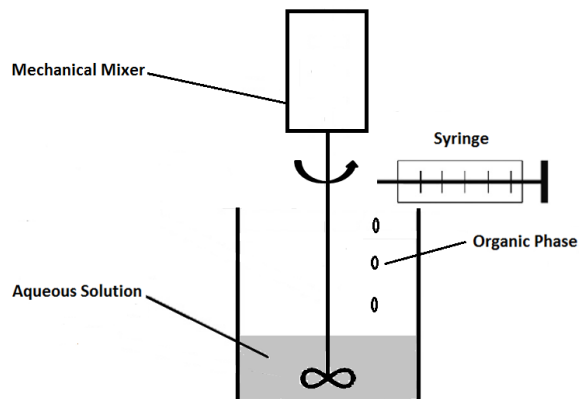
Figure 1. CLAs generation process

Copper Solution Preparation

Different concentrations (10 ppm, 20 ppm, 50 ppm, and 100 ppm) of copper solution were prepared by dissolution of $CuSO_4$ (FW:159.61) in 1 L distilled water, stirring for about 2 hours and the pH of the solution was lowered to 3.9-4 (similar pH to AMD) using sulfuric acid.

Copper Extraction Experiments

In PDSE experiments, 10 mL of CLAs were added to 10 mL of Cu (II) solution in a centrifuge tube. The mixture was mixed for 30 seconds followed by phase separation in a centrifuge (10 min, 4400 rpm). After centrifuging, the aqueous phase was removed and diluted in order to analyze the copper ion concentration with atomic absorption spectrometer (AAS) and finally, the percentage of copper removed (R) calculated using the following equation:

$$R = \frac{(C_0 - C)}{c_0} \times 100 \tag{1}$$

C_0 is the initial concentration of copper (ppm) calculated with regard to dilution factor and C is the final concentration of copper (ppm) as determined by AAS. All the experiments were repeated 5 times to ensure the repeatability and errors calculated at the 95% confidence level. In order to calculate the dilution factor, the initial mass of copper solution, mass of CLAs added to the solution and final dilution of the sample was taken into account.

Copper Extraction Characterization of CLAs

In order to investigate the size distribution of CLAs preliminary observations were carried out using light microscopy Leitz Laborlux 12 Pol (Germany). CLA dispersions generated with three different phase volume ratio were studied during these experiments and initial extractant concentration, anionic surfactant concentration, stirring time and speed, pH and temperature were kept constant. Due to high turbidity of CLA dispersions, the samples were diluted (1:10 volume distilled water).

RESULTS AND DISCUSSION

Structure and size distribution of CLAs

Light micrographs of diluted CLA dispersions at the PVR of 1, 4 and 10, respectively are shown in Figure 2. According to the observations, CLAs at the dispersed state are micron-sized droplets and size of CLAs decreases and their number increases by increasing phase volume ratio of aphrons.
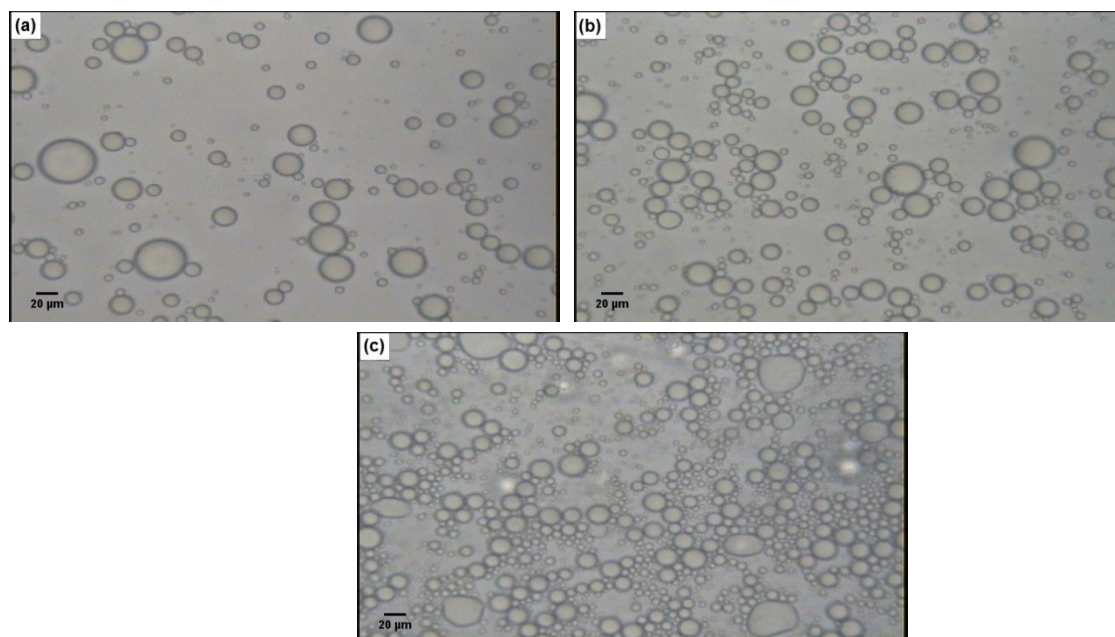

Figure 2. Optical micrographs of CLAs, LIX 984N 0.5 % (w/v kerosene), SDS 0.5 % (w/v), and Tergitol 0.1 % (v/v): (a) PVR 1; (b) PVR 4; (c) PVR 10

Copper removal

Effect of phase volume ratio and initial copper concentration

Figure 3 shows the copper removal percentage of CLAs generated in different phase volume ratios. All experiments were carried out for the solutions with different initial copper concentrations.

