The use of foaming agents and foam stabilizers to improve heavy metal removal properties of acrylic acid/acrylamide hydrogels for use in wastewater remediation

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Abstract

Contamination of waterways is a prominent problem in today's world. Contaminants can enter the water stream through many avenues such as agricultural runoff, industrial waste, and municipal wastewater. One way to protect waterways, and therefore the plants and animals that rely on the waterway, is to treat wastewater before it enters the waterway. Wastewater treatment plants are designed to remove solids and to reduce pathogens. However, wastewater treatment techniques can also remove contaminants, such as heavy metals, hormones, and personal care products. A variety of physical, chemical, and biological treatments that are currently in use at water treatment facilities have been tested over time to assess their effectiveness at contaminant removal. Thanks to these processes, biological treatments or adsorption have proved to be the most effective. Adsorption in wastewater facilities is usually performed by adding traditional adsorbents such as activated carbon to the water, however, polymer adsorbents such as hydrogels show a great potential for wastewater remediation under laboratory conditions. Hydrogels are 3D polymeric networks that can absorb hundreds of times their weight in water or other fluids. They can be made from a variety of monomers such as petrochemical monomers or natural monomers including starch and protein. Several different factors, including monomer composition and pore structure, will affect the hydrogel's ability to adsorb contaminants such as heavy metals. The subject of this thesis is the synthesis of three acrylic acid/acrylamide hydrogels with differing pore structures and the testing of their physical and chemical properties to determine which is the best adsorbent.

The three structures (non-porous, superabsorbent, and super porous) were synthesized using the same monomers, initiation system and crosslinker. A foaming agent and foam stabilizer were used to introduce differences in pore structure. The difference in structure led to differences in the final physical and chemical properties of a hydrogel. These differences were evident when measuring the 24-hour swelling capacity of the hydrogels and the heavy metal adsorption. The hydrogel synthesized with a foaming agent, and a foam stabilizer had the highest swelling capacity (256 g/g). Additionally, this project aimed at comparing the ion removal capacity for copper (II), cadmium (II), and nickel (II) under competitive and non-competitive conditions. The use of a foaming agent significantly increased the ion removal capacity of the hydrogel, with there being little difference between the stabilized and non-stabilized foam structures (103 mg/g and 104 mg/g copper (II)). Under competitive conditions, the hydrogel preferentially removed cadmium>

copper> nickel. The conclusion of this project was that the use of a foaming agent could greatly increase the heavy metal removal capacity of acrylic acid/acrylamide hydrogels. They could be used for wastewater remediation.

Résumé

La contamination des cours d'eau est un problème important dans le monde d'aujourd'hui. Les contaminants peuvent entrer dans le cours d'eau par de nombreux moyens tels que le ruissellement agricole, les déchets industriels et les eaux usées municipales. Une façon de protéger les cours d'eau, et donc les plantes et les animaux qui dépendent de l'eau, est de traiter les eaux usées avant d'entrer dans le cours d'eau. Les usines de traitement des eaux usées sont conçues pour éliminer les solides et réduire les agents pathogènes. Les techniques de traitement des eaux usées peuvent également éliminer un certain pourcentage des contaminants. Ces contaminants comprennent les métaux lourds, les hormones et les produits de soins personnels. Divers traitements physiques, chimiques et biologiques qui sont actuellement utilisés dans les installations de traitement de l'eau ont été mis à l'essai au fil du temps pour tester leur efficacité à éliminer les contaminants. Grâce à ces expériences, les traitements biologiques et l'adsorption se sont montrés les plus efficaces. L'adsorption dans les installations de traitement des eaux usées est généralement effectuée en ajoutant des adsorbants traditionnels tels que du charbon actif. Cependant, les polymères adsorbants, tels que les hydrogels, démontrent un grand potentiel d'assainissement des eaux usées dans des conditions de laboratoire. Les hydrogels sont des réseaux polymères 3D qui peuvent absorber des centaines de fois leur poids dans l'eau ou d'autres fluides. Ils peuvent être fabriqués à partir d'une variété de monomères tels que les monomères pétrochimiques ou les monomères naturels, y compris l'amidon et les protéines. Plusieurs facteurs, dont la composition des monomères et la structure des pores, affectent la capacité de l'hydrogel à adsorber des contaminants tels que les métaux lourds. Le sujet de ce mémoire est la synthèse de trois hydrogels d'acide acrylique/acrylamide avec des structures différentes, et la détermination de leurs propriétés d'adsorption de métaux lourds.

Ces trois structures (non poreux, superabsorbant et super poreux) ont été synthétisées avec les mêmes monomères, système d'initiation et réticulant. Un agent moussant et un stabilisateur de mousse ont été utilisés pour introduire des différences dans la structure des pores. La différence de structure a entrainé des différences au niveau des propriétés physiques et chimiques de l'hydrogel. Ces différences étaient évidentes lors de la mesure de la capacité de gonflement (période de 24 heures) des hydrogels et de l'adsorption des métaux lourds. L'hydrogel synthétisé avec un agent moussant, et un stabilisateur de mousse a eu la capacité de gonflement la plus élevée (256 g/g). De plus, ce mémoire compare la capacité d'élimination des ions pour le cuivre (II), le cadmium (II) et le nickel (II) dans des conditions concurrentielles et non concurrentielles. L'utilisation d'un agent moussant a considérablement augmenté la capacité d'élimination des ions de l'hydrogel, avec peu de différence entre les structures de mousse stabilisées et non stabilisées (103 mg/g et 104 mg/g de cuivre (II)). Dans des conditions compétitives, l'hydrogel a éliminé de préférence le cadmium> le cuivre> le nickel. Ce mémoire permet de conclure que l'utilisation d'un agent moussant pourrait augmenter considérablement la capacité d'élimination des métaux lourds des hydrogels d'acide acrylique/acrylamide à utiliser pour l'assainissement des eaux usées.