According to the experimental results, the phase volume ratio is one of the major contributing factors to the extraction of copper ions by CLAs. The increasing trend of copper removal by increasing PVR is obvious in higher initial copper concentrations. In solutions with 100 ppm initial copper concentration, 45 % of copper ions were removed by addition of CLAs of PVR 1, however, CLAs of PVR 10 were able to remove as high as 97 % of the copper. The significant difference between removal efficiency in different copper concentrations can be attributed to the loading capacity of extractant. As described in the experimental section, equal volumes of CLAs (10 ml) were added to each sample of copper solution which had different copper concentrations. Therefore, for each unit of LIX 984N there are more copper ions to be extracted in 100 ppm copper solution compared to 10 ppm solution.
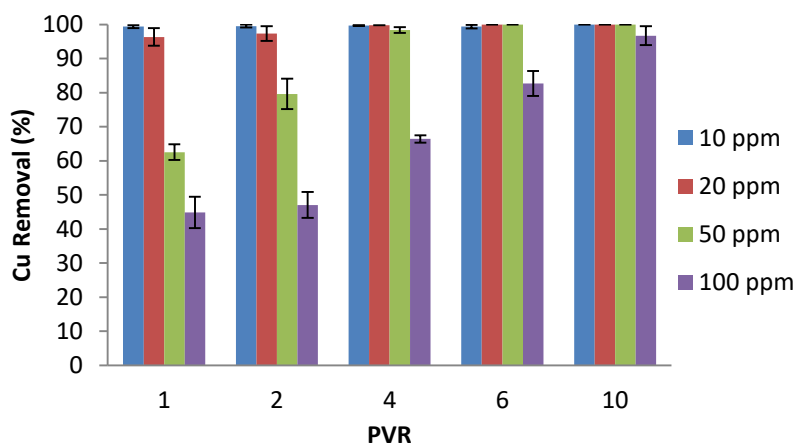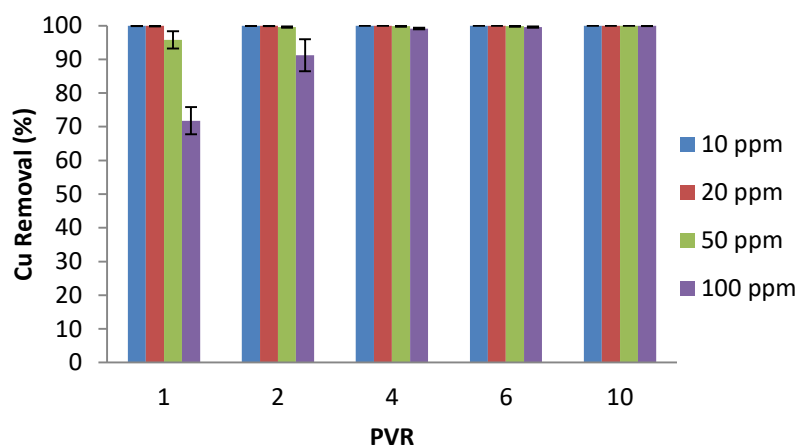
Figure 3. Effect of phase volume ratio on the copper ions removal. Initial pH of copper solution: 4, initial LIX 984N concentration: 0.2 % (w/v), SDS concentration 0.5 % (w/v), and Tergitol concentration 0.1 % (v/v). Error bars denote 95% confidence interval.

Effect of initial extractant concentration

In order to determine the effect of LIX 984N (extractant) concentration on the extraction efficiency of the CLAs, similar experiments were carried out using colloidal liquid aphrons generated from different LIX 984N concentrations. The results are shown in Figure 4 and Figure 5.
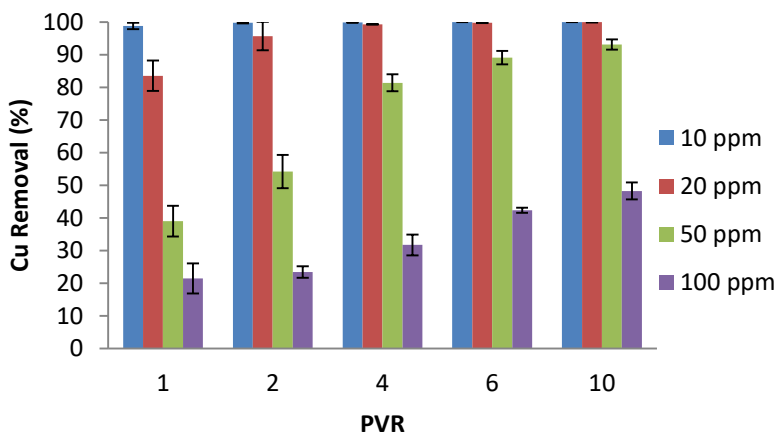
Figure 4. Initial pH of copper solution: 4, initial LIX 984N concentration: 0.1 % (w/v), and SDS concentration 0.5 % (w/v), and Tergitol concentration 0.1 % (v/v). Error bars denote 95% confidence interval.
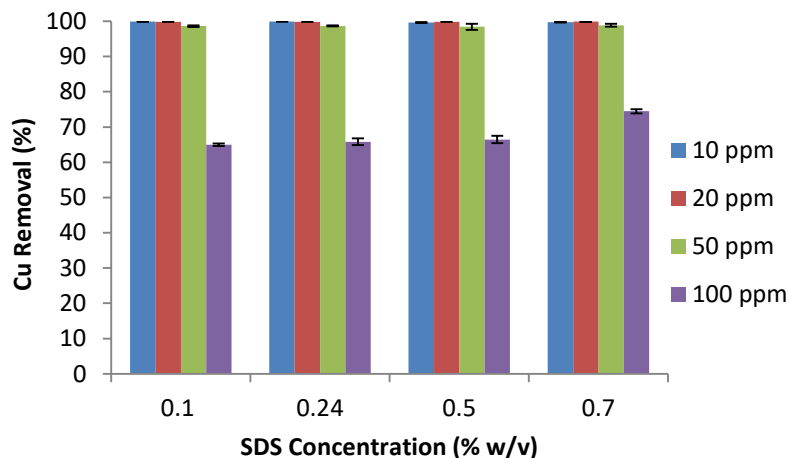
Figure 5. Initial pH of copper solution: 4, initial LIX 984N concentration: 0.5 % (w/v), and SDS concentration 0.5 % (w/v), and Tergitol concentration 0.1 % (v/v). Error bars denote 95% confidence interval.

It can be seen from the results that initial extractant concentration is a key effective parameter in the extraction of copper ions from dilute solutions. Increasing the initial extractant concentration results in the higher copper removal to reach almost 100 % in the 0.5 % (w/v) of LIX 984N concentration for all the copper concentrations in PVR 4, 6, and 10. However, the maximum initial LIX concentration used in these experiments was significantly lower than the conventional solvent extraction processes (Alguacil, 1999; Alguacil & Navarro, 2002; Cognet, Vaissiere, & Renon, 1977; Dukov & Guy, 1982; Fouad, 2009; Navarro & Alguacil, 1999; Sastre & Alguacil, 2001; Sridhar, Verma, & Kumar, 2009; Xie & Dreisinger, 2010).

Effect of ionic surfactant concentration

Figures 6 and Figure 7 indicate the effect of ionic surfactant (SDS) concentration on the extraction efficiency of CLAs. The experiments were carried out using two different LIX 984N concentrations, 0.2 % and 0.5 % (w/v) in the PVR of 4 in CLAs generation process.

Figure 6. Effect of SDS concentration on the copper ions removal. Initial pH of copper solution: 4, initial LIX 984N concentration: 0.2 % (w/v), PVR 4, and Tergitol concentration 0.1 % (v/v). Error bars denote 95% confidence interval.
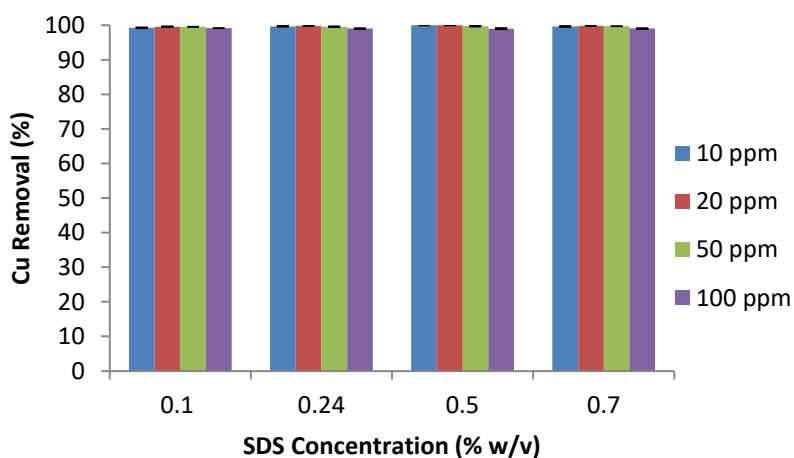
Figure 7. Effect of SDS concentration on the copper ions removal. Initial pH of copper solution: 4, initial LIX 984N concentration: 0.5 % (w/v), PVR 4, and Tergitol concentration 0.1 % (v/v). Error bars denote 95% confidence interval.

No significant difference between copper ion extraction with respect to SDS concentrations was observed. The slight increase in removal may result from attractive forces between positively charged copper ions and the anionic surfactant (SDS). This suggests that the major contributing factors in predispersed solvent extraction of dilute copper solutions are related to extractant, which are initial extractant concentration and phase volume ratio. Therefore, the major mechanism involving in extraction of copper ions using PDSE method is ion exchange between LIX 984N and copper bearing aqueous solution as expressed by the following equation:

$$Cu^{2+}_{(aq)} + 2HR_{(org)} \Longleftrightarrow CuR_{2(org)} + 2 H^+ \tag{2}$$

where HR represents the active substance of the LIX 984N, aq and org are the respective aqueous and organic phases.

Thus, the ionic surfactant plays the role of making the initial contact between CLAs copper ions by electrostatic interactions and the effect of concentration on extraction is negligible.

Conventional solvent extraction

Solvent extraction tests in the absence of surfactants were done in the same way as predispersed solvent extraction tests in two different LIX 984N concentrations. The results are illustrated in Figure 8.
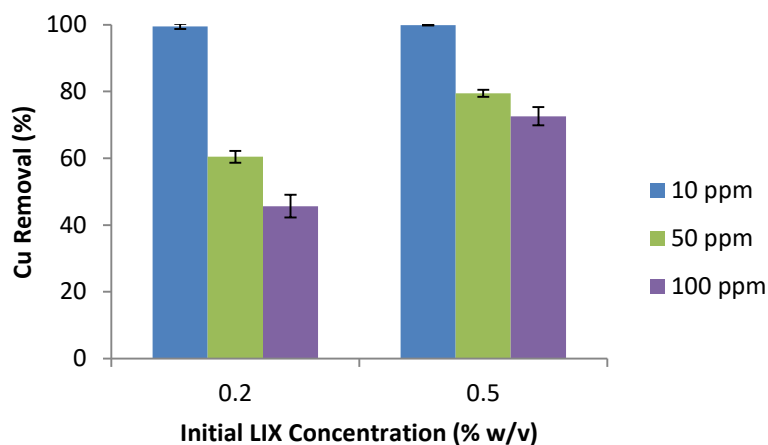
Figure 8. Conventional solvent extraction in the absence of surfactant. Initial pH of the copper solution: 4. Error bars denote 95% confidence interval.

By comparing the results in Figure 8 with the results from predispersed solvent extraction, it can be concluded that higher removal is obtainable using PDSE method. For example, in 100 ppm copper solution, the conventional method was able to extract 45% and 72% of copper at 0.2% and 0.5% LIX 984N concentrations, respectively. However, by using PDSE at these LIX concentrations, 67% and more than 99% of copper ions were removed from the solution, respectively.

CONCLUSIONS

The extraction behavior of copper from dilute solutions using predispersed solvent extraction method was studied, and the effect of phase volume ratio, initial extractant concentration and initial surfactant concentration on the extraction efficiency of colloidal liquid aphrons were investigated. It was shown that phase volume ratio and initial extractant concentration are the major contributing factors on the extraction of copper ions using CLAs. The effect of surfactant concentration is not significant. Also, by performing conventional solvent extraction tests it was concluded that PDSE method was more effective than conventional method.

Microscopic observations show that CLAs are micron-sized droplets that their size decreases and their number increases by increasing phase volume ratio of aphrons.

Under the studied conditions, optimum conditions for cupper ion extraction in PDSE were found as initial LIX 984N concentration of 0.5 % (w/v) and PVR of 4.