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Glossary

CEC: Contaminants of Emerging Concern PPCP: Pharmaceuticals and Personal Care Products EDC: endocrine disrupting compounds BH: Base Hydrogel FAH: Foaming Agent Hydrogel FAFSH: Foaming Agent Foaming Stabilized Hydrogel R BH: Regenerated Base Hydrogel R FAH: Regenerated Foaming Agent Hydrogel R FAFSH: Regenerated Foaming Agent Foaming Stabilized Hydrogel AA: Acrylic Acid AM: Acrylamide SEM: Scanning Electron Microscopy BET: Brunauer, Emmett, and Teller Surface Area TGA: Thermogravimetric Analysis

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Contribution of Authors

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Chapter 1 Introduction

General Introduction

Pollution is one of the main issues that threaten waterways. Heavy metals are one of the main water contaminants. They are produced by a wide range of industries including technology and agriculture. Heavy metals enter the environment in many ways, such as exhaust gases, fertilizer and pesticide use, and the spreading of municipal and industrial wastes such as sewage [1, 2]. Common examples of heavy metals include cadmium, copper, lead, nickel, and zinc [3]. Exposure to heavy metals can cause serious health issues. They accumulate in the body and can disrupt organ and gland function. Affected organs include the heart, brain, kidneys, bone, and liver. They also displace nutritional minerals, which hinders biological processes [4]. Contact with heavy metals can occur through the ingestion or use of water from contaminated sources. It is therefore vital to treat water that will come into contact with the population.

Contaminated water is often treated in municipal water treatment facilities; however, the goal of the treatment is to remove solids and inactivate bacteria. Heavy metals are not fully removed from wastewater as they are not targeted by the treatment plant [5]. While chemical treatment can partially remove some heavy metals, the most effective removal treatments are biological [6]. However, the use of adsorbents such as activated carbon [7] and hydrogels [8-10] are suitable.

Hydrogels are 3D chemically or physically crosslinked polymeric networks that can absorb hundreds of times their weight in water. They have previously been used for soil and water remediation, including the removal of heavy metals such as copper [8, 9], zinc, and nickel [9, 11]. Hydrogels can be categorized by their composition and their structure. A hydrogel's structure is determined by the porosity and shape of the pores. There are 3 structures of hydrogel reported in the literature: non-porous, superabsorbent and super porous [12]. All 3 can be made by using the same base composition but varying the use/non-use of foaming agents and foam stabilizers [13]. This causes a variation in physical and chemical properties that affect the final properties, such as the swelling rate of the hydrogel [14].

Study Objectives

Municipal wastewater is a large source of contaminants entering the water stream. Traditional water treatment plants focus on the removal of solids and elimination of pathogens from wastewater, but do not target harmful contaminants such as heavy metals. One of the most efficient ways to remove heavy metals is the use of adsorbents such as activated carbon. Polymer adsorbents such as hydrogels can be tailored to remove large amounts of specific contaminants. The general objective of this thesis was to determine the effect that the pore structure of the hydrogel has on the swelling capacity and heavy metal removal capacity of the hydrogels. Specific objectives for this thesis are listed below:

- I. Synthesize three hydrogel structures: without any additives, with a foaming agent, and with a foaming agent and foam stabilizer.
- II. Quantify the swelling capacity and physical properties of the hydrogels under relevant conditions (fresh and regenerated, various pH and ionic concentration)
- III. Determine ion removal capacity of the three original and three regenerated structures in competitive and non-competitive conditions.

Literature Review

1.1 Introduction

Over the past 40 years, the treatment of wastewater has grown in prevalence and in intensity. In Canada, the percentage of homes that are connected to sewers with secondary sewage treatment has increased from 40% in 1983 to 69% in 2017 [15]. Municipal wastewater treatment is usually comprised of two steps; primary and secondary treatment that can be followed by disinfection. Depending on the characteristics of the wastewater, additional treatment steps may also be included with the goal of removing specific contaminants.

The purpose of primary treatment is to remove large objects (such as baby wipes) through filtration as the water enters the facility. The wastewater then passes into a grit chamber that consists of a large tank where heavy solids such as rocks and sand settle to the bottom. The wastewater then moves into a sedimentation tank where the flow of water is slowed, and suspended solids (small particles) settle at the bottom to the tanks, forming a layer called raw primary biosolids or sludge. This layer is pumped out of the tank and can be reused, disposed of in a landfill, or incinerated. While primary treatment removes the majority of solids from wastewater, it fails to bring water to the cleanliness required for reuse, thus the need for secondary treatment [16].

In some cases, the load of wastewater is higher than the plant capacity (e.g., storm events, seasonal melt, etc.) therefore water cannot be held in sedimentation tanks for the time required for proper sedimentation. Chemically enhanced primary treatment (CEPT), which involves processes called coagulation and flocculation, will sometimes be used to remedy this issue. During coagulation, a coagulating agent (in most cases a metal compound such as alum and aluminum or ferric sulfide) is introduced to the wastewater, disrupting the net surface charge and the repulsion between the pollutants and the coagulants. Flocculation, a method of mixing that promotes the formation of agglomerations, is used to increase the size of the metal particles allowing them to be removed from the solution by filtration of settling [17]. This process greatly decreases the load on the biological treatment performed during secondary treatment, however there are disadvantages. The efficacy of the coagulating agents depends on the chemical agent itself, the temperature of the water, and the pH, among other factors. This means metal ions, metal byproducts and polymer byproducts produced by the coagulants and other chemicals are likely to

be present at the end of the treatment process. The release of all these chemicals can affect the surrounding environment [18].