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A DESIGN OF EXPERIMENTS INVESTIGATION INTO PREDISPERSED SOLVENT EXTRACTION OF NICKEL IONS FROM DILUTE SOLUTIONS USING FRACTIONAL FACTORIAL DESIGN

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ABSTRACT

Solvent extraction is the one of the most common techniques for recovering metal ions from aqueous systems. However, it is not efficient in the extraction of low concentration metal ions from aqueous solutions. Predispersed solvent extraction is an alternative method for solvent extraction which implies colloidal liquid aphrons as extracting agents in order to reach higher interfacial area and lower reagent consumption. This work investigated important parameters in predispersed solvent extraction of nickel ions from dilute aqueous solutions by fractional factorial design of experiments. Four experimental parameters, the initial extractant concentration, initial surfactant concentration, equilibrium pH and phase volume ratio (organic to aqueous ratio) were investigated. The important parameters were determined as well as important interactions between these parameters. It was found that extractant concentration, phase volume ratio, and equilibrium pH are the most significant experimental parameters. However, the interaction between surfactant concentration and other parameters was determined as significant interactions.

KEYWORDS

Predispersed solvent extraction, nickel, design of experiments

INTRODUCTION

Nickel is one of the key components found in cars, mobile phones, rechargeable batteries, kitchen appliances, and steel industry (Anyadike, 2002). It is one of the most important metals produced by Canada which is in the five top nickel producers in the world. Despite a 24% decrease in the nickel prices from 2011 to 2014 the nickel global mine production increased by 36% between these years (*Mineral commodity summaries 2015*, 2015; "Nickel - Statista Dossier," 2015), which shows the increasing demand for nickel. This high demand leads producers to consider the production of nickel from low grade ores and other secondary sources such as process wastewaters. The removal of nickel ions from process wastewater is also important due to environmental considerations. Nickel is known to be a human carcinogen and it may cause serious lung and kidney problems, pulmonary fibrosis, gastrointestinal distress, and skin dermatitis if it exceeds the critical level (Borba *et al.*, 2006; Fu & Wang, 2011).

Solvent extraction of pregnant leach solutions is one of the common ways to concentrate nickel ores. Solvent extraction is a well-established technique for removing metal ions using hydrometallurgical processes. In this

technique, the pregnant solution is contacted with an immiscible organic metal extractant and metal ions transfer into the organic phase. Solvent extraction has a wide application in metal industries because of its simplicity and selectivity (Bullock & King, 1975; Doungdeethaveeratana & Sohn, 1998; Sengupta *et al.*, 2009). However, it has some limitations which impact its efficiency in some applications. One of these limitations is a high reagent consumption and low recovery at low metal concentration (<500 ppm) which makes it economically infeasible for dilute streams.

Predispersed solvent extraction (PDSE) is a modified solvent extraction technique which has shown promise in the removal of metal ions from dilute solutions. In PDSE the organic phase including the extractant are predispersed into micrometer sized globules termed colloidal liquid aphrons (CLAs). By using CLA in PDSE process lower extractant consumption and faster extraction can be reached due to an increase in the interfacial area of organic phase resulted from small size of CLAs (Michelsen *et al.*, 1986; Wallis *et al.*, 1986).

Colloidal liquid aphrons are micrometer sized multilayer droplets which consist of an oil core encapsulated by a thin soapy (aqueous) shell (Sebba, 1987). The oil core carries the organic phase including organic extractant and oil soluble surfactant. The aqueous shell contains a water soluble surfactant which makes the CLAs surface hydrophilic and allows them to disperse easily in feed phase. A mixture of non-ionic and ionic surfactants makes CLAs stable by forming three distinct interfaces (Molaei & Waters, 2015a). They can be stored for a long period of time without any noticeable change in their properties (Matsushita *et al.*, 1992; Molaei & Waters, 2015b; Sebba, 1987) and also can be transported through pumping without destroying the structure (Lee *et al.*, 2002; Sebba, 1987). In addition, the small size of CLAs provides large interfacial area available for mass transfer. Figure 1 shows the structure of a CLA.
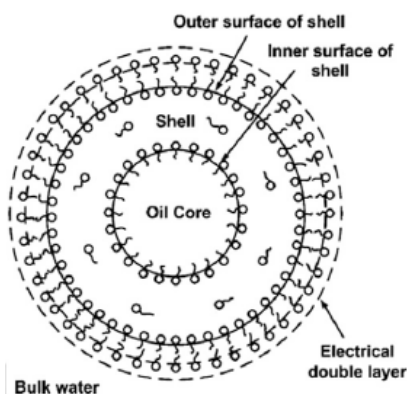
Figure 1. Structure of a colloidal liquid aphron (Molaei & Waters, 2015a)

Since 1985 in which the idea of using of CLAs in PDSE process was first proposed by Sebba (Sebba, 1985), there have been a number of articles published on this topic. For instance, in 1986 Michelsen *et al.* (Michelsen *et al.*, 1986) compared PDSE with conventional solvent extraction. They reported that the PDSE process was 5 to 10 times more effective in removing ortho-dichlorobenzene from water than conventional solvent extraction using in identical tests with a similar quantity of solvent. Wallis *et al.* (Wallis *et al.*, 1986) also reported 20% higher ethanol extraction with CLAs in PDSE compared to conventional solvent extraction. Later works on the PDSE were carried out to extract metal ions from water (Hahm *et al.*, 2003; Luo *et al.*, 2013; Molaei & Waters, 2015b); and organic dyes, acids and drugs from aqueous solutions (Hong *et al.*, 2001; Kim *et al.*, 2004a; Kim *et al.*, 2004b; Kim *et al.*, 2002; Lee *et al.*, 2000; Lye & Stuckey, 2000) however, there is not any study about the predispersed solvent extraction of nickel ions from dilute solutions.

Predispersed solvent extraction method showed promising results in the extraction of low concentration copper ions from aqueous solutions in the recent study performed by authors (Molaei & Waters, 2015b). In this work PDSE of nickel ions in three different initial concentrations was studied and the effects of four process parameters (initial extractant concentration, phase volume ratio, initial surfactant concentration, and equilibrium pH,) on the extraction of nickel ions were investigated. The main purpose of this study was to determine the most significant

parameters and their interactions, using fractional factorial experimental design, to better understand the process and screen the factors for the optimization stage.

MATERIALS AND METHODS

Materials

Nickel (II) solutions were prepared by dissolving Nickelous Sulfate (NiSO4.6H2O) (Anachemia, USA) in reverse osmosis purified water. For the CLA dispersion formulation, the oil phase consists of LIX 984N (BASF, Germany) as nickel extractant and Kerosene (Sigma-Aldrich, USA) and Tergitol 15-S-3 (Talas, USA) as a LIX diluent, and oil soluble surfactant respectively. LIX 984N reagent is a 1:1 volume blend of LIX 860N (5-nonyl salicylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone oxime with the specific gravity of $0.935 - 0.955$ g/cm³ in 25 ˚C and the flash point greater than 170 ˚F.

The aqueous phase was comprised of anionic sodium n-dodecyl sulfate (SDS) (99%, Avocado, UK), as a water soluble surfactant. Sulfuric acid (Fisher Scientific, Canada) and sodium hydroxide (Fisher Scientific, Canada) were used to modify pH; and 4% nitric acid (Sigma-Aldrich, USA) was used to dilute samples before nickel concentration analysis. All aqueous phases were prepared from reverse osmosis purified water at ambient temperature.

Preparation of CLAs

The CLA dispersion was prepared by the slow drop-wise addition of the oil (organic) phase containing LIX 984N, kerosene, and oil soluble surfactant into a foaming aqueous solution containing the water soluble surfactant (SDS). 10 ml of aqueous solutions was placed in beaker and mixed at a rate of 800 rpm for 10 minutes to make initial foams, followed by the gradual addition of the organic phase at a flow rate of 2 ml/min to the mixing aqueous phase, until the desired phase volume ratio was reached (PVR = V_{org}/V_{aq}). The resulting CLA dispersions were in the micro meter size range, viscous and had a creamy white appearance, showing no phase separation over a period of months. The schematic view of the CLA generation process is shown in Figure 2.
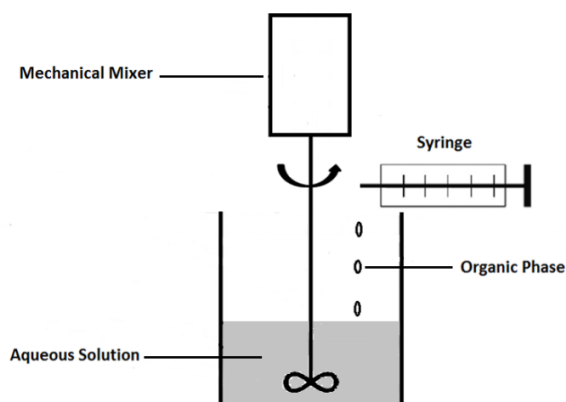
Figure 2. CLAs generation process (Molaei & Waters, 2015b)

The CLA dispersions were prepared freshly every day and kept for maximum of 24 hours. However, according to Molaei and Waters (Molaei & Waters, 2015b), CLAs can be stored for at least 2 months without any change in their extraction ability.

Extraction process

Nickel extraction experiments were conducted in 100 ml beakers with 15 ml of CLAs added to 15 ml of Ni (II) solution. The mixture was stirred while the pH was adjusted to the required value. Once the pH was adjusted, the solution was transferred to centrifuge tube and centrifuged for 5 min at 4200 rpm to ensure a rapid phase separation.

Following the phase separation, the raffinate was removed and diluted with 4% nitric acid to analyze the remaining nickel concentration using inductively coupled plasma emission spectroscopy (ICP-ES, Thermo Scientific 6000 series). Ultimately, the percentage of removed nickel was calculated using Eq. (1):

$$\text{Ni removal \%} = \frac{(C_0 - C)}{C_0} \times 100 \qquad \qquad (1)$$

Where C_0 is the initial concentration of nickel (ppm) and C is the final concentration of nickel (ppm) in the raffinate, as measured by ICP-ES.

Fractional factorial design

Fractional factorial design (FFD) is a statistical approach in designs of experiments which consists of a fraction runs of a full factorial design to determine the significant experimental parameters with a minimum number of experiments (Antony, 2014; Montgomery, 2012).

Factorial designs are widely used in experiments involving several factors where it is necessary to investigate the interaction effects of the factors (parameters) on a response. Fractional factorial tests are mostly used in the screening stage in order to determine the most significant factors and interactions and screen the factors to minimum for the optimization stage (Montgomery, 2012).

In this study, the experimental procedure was performed according to 2^{4-1} fractional factorial design, which is a series of experiments involving 4 factors, each of which has two levels ('low' and 'high'). The factors and their levels are represented in Table 1.

Table 1. Factors and their levels

Factor	Term	Low level (-1)	High level (+1)
Extractant concentration (% w/v)	A	0.1	1
Phase volume ratio (PVR)	B	1	10
Surfactant concentration (% w/v)	C	0.1	0.7
Equilibrium pH	D	4	10

According to half factorial design (2^{k-1}) with two replicate for each point and three replicates at the center total number of experiments was calculated as 19. Table 2 shows the complete experimental design and actual responses of the experiments.