Secondary treatment encompasses many processes that use microorganisms to remove organic matter and capture contaminants. The treatment can be performed with the use of activated sludge in a sedimentation tank (the most popular), or by passing the wastewater through a filter medium which contains microorganisms, with several variations of these developed over time [19]. Biological treatments generally have a high removal efficiency and a low cost, but they require a skilled operator and a large space. Additionally, they are very sensitive to temperature and pH [20], and the strains of bacteria present can have an important effect on the removal of specific contaminants. A study performed by O'Grady et al. showed that while *Rhodococcus erythropolis*, a common wastewater bacterium, removed up to 47% of the synthetic steroidal estrogen 17 α -ethinylestradiol (EE2) present, both *Rhodococcus rhodochrous* and *Rhodococcus zopfii* showed no significant removal [21]. Therefore, an in-depth understanding and control of the bacteria that are present is essential for the removal of contaminants.

Disinfection is the primary method of pathogen inactivation and is performed after primary and secondary treatment [16]. There are several methods of disinfection currently in use, all requiring water with minimal organic matter present, as disinfection will break down organic waste before attacking other pathogens. Therefore the more successful the secondary treatment, the more effective the disinfection [22]. Some disinfection methods are capable of degrading contaminants in wastewater; however, they can produce harmful byproducts, therefore the removal of contaminants before this step would be preferred.

Many contaminants are resistant to degradation or removal by the conventional water treatment process. In the case that these contaminants are harmful, additional water treatment steps must be used to ensure proper removal. Many additional treatment options, such as membrane filtration, can also be used as a part of secondary treatment. However, some options, such as physiochemical or electrochemical treatments, require substantial infrastructure and others, such as Fenton oxidation, and the use of harsh chemicals to remove contaminants which can be considered undesirable. A diagram of the steps involved in municipal water treatment is presented in Figure 1.1.



Figure 1.1: Typical Water Treatment Process

The term contaminant of emerging concern (CEC) covers a wide range of chemicals, with the list being updated constantly. To be considered a CEC, the chemical has to have one of three criteria; i) be a true emerging contaminant, something that has not been recorded, or very recently recorded in scientific literature ii) a contaminant of emerging interest that was known to be present before but whose impact on the environment was not assessed iii) a well-known contaminant about which new information has been discovered, changing the way that we understand its health and environmental risks [23]. Although they are generally found in water in low concentrations (ppb or ppt), CECs can pose significant health risks such as intellectual impairment or developmental disruption. Currently, water treatment plants are not properly equipped for CEC removal [24].

One category of contaminants that are considered to be CECs are endocrine disrupting compounds (EDC) [25]. EDCs interfere with hormone actions and can therefore affect growth and development at very low concentrations [26]. EDCs include hormones, personal care products, and heavy metals that are often found in wastewater [5, 25]. This review will focus on these three categories of EDCs.

Many CECs, including ibuprofen, caffeine, carbamazepine and antibiotic sulfamethoxazole were detected in the Yamaska river of Québec [10]. This is consistent with other areas in North America where (PPCPs) have been detected in similar concentrations. Generally, the concentration of CECs increase as the nearby population increases [10] because municipal effluent is a significant source of pollution. While most wastewater undergoes thorough treatment, the process is mainly focused on removing organic matter and killing bacteria that could harm the population [16], it does not normally focus on the removal of CECs or EDCs.

Alternate materials, such as hydrogels, could be used for CEC and EDC removal in water treatment facilities. Superabsorbent hydrogels are polymeric matrices which are known for their swelling ability. They are often used for hygienic applications but have demonstrated high heavy metals adsorption capacities in recent years [9, 27]. This review explores how hydrogels can be used in the water treatment process to increase removal efficiencies for contaminants of emerging concern.

1.2 Contaminants

1.2.1 Heavy Metals

Heavy metals occur naturally in the earth's crust. However, the concentration found in waterways is increasing due to anthropogenic events. The most common heavy metals in wastewater include arsenic, lead, mercury, cadmium, chromium, copper, nickel, silver, and zinc [28]. These metals are persistent in the environment as they are not degraded in the same fashion as organic pollutants. They can only be removed or be transformed into inert compounds that have a lower bioavailability, therefore lowering their ability to cause harm. A metal is bioavailable when existing as an ionic species and is achieved when dissolved in water or in the gut or an organism. In organic soils, the metals generally become fixed and therefore have a reduced bioavailability [29]. Despite this, they can be up taken by plants, which are then eaten by herbivores and move through the food chain, with humans and other animals at the top at the greatest risk for accumulation. Heavy metals are toxic and have increasingly negative health effects as accumulation increases [30]. In some cases, heavy metals displace essential metals from important cellular cites, therefore causing cellular malfunction. In other cases, heavy metals can bind to DNA and nuclear proteins, causing the oxidative deterioration of macromolecules [31]. This can cause a variety of symptoms including cognitive impairment and nervous system disorders [31].

A study performed by Bouchard et al. found that increasing manganese concentrations in tap water led to increased accumulation of said metal in the hair of children. Higher concentrations of manganese in hair were negatively correlated with IQ, with a 10x increase in concentration correlating to a two-point drop in IQ [32]. This data supported Bouchard et al.'s hypothesis that the current concentration of manganese in drinking water is harmful, as it is above the concentration at which cognitive impairment could be observed [32]. Other heavy metals such as lead, in particular, is neurotoxic at very low levels (blood lead concentration of under 7.5 μ g/dL)

and children are particularly vulnerable. A study by Lanphear et al. found that high lead levels lead to a decrease in IQ, with an increase from blood levels of 2.4 to 30 μ g/dL, leading to a decrease of 6.9 IQ points. However, an increase from blood levels of 2.4 to 10 μ g/dL lead to a decrease of 3.9 IQ points, suggesting that very low doses could cause significant damage [33].

There are many industries, such as mining and battery manufacturing, that produce wastewater which contain heavy metals, particularly copper and cadmium, as a byproduct [34]. The main methods of removal for heavy metals include membrane separation (reverse osmosis, nanofiltration, ultrafiltration) and adsorption. Due to the cost of adsorbents, adsorption models are often used to predict the specific amount of adsorbent required to adsorb a certain amount of contaminant in order to minimize wastes. The adsorption models are calculated using experimental data to determine adsorption coefficients. This data is then compared to various models to determine which is the best fit [35]. The adsorption of heavy metals by an adsorbent can be quantified using the Freundlich and Langmuir isotherms [36]. The Langmuir isotherm is considered to be monolayer adsorption, where the maximal adsorbance is calculated per unit mass as well as the Langmuir constant, which shows the solutes affinity for the solvent. The Freundlich adsorbed per unit mass increases with time [35].

1.2.2 Hormones

Hormones are an important class of CECs. They can enter the wastewater stream as a result of human consumption, or can be the result of runoff from agricultural fields where manure has been applied as a fertilizer [37]. These hormones are estrogenic EDCs and disrupt the growth and reproductive cycles of aquatic life [24]. Estrogenic EDCs currently affect wildlife, including invertebrates, fish, amphibians, reptiles, birds, and mammals, in a variety of ways such as abnormal blood hormone levels, altered gonadal development (e.g., imposex and intersex), induction of vitellogenin gene and protein expression in juveniles and males, masculinization/feminization, hermaphroditism, and decreased fertility and fecundity [38-41]. Even at the low quantities currently measured in wastewater effluent, a mix of estrogenic EDCs have been found to disrupt the development of rat testicles [42].

There are several estrogenic EDCs, however the main estrogens of concern are 17 β estradiol (E2) which is the primary natural estrogen, and the synthetic steroidal estrogen 17 α - ethinylestradiol (EE2), which is the main component in birth control pills. The overall estrogenicity of EE2 overshadows that of E2 in municipal wastewater. A study by Snyder et al. found that E2 concentration in water ways near wastewater treatment plants was as high as 324 ng/ml, while EE2 levels could reach 71260 ng/ml [43]. These two compounds are the main causes of feminization, induction of vitellogenin, and altered gonad development [24].

Seasonal variation in hormones, specifically E2 and EE2, can have important impact on the environment. Estrogen removal techniques tend to work better during the summer months, however the concentration of estrogen downstream from water treatment facilities increases in the summer months [44]. It is hypothesized that this is because rivers have a lower flow rate in the summer, leading to the effluent making up a greater portion of the river's flow. This leads to high concentrations in river sediment, as a lower flow rate allows particles containing estrogen to settle out of the water, and highlights the need for a system that can handle seasonal variations of hormone concentrations [44]. The removal of hormones from wastewater is currently done through four main treatments: exclusion by a filter, oxidation, bacterial degradation and adsorption. The adsorption of estrogens can be quantified using Freundlich and Langmuir isotherms [45].

1.2.3 Pharmaceuticals and Personal Care Products (PPCP)

Veterinary medicine, prescription drugs, and over-the-counter drugs are all classified as pharmaceuticals and are used to treat medical conditions. Personal care products (PCP), in contrast, are products that are designed to increase the quality of life of the user. These products include shampoos, sunscreens, and soaps. PCPs contain a variety of chemicals such as UV stabilizers and disinfectants. Concern over the unintended release of pharmaceuticals and personal care products (PPCP) into the environment has been increasing in recent years [46].

A list of 33 priority contaminants was first established in 2000 by the EU Water Framework Directive [47]. These contaminants were judged to be disruptive to the ecosystems they were released into, and therefore worth monitoring. In 2007, PPCPs such as musks and diclofenac (Voltaren, a nonsteroidal, anti-inflammatory drug) were added to this list. Other prominent PPCPs include ibuprofen, caffeine and triclosan (antibacterial, antifungal agent present in many PCPs) [46].

This category of contaminants is extremely diverse and can have varied effects on the environment. PPCPs are harmful as they can be persistent, bio accumulative, and toxic. They are

not easily removed by the water treatment process and are therefore present in drinking water and in the aquatic environment. While not all PPCPs are persistent, non-persistent PPCPs are still an area of concern as they are a component of many people's everyday routine and are therefore constantly being released into the environment, leading to a pseudo-persistence. Ibuprofen is a prime example of a compound that has a low persistence (3–7 days) however, due to its constant release, it is continually found in the environment [46].

PPCPs have an important effect on aquatic life as they, and their metabolites, are biologically active. Over 145 PPCPs, including caffeine and triclosan, have been measured in aquatic organisms such as fish and clams [46]. The toxicity of these compounds is an area of high concern because many of the compounds are designed to be the most effective at low concentrations. They can interfere with endocrine systems of aquatic organisms and cause undesirable effects to the organism or its offspring. Additionally, mixing of different PPCPs at low concentrations may cause synergistic effects leading to a higher toxicity [46]. Moreover, anti-infective substances such as trisoclan may contribute to antibiotic resistance. Release at low levels expose bacteria present in the ecosystem to levels that can allow for the development of a resistance which can have an indirect effect on human health [48]. Though the presence of PPCPs is detrimental for human health, their presence can be useful as the presence of certain PPCPs can signify that other harmful contaminants are present, and therefore be used for surveillance. For example, caffeine is a good indicator of human fecal contamination [49].