Table 2. Experimental design and responses

Run Order	Coded level of factors				Actual level of factors				Response (Extraction, %)		
	A	B	C	D	Ex Con	PVR	S Con	Eq pH	20 ppm	100 ppm	300 ppm
1	-1	-1	1	1	0.1	1	0.7	10	4.33	1.71	0.00
2	0	0	0	0	0.55	5.5	0.4	7	90.56	78.02	60.20
3	-1	1	-1	1	0.1	10	0.1	10	64.47	76.39	84.08
4	-1	-1	1	1	0.1	1	0.7	10	7.40	0.00	1.15
5	-1	1	1	-1	0.1	10	0.7	4	83.04	67.56	35.34
6	0	0	0	0	0.55	5.5	0.4	7	91.98	81.12	58.41
7	-1	1	1	-1	0.1	10	0.7	4	78.66	69.42	43.98
8	1	-1	-1	1	1	1	0.1	10	11.73	35.49	74.46
9	1	1	1	1	1	10	0.7	10	86.92	95.50	88.81
10	1	1	-1	-1	1	10	0.1	4	65.05	74.03	33.25
11	1	-1	-1	1	1	1	0.1	10	9.95	38.88	71.41
12	1	1	1	1	1	10	0.7	10	79.06	91.61	90.72
13	-1	-1-	-1	-1	0.1	1	0.1	4	78.30	75.21	0.00
14	1	-1	1	-1	1	1	0.7	4	89.51	95.32	63.82
15	-1	-1	-1	-1	0.1	1	0.1	4	70.33	79.37	0.00
16	-1	1	-1	1	0.1	10	0.1	10	59.47	81.08	80.67
17	1	1	-1	-1	1	10	0.1	4	70.46	79.15	40.85
18	1	-1	1	-1	1	1	0.7	4	88.34	98.63	58.88
19	0	0	0	0	0.55	5.5	0.4	7	87.73	80.53	57.61

In fractional factorial design the higher order interactions (third order and higher) are assumed as not being important and aliased with lower order interactions. In this work a half factorial design with resolution IV was selected. In this resolution, two-factor interactions are aliased with other two-factor interactions and main effects are aliased with three-factor interactions. The aliasing pattern for two and three-factor interactions follows:

A = BCD, B = ACD, C = ABD, D = ABC, AB = CD, AC = BD, and AD = BC

After obtaining the experimental results a linear regression model was generated. The model is given in Eq. (2).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon$$

(2)

where y is the predicted response, x_i and x_j are the variables; β_0 is the constant coefficient; and β_{ij} represents the interaction effect, between the ith and jth variables.

The proposed model was then analyzed with the Fisher's statistical test for the analysis of variance (ANOVA) to obtain the coefficients and assess the quality of "goodness of fit". All statistical analyses were produced using "Minitab® 17 statistical software".

<div align="center">

RESULTS AND DISCUSSION

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Statistical model for nickel extraction

The designed experiments were performed separately for three initial nickel concentrations in a randomized order (Table 2) and the results (responses) were calculated. Using the results, a regression model for each concentration was constructed. Equations (3), (4) and (5) present the coded model at 20, 100 and 300 ppm nickel concentration respectively.

Extraction (%) = 59.189 +3.439 Ex Con + 14.203 PVR + 5.469 S Con − 18.772 Eq pH − 1.458 Ex Con*PVR + 17.861 Ex Con*S Con + 3.060 Ex Con*Eq pH + 2.14 Ct Pt   **(3)**

Extraction (%) = 66.209 + 9.867 Ex Con + 13.133 PVR − 1.241 S Con − 13.627 Eq pH − 4.137 Ex Con*PVR + 20.429 Ex Con*S Con + 2.921 Ex Con*Eq pH + 1.54 Ct Pt   **(4)**

Extraction (%) = 47.964 + 17.311 Ex Con + 14.249 PVR − 0.126 S Con + 13.449 Eq pH − 16.116 Ex Con*PVR + 10.409 Ex Con*S Con + 2.626 Ex Con*Eq pH + 1.94 Ct Pt   **(5)**

The presented fractional factorial models resulted in predicted R^2 value of 99.33 %, 99.60 % and 99.45 % for 20, 100 and 300 ppm respectively. This high R^2 values indicate the good fit of the proposed models. Furthermore, *F*- test applied to validate the models yielded *p*-values of 0.000 for all three concentrations which confirm the goodness of fit for the models.

Analysis of factors

The first step in the analysis of variables is to identify the most important factors which influence the extraction percentage of nickel at each concentration. A Pareto chart of factors effects was constructed for each concentration. Pareto charts show the relative significance of factors and interactions (Antony, 2014).

Plotting the normal probability plot is another way to determine the significance of factors and interactions. The effects that are not significant will fall along a line and the significant effects will stay farther from the line. Distance from the normal line shows the significance, the farther from normal line the more significant factor. Normal plot also determines the sign of effects; either they have positive effect in response or negative one.

Figures 3 to 5 show the Pareto chart and normal plot of standardized effects at 20, 100 and 300 rpm respectively.
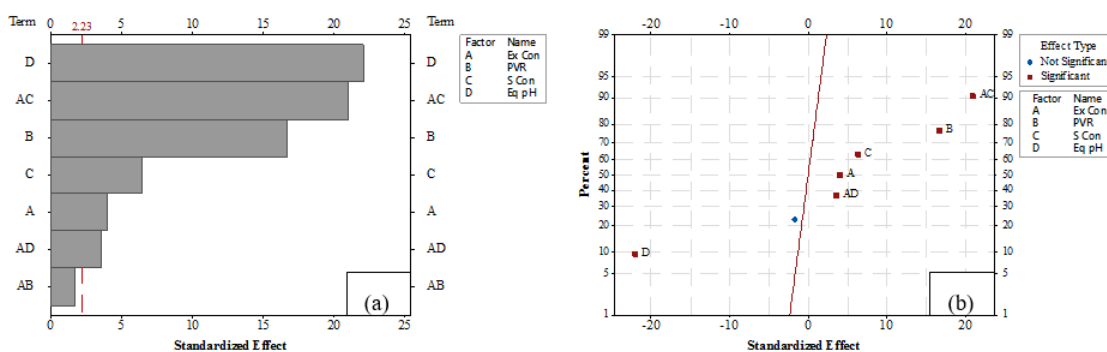
Figure 3. Pareto chart (a) and normal plot (b) of the standardized effects (α= 0.05) at 20 ppm nickel concentration
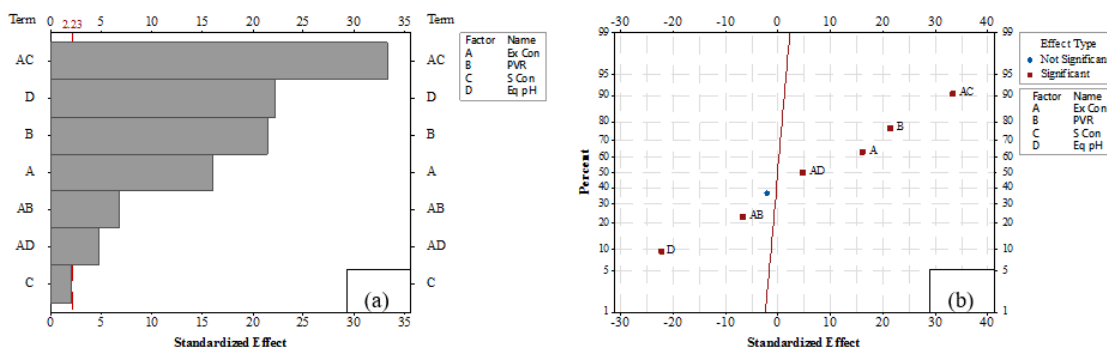
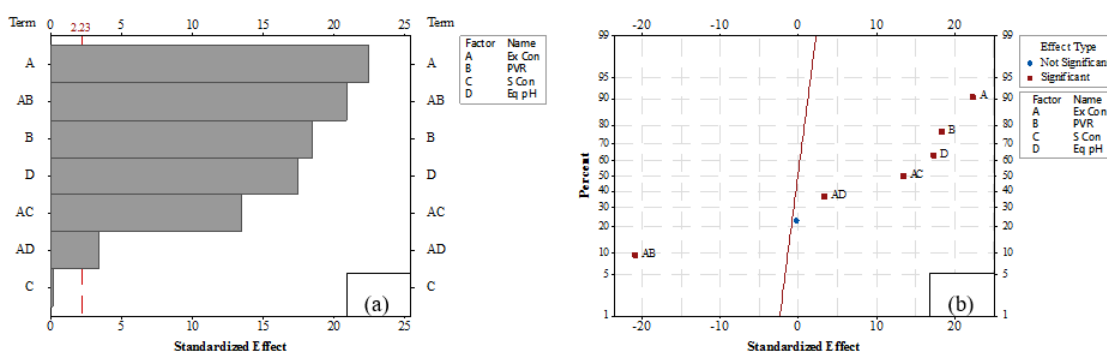**Figure 4**. Pareto chart (a) and normal plot (b) of the standardized effects (α= 0.05) at 100 ppm nickel concentration