Personal care products are removed from water in the same fashion as estrogens. However their kinetic removal models may vary between Freundlich and Langmuir isotherms, and Dubinin-Ashtakhov isotherms depending on the chemicals being studied [50]. The Dubinin-Ashtakhov isotherm is based on a model for microporous adsorption[51] which has been used in the past for gases and vapors [52, 53] as well as for the adsorption of organic solutes from aqueous solutions on porous substrates [54].

1.3 Legislation

The World Health Organization cannot force countries to implement legislation limiting water pollution but has released several guidelines for water quality over the years. In 1987, guidelines for the reuse of wastewater were established by "The Scientific Group on Health Guidelines for the Use of Wastewater in Agriculture and Aquaculture" [55]. These guidelines

established three categories of water reuse; A—irrigation of crops that are likely to be eaten raw, sports fields and public parks, B–irrigation of cereal crops, industrial crops, fodder crops, pasture and trees and, C—localized irrigation of category B crops if no public or worker exposure occurs. These recommendations set limits on the allowable concentrations of nematodes, fecal coliforms, and microbiological colonies for each category. Categories with a higher level of human exposure, such as A, have much lower permissible limits of contaminants. In 1989, the World Health Organization (WHO) issued guidelines for water quality, building on their previous guidelines, becoming the reference for other subsequent guidelines such as those released by the WHO in 2006 [56] and the EPA in 2012 [57] for water reuse, and the 2018 EPA guidelines for drinking water contamination (Table 1.1) [58]. Targets for different contaminants can be seen in Table 1.1. Despite the publication of these guidelines, they are not legally binding, and each state/country is able to set their own limitations based on category of reuse (irrigation of different crops, release into environment, etc.), cost and societal norms, leading to a large difference depending on the region. Developed countries tend to have stricter regulations concerning water, this is partly because they have the infrastructure to meet stricter targets.

In developed countries such as Switzerland and the United States there are defined regulations for limits on pollutants in wastewater. Compounds such as carbamazepine, DEET and estrone are monitored as they indicate that other CECs may also be present. In the EU the Water Framework Directive (WFD; 2000/60/EC) and subsequent regulations (2013/39/EU, Decision 2015/495 and Decision 2018/840), lists CECs such as 17 alpha-ethinylestradiol (EE2), 17 beta-estradiol (E2), estrone (E1), erythromycin, clarithromycin, azithromycin, ciprofloxacin and amoxicillin as compounds to be monitored for possible future regulation [59-62]. By contrast in developing countries the environmental pollution is managed under both general and specific laws. For example, in Kenya, two main laws (the National Environment Management and Coordination (amendment) Act, 2015, and the Water Act, 2016) govern water pollution management [63, 64]. Due to the variety of regulatory frameworks around the globe, permissible levels of CECs vary greatly.

Contaminant	WHO 2006	EPA 2012	EPA 2018
Helminth Eggs	<1 g/L	-	-
E.Coli or Fecal Coliforms	<10^3	Bellow	Bellow
	bacteria/100 ml	Detectable	Detectable
		Limit/100 ml	Limit/100 ml
Soil Concentration of Heavy	0.2 - 635 mg/kg	-	-
Metals			
Soil Concentration of Organic	0.0012 -	-	-
Pollutants	13733 mg/kg		
Heavy Metal Concentration in	-	0.01-5 mg/L	0-0.8 mg/L
Water			
Organic Pollutant Concentration	-	-	0-0.7 mg/L
in Water			
Biochemical Oxygen Demand	-	<10 mg/L	-
Radioactive Elements	_	-	0 mg/L

Table 1.1: Water Quality Guidelines (2006–2018)

1.4 Water Treatment Methods

1.4.1 Physical, Chemical and Electric Treatments

Physical, chemical, or electric contaminant removal methods can be employed as a part of primary treatment (e.g. coagulation and flocculation or electrocoagulation) or used to remove specific contaminants. These methods primarily rely on chemical treatment, physical barriers, or electric charge. The efficiencies of common physical, chemical, or electric removal are presented in Table 1.2.

Table 1.2: Removal Efficiencies of Physical, Chemical or Electric Methods for Common CECs [34, 65-77]

Removal Methods	Heavy Metals	Estrogens	PPCPs
Chemical Precipitation, Coagulation and	60–99%	-	75–77%
Flocculation			
Membrane Filtration	82-99%	90%	>99%
Ion-Exchange	95-100%	-	90%
Electrocoagulation	>99%	87–98%	34%
Electrodialysis	67–100%	57-72%	57-72%

1.4.1.1 Chemical Precipitation, Coagulation and Flocculation

Chemical precipitation is one of the most commonly used methods of heavy metals removal in industry and generally used for inorganic effluents. This method produces "insoluble precipitates of heavy metals" [17] which are formed by reacting the dissolved metals with other chemicals to generate very fine particles. Coagulation and flocculation are being used to increase the size of the particles, encouraging them to settle out of solution. One of the most commonly used precipitation processes is the addition of lime, which forms metal hydroxides as precipitates [17]. This process has a removal efficiency ranging from 60 to 99%, depending on the pH of the wastewater and the concentration of precipitants used [65]. The advantages of this process include simple, inexpensive operations, and the ability to remove most of the heavy metals from the solution. However, this process creates a large amount of chemical sludge and there is an extra cost incurred for the disposal of this waste [7]. This process can also be used for the removal of personal care products. A study performed by El-Gohary et al. used wastewater from Unilever Mashreq Company, a PPCP manufacturing company, containing components found in many PPCPs such as sorbitol, stearic acid niacinamide and dimethyl ammonium. They found that 75 to 77% these components could be removed, depending on the coagulant used [66].

1.4.1.2 Membrane Filtration

There are several kinds of membrane filtration, with the most common-being ultrafiltration, reverse osmosis and nanofiltration. The working process behind these methods is to pass the water through a semipermeable membrane to remove contaminants. This is effective at removing dissolved solids, heavy metals and organic contaminants [17].

Reverse osmosis (RO) is a process that was developed to remove salt from brackish and sea water. It is performed by pumping water through a semipermeable membrane. This system relies on hydraulic pressure to force water in the incoming stream through the filter to the filtered side. The pressure used in RO varies depending on the kind of water being filtered [78]. Fresh or brackish water requires 0.2-1.7 MPa while sea water requires 4–7 MPa as it must overcome its natural osmotic pressure of 2.4 MPa. RO systems can filter out particles as small as 0.1 nm [78]. Nanofiltration was also developed to reduce the salinity of water. It has previously been used to remove pesticides and other micropollutants such as dyes from wastewater [34]. It is very similar

to reverse osmosis; however, it uses a larger mesh size for the filter and as a result nanofiltration requires a lower pressure and therefore less energy. Nanofiltration also tends to have a lower filtering capacity, only being able to filter out particles as small as 1 nm [78]. Ultrafiltration (UF) uses a semipermeable membrane to separate contaminants from wastewater based on pore size and molecular weight. Depending on membrane specifications, it can achieve up to 90% removal of contaminants at pressure ranging from 2 to 5 bar, which is low pressure when compared to reverse osmosis. Polymer-supported ultrafiltration is a variation of ultrafiltration that uses water soluble polymeric ligands to bind with contaminants present in wastewater. These form large complexes allowing the contaminants to be filtered out more effectively and easily. Additionally this can make the process more selective as ligands can be selected to bind to specific contaminants [17]. Generally, membrane filtration has a high operational cost due to fouling of the membrane, but requires little space and the membrane can be selected to target specific contaminants [7].

A study by Qdais and Moussa found that reverse osmosis has a removal efficiency for copper ions of 97%, and a removal efficiency for cadmium of 98.5% (initial concentrations ranging from 25 to 200 ppm) [34]. Authors of the same study used an analog for wastewater containing both ions, and it was found that the reverse osmosis membrane was effective at removing both simultaneously. The original effluent contained a total of 500 ppm of heavy metal ions and the reverse osmosis membrane reduced the effluent to 3 ppm (99.4% efficiency). Additionally, Qdais and Moussa found that the removal efficiency of copper ions by nanofiltration varied from 84 to 96%, and that the removal efficiency of cadmium varied from 82 to 97%. Removal efficiencies were dependent on the initial concentration of ions in solution (25 to 200 ppm). When a solution containing copper and cadmium ions (500 ppm) was treated using nanofiltration, a 97.4% removal was measured (effluent with 13 ppm). Finally, Qdais and Moussa hypothesized that higher removal efficiencies could be achieved by both reverse osmosis and nanofiltration by increasing the pressure of the systems [34].

Membrane filtration is an effective way of removing PPCPs from wastewater. However, its efficiency is highly dependent on the membrane and method chosen. While some membrane systems, such as ultrafiltration did not reject most PPCPs, reverse osmosis was effective. According to Snyder et al., only trace amounts of a wide range of PPCPs such as caffeine, triclosan, and diclofenac were found in effluent using reverse osmosis. The similarly small pore size of nanofiltration filters suggests that nanofiltration would also be effective [67]. Membrane filtration

can achieve 90% estrogen removal when using reverse osmosis and nanofiltration that have tightly knit membranes with small pore size [68, 69].

1.4.1.3 Ion-Exchange

Ion exchanges attract soluble ions from a liquid phase to a solid phase. One of the most common forms of ion exchangers is the synthetic organic ion exchange resins. These resins will adsorb ions, replacing them with organic ions of the same charge such as sodium and sulfate. It is very effective at low concentrations of ions [17]. This process has a high regeneration of required materials. Additionally, it is highly selective and depending on pH, it can be used to target a specific ion. However, it has a lower removal efficiency than other methods at high concentrations of ions, and it is expensive [7].

This process is effective for the removal of heavy metals such as copper, cobalt, lead, cadmium [79-81], and nickel, with 95–100% nickel removal achieved after three hours contact time in a batch reactor [70]. The removal of diclofenac (a common pharmaceutical) from human urine using ion exchange membranes has been measured in laboratory settings with an efficiency above 90% for anion membranes. However this removal efficiency was affected by the characteristics of the solution such as the presence of other ions [71].

1.4.1.4 Electrocoagulation

Electrocoagulation is a process where a current is passed through contaminated water. The current is initiated by electrolytic oxidation of an appropriate anode material, which removes the need for chemical addition [17]. In theory, it has the advantage of removing particles with smaller sizes than chemical coagulation as the particles are more excited by the electric field, causing them to collide and coagulate [82].

This process can remove several CECs. Heavy metals are removed at the anode, and can result in the recovery of pure metals [17]. This process has been used to remove cadmium, copper and nickel from simulated wastewater with removal rates over 99%. The removal of heavy metals is affected by the pH, initial metal concentration and the current density of the system [72]. Moreover, studies have shown that the method was effective at removing estrogens, including a study by Maher et al. which demonstrated a removal efficiency of 87% for E2 and 97% for EE2 [73]. This method has also been used with limited success for the removal of pharmaceutical

components from wastewater produced by Osvah Pharmaceutical Company located in Tehran, Iran. A study conducted by Farhadi et al. reported a removal efficiency of about 34% [74]. However, there are disadvantages, such as high initial and operational costs associated with this method. Additionally, the pH and the density of the initial solution must be adjusted complicating the process and increasing the amount of chemicals used [7].