Figure 5. Pareto chart (a) and normal plot (b) of the standardized effects (α= 0.05) at 300 ppm nickel concentration

Looking at Pareto chart and normal plot at 20 ppm (Figure 3), all the main factors are assumed to be significant. However, equilibrium pH (D) and PVR (B) are the most significant ones. In the case of interactions, the interaction between extractant concentration and surfactant concentration (AC) is the most significant interaction, while the other interactions have very little importance compared to this one.

At 100 ppm (Figure 4), among the main factors, equilibrium pH (D), PVR (B) and extractant concentration (A) are significant, respectively. Surfactant concentration (C) is considered as non-significant factor; whereas the interaction of this factor with extractant concentration (AC) is very important. Therefore, this factor cannot be omitted for the optimization stage.

At 300 ppm (Figure 5), extractant concentration (A), PVR (B) and equilibrium pH (C) are again the significant parameters but the order of their significance is different from 100 ppm. While the first two parameters (A and B) have the most influence on the response individually, their interaction (AB) is also very effective and considered as the most significant two-way interaction in this concentration.

DISCUSSIONS

According to recent research performed on the PDSE of copper from dilute solutions (Molaei & Waters, 2015b), electrostatic interactions and ion exchange are determined as the two major contributing mechanisms in the PDSE of positively charged metal ions using colloidal liquid aphrons. The former causes the initial contact between CLAs charged surface and metal ions by physical attraction, and the latter leads to complete extraction of metal ions from solution by means of LIX 984N molecules (Equation 5).

$$Ni^{2+}_{(aq)} + 2\,HR_{(org)} \longleftrightarrow NiR_{2\,(org)} + 2\,H^{+} \qquad \textbf{(5)}$$

where R represents the active component of the extractant (LIX 984N).

This equation reveals why the equilibrium pH (D) and the extractant concentration (A) are the most significant factors 20ppm, 100 ppm, and 300 ppm respectively. When the concentration of nickel is low (20, 100 ppm), a small amount of extractant is needed to extract all the existing nickel ions therefore the extractant concentration is not considered as a significant factor however equilibrium pH was the most significant factor because it controls the direction of equation. At a higher concentration (300 ppm) the extractant concentration became the most significant factor and PVR which is also related to extractant concentration and the structure of CLAs become the second important parameter.

In case of surfactant concentration, it is reported that the water soluble surfactants have two major rules in the CLAs structure: first, to make the structure stable; and second, make the surface of CLAs charged (Beyer *et al.*, 1986; Matsushita *et al.*, 1992; Sebba, 1985). Therefore, the electrostatic interaction between CLAs and nickel ions are controlled by water soluble surfactant type and concentration. Although the surfactant concentration (C) was not among the most important parameters for all three concentrations due to its important interaction with extractant concentration it should be considered in optimization stage.

In the case of phase volume ratio (PVR) (B) of CLAs, an increase in PVR resulted in a decrease in CLAs size (Molaei & Waters, 2015b) and consequently increasing in the surface area of CLAs. This increase in the surface area eventuates to enhance the extraction. This is why PVR is one of the significant factors for all three concentrations.

CONCLUSIONS

Using CLAs made from an anionic water soluble surfactant (SDS), and an extractant (LIX 984N) can be an alternative method for conventional solvent extraction technique. Predispersed solvent extraction showed promising results for copper extraction (Molaei & Waters, 2015b) and when compared to conventional solvent extraction PDSE had higher removal percentage in the similar conditions (Molaei & Waters, 2014). According to the results presented here, PDSE is an effective method on the extraction of low concentration nickel ores from aqueous solutions as well. The results show that more than 90 % of extraction percentage at each nickel concentration could be reached if the factors were chosen properly.