1.4.1.5 Electrodialysis

During this process, ions pass through an ion exchange membrane. As the water enters the cell where multiple membranes (alternating anion and cation characteristics) are contained, the ions will be attracted to the anode or the cathode, passing through the membranes, exchanging heavy metals for other ions [17]. This process has a high separation selectivity and can therefore be used to remove a specific ion. However, it also has a high operational cost due to membrane fouling and energy consumption. It has been used to remove cadmium and tin from water produced by the electroplating industry, with maximum removal efficiencies reported at 78.5% and 67.3% respectively [75]. This method has also been used to remove lead from aqueous solutions, reaching almost 100% removal [76].

Electrodialysis can also be used to remove a range of emerging contaminants such as estrogens and pharmaceuticals, including bisphenol A and oxybenzone (a sunscreen compound) from wastewater. Removal efficiencies varied greatly depending on whether anionic or cationic membranes were used. Anionic membranes resulted in higher removal efficiencies that ranged between 57 and 72% [77].

1.4.2 Disinfection/Oxidation Treatments

Disinfection is used primarily to deactivate bacteria and viruses; however, it can provide added benefits in the form of CEC destruction or removal. These processes can produce harmful by-products that are important to be aware of. The removal efficiencies of these methods can be seen in Table 1.3.

Removal Methods	Heavy Metals	Estrogens	PPCPs
Chlorination	-	99% (harmful by-	90%
		products)	
Ozonation	-	57–99%	90% (harmful by-
			products)
UV Radiation	26–99%	60–95%	90%
Ferrate	18–99%	99%	90%
Fenton and Fenton like	-	95%	10–99%
Oxidation			

Table 1.3: Removal Efficiencies of Disinfection/Oxidation Methods for Common CECs [83-94]

1.4.2.1 Chlorine

The most popular way to disinfect wastewater is through the addition of chlorine. It is used to kill pathogenic bacteria (99%) and reduce odors. However, there are issues with chlorine polluting surrounding surface waters [16] as well as harmful byproducts that can be present after the disinfection process [22]. Some regions require excess chlorine to be removed prior to the water being released into the environment, increasing the process cost. Additionally, chlorine can be difficult to transport, handle and store. For this reason, some plants use alternative methods of disinfection such as ozone or ultraviolet light [16].

Chlorination can be used to kill pathogens with up to 99% deactivation when done correctly [16] and can also be used to remove other contaminants such as estrogens. At ideal conditions, such as high temperature and an excess of free chlorine, 99% removal of estrogen can be achieved [83]. Chlorination generally decreases the estrogen levels of wastewater, however the degradation of estrogens by chlorine can form carcinogenic byproducts such as 4-chloro-E2 and 4-chloro-EE2. Therefore, despite its potential for estrogen deactivation, the use of chlorine to degrade estrogens must be closely monitored, and the byproducts must be well known before it can be used for large-scale plants [95-97].

Chlorination can be effective for the removal of personal care products from wastewaters. For some amine substituted antibiotics, it has up to 90% removal efficiency. However it also has a high possibility of reacting with the compounds present to form byproducts that have the potential to be more harmful [84].

1.4.2.2 Ozonation

Ozone is an unstable gas that is a strong disinfectant with a high oxidation potential. When ozone comes into contact with water, it dissociates and forms hydrogen peroxide and hydroxyl groups [22]. This inactivates bacteria by oxidizing their bacterial membrane, leading to cell lysis [98]. The mechanism of inactivation varies with other contaminants such as viruses and protozoans. One possible method is to damage the constituents of the DNA and RNA which can be done directly or by energizing DNA causing the fusion of two base pairs, or indirectly by exciting oxygen [99]. This causes a reactive oxygen which can cause a guanine to thymine transversion [100].

Generally, the effectiveness of ozone is dependent on the concentration of ozone and exposure time. Effluent from secondary treatment is mixed with ozone in a contact tank (after ozone generation, the air mixed with effluent generally contains 0.3-0.5 % ozone). The ozone is left in contact with the solution for 10 to 30 minutes, a relatively short contact time as compared to other methods of disinfection [22]. This process is less effective on effluent with a high organic matter content, as ozone will preferentially degrade organic matter over bacteria. Therefore, it works best on effluent that has undergone secondary treatment. Despite its strong disinfection power, ozone is potentially toxic and explosive. Additionally, the method is costly and should be generated on site, thus limiting its use [98].

Ozonation has been found to remove 62-98% of estrone and 57-100% of estradiol [85]. A study performed by Ternes et al. showed that ozonation with a contact time of 18 minutes led to levels of estrone (a natural estrogen) falling below detectable levels, which is promising. However, the products of the ozonation process are difficult to study. Generally, ozonation increases the number of functional groups on the molecule and therefore its biological activity. A hydroxylated estrone will lose its affinity for the estrogen receptor and thus greatly reduce the estrogenic activity of water [85]. This is consistent with a study performed by Nasuhoglu et al. that found that ozonation of wastewater in normal disinfection doses removed up to 98% of estrogenic activity [86]. In 2012, a study by Larcher et al. focused on identifying the byproducts that resulted from the reaction of E2 and EE2 with ozone. It was found that the byproducts included two compounds with phenolic rings. The estrogenic activity of these compounds was greatly reduced when compared to the parent compounds [101]. A study by Bila et al. found that the byproducts of E2 degradation were highly dependent on pH. Byproducts formed at pH 11 include 10 ε -17 β -

dihydroxy-1, 4-estradieno-3-one (DEO) and 2-hydroxyestradiol.[102] However E2, EE2 and the byproducts of EE2 had a negative effect on the production of testosterone in rat testes, with the byproducts having the largest negative effect [101].

A study performed by Lassonde et al. showed that the mix of synthetic and natural estrogens currently found in wastewater disrupted the development of rat testicles, greatly reducing their growth. When water was treated with ozone, the mix of estrogens was removed. When rat fetuses were exposed to the treated water, they showed no ill effects [42]. While the team was successful at removing the parent estrogens, the team did not focus on assessing what byproducts may be present and their possible negative effects.