By analyzing the statistical data obtained from proposed regression models, it can be concluded that:

- At 20 ppm all the main factors are important; however, the factor C (surfactant concentration) is not significant at 100 and 300 ppm nickel concentration.
- Factors following the sequence of increasing the significance: A < C < B < D, C< A < B < D, and C < D < B < A at 20, 100 and 300 ppm initial nickel concentration respectively.
- AC is only significant interaction at 20 ppm, while at 100 ppm all the interactions became significant but still AC is the most significant one and at 300 ppm AB and AC became significant respectively.
- Although factor C (surfactant concentration) is not significant factor neither at 100 ppm nor 300 ppm, but due to significance of its interaction with other factors cannot be omitted for the optimization stage.

In general, fractional factorial design is an efficient method in order to recognize the significant factors and interactions. However, FFD is not an efficient way to construct a model for process, define optimum conditions, and predict response in different level of factors. In order to find proper level of factors and optimize the process, more detailed experiments in different points should be done which is the next step in investigating the nickel ion removal from dilute solutions using PDSE. In optimization process more accurate methods such as response surface methodology (RSM) need to be applied. The future work will be to apply the RSM technique to this process in order to optimize the factors and process and to validate optimum condition by conducting a new set of experiments in the optimal points.

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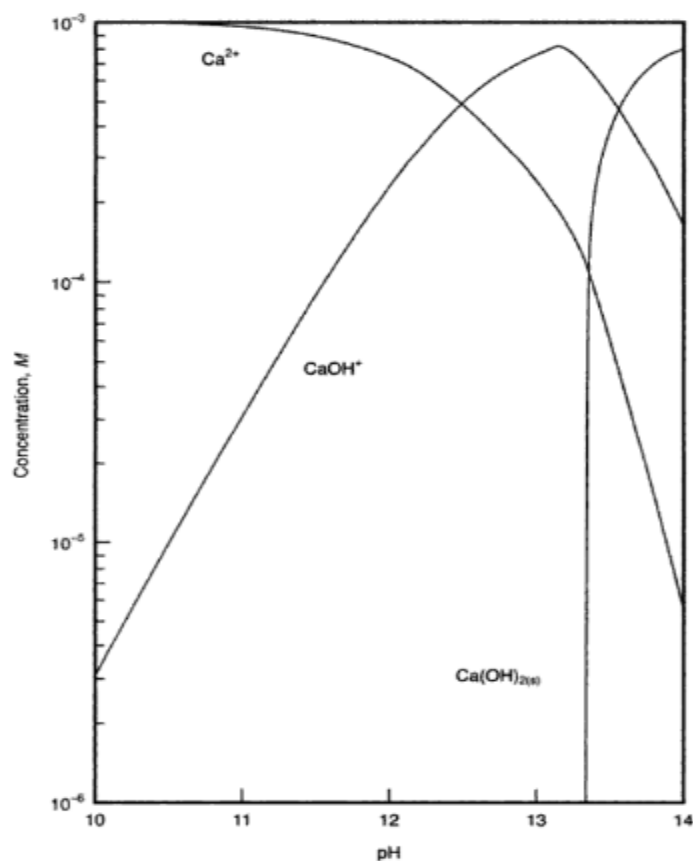
Speciation diagrams of copper, nickel and cobalt
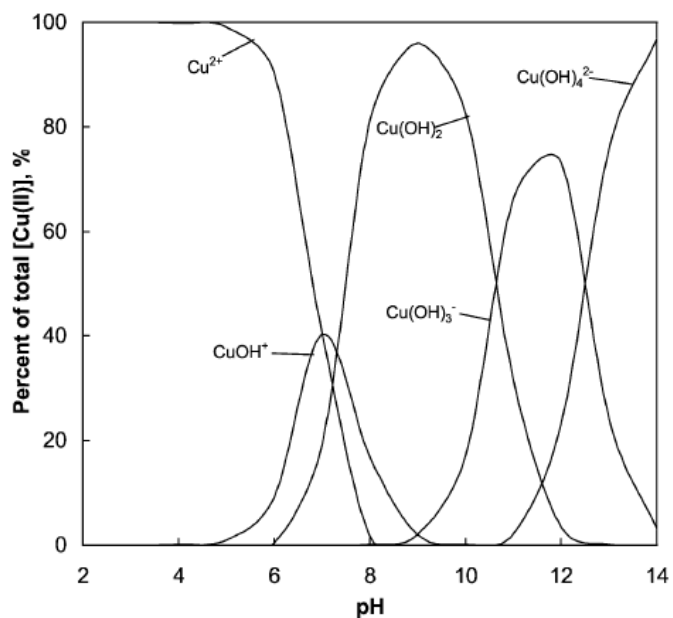
Figure 1: Speciation diagram of copper (II) (Doyle & Liu, 2003).
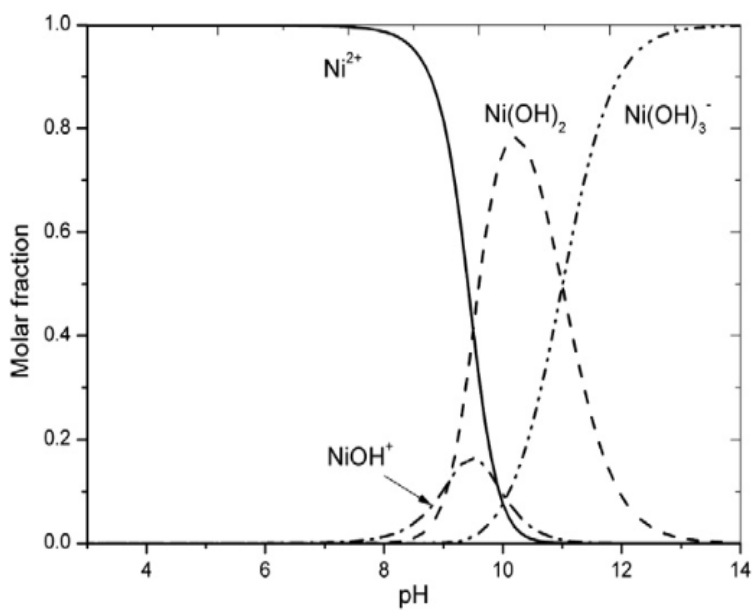
Figure 2: Speciation diagram of nickel (II) (Bhatnagar *et al.*, 2012).

Figure 3: Speciation diagram of calcium (II) (Fuerstenau *et al.*, 2007)

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