Ozone is also an option that has shown potential for the removal of PPCPs from wastewater. It reportedly has a removal efficiency of over 90% for many prominent PPCPs such as antibiotics, nonsteroidal anti-inflammatory drugs, preservatives and disinfectants [87]. A study performed by Kolosov et al. found that ozonation removed between 45 and 73% of ibuprofen in a synthetic wastewater solution with an adjusted pH of 10 [88]. It can be combined with chemical catalysts which decrease the reaction time. However, ozone can cause the formation of intermediate chemicals as the PCPs degrade. These intermediate chemicals can be equally or more toxic than the initial chemical. In order to safeguard the water supply from this toxicity, ozonation must be paired with a filtration system (biological or membrane) to ensure that any toxic intermediates are removed [103].

1.4.2.3 UV Radiation

Ultraviolet (UV) disinfection is a physical method of pathogen inactivation. UV disinfection systems use electromagnetic energy from mercury arc lamps to disrupt DNA and RNA's crystalline structure, therefore deactivating the living cells [104]. The effectiveness of the system depends on the contact time, type of mercury lamp, turbidity of the wastewater and the type of reactor [105].

Mercury UV lamps are typically composed of mercury and a gas such as argon. There are two main types: low-pressure lamps (LP) and medium pressure lamps (MP). LPs typically operate at 1 Pa. They have a radiation peak at 265 nm which is optimum for pathogen inactivation, however, radiation at 254 nm will work well for a typical UV disinfection process. The wall temperature of this process typically varies between 30 and 50 °C. The efficiency of UVC

generation in this system varies between 25 and 40%, however, it is greatly influenced by ambient temperature. LP Amalgam lamps are a subset of LPs. They use an amalgam of mercury (normally mercury/indium) rather than pure mercury. They operate at 1 Pa and 100 °C. They have a much higher output of UVC-flux per unit length (1000 as compared to <350 for standard LP). Additionally, the higher temperature output of the light means that the ambient temperature has a lower effect on UVC generation. As for MPs, they operate at 100 kPa because they have a higher electrical power input. They have a continuous UV output spectrum but operate at temperatures between 500–950 °C, which can cause issues with other equipment. They have a higher UV flux per length than amalgam LPs but have a much lower UVC efficiency at 5–15% [104].

Due to their higher power density, MP lamps are often chosen for municipal water treatment facilities. UV light is a line-of-sight treatment, meaning that the bacteria must be directly exposed to the radiation. To achieve optimum line of sight, lamps can either be submerged in wastewater (with thermal protection) or suspended above a transparent conduit. UV light is adsorbed by water; therefore, the treatment is most effective close to the lamps. Both submerged and suspended lights require contact time of 10–30 seconds. While UV disinfection is extremely effective and does not produce harmful byproducts, high suspended solid counts render the treatment ineffective as the solids block the transmission of UV. Additionally, bacteria can sometimes repair damage in a process known as "dark repair", making the process ineffective [105].

UV radiation is an effective method for inactivating bacteria and viruses [105] as well as estrogens and PPCPs. For PPCPs such as antibiotics, nonsteroidal anti-inflammatory drugs, preservatives, and disinfectants, it generally has removal efficiencies of over 90%. However, this varies depending on the PPCP being targeted [87].

UV radiation has a removal efficiency ranging between 60 and 95% for estrogens [87]. It is capable of causing the complete degradation of 1 mmol of estrogen within 6 hours [106], however this is a much longer contact time than the norm in water treatment (10–30 s). When UV disinfection is combined with ozonation, it increases the efficiency of the process and reduces the required contact time [107]. UV disinfection can also be used with other oxidizers such as TiO₂ to increase efficiency [108]. It has been used with photocatalysts to remove contaminants such as specific heavy metals. This achieves removal efficiencies ranging from 26 to 99.9% depending on pH and contaminant type (lead or cadmium) [89].

1.4.2.4 Ferrate

Ferrate is an oxidizer and a coagulant. In acidic conditions, ferrate has a higher oxidizing potential than ozone [109]. It has been investigated to remove E2 and EE2, showing high removal capacities (99%) however, the dose required is highly dependent on the quality of wastewater. An increase in the amount of dissolved organic matter contained in the water requires an increase in the dose of ferrate [90]. Ferrate also shows a promising ability to oxidize acidic pharmaceuticals, demonstrating over 90% removal for 7 out of 14 tested pharmaceuticals (including Diclofenac) [91].

Additionally, ferrate is effective for the removal of certain heavy metals from wastewater. In a study performed by Lim and Kim, heavy metal removal (copper, zinc, magnesium) efficiencies ranged between 18 and 99%. The removal percentages were highly dependent on the dose of ferrate used and the characteristics of the wastewater such as pH [92].

1.4.2.5 Fenton Oxidation

Fenton oxidation is a chemical reaction which is performed using acidic conditions, iron salts and hydrogen peroxide. It relies on hydroxyl radicals to oxidize contaminants. This system can be used for PPCPs such as antibiotics, nonsteroidal anti-inflammatory drugs, preservatives and disinfectants with an efficiency ranging from below 10% to 99% depending greatly on the PPCP being targeted [87]. A study performed by Sabri et al. found that traditional Fenton oxidation removed 95% of ibuprofen from wastewater in laboratory conditions [93]. However, the parent compound was degraded into several by-products whose effects need to be studied further. Fenton, like oxidation of estrogens, has been used for the removal of E2 and EE2 from wastewater. It achieved removal efficiencies of over 95% for both estrogens using ferric concentrations of 1 mmol/L [94].

1.4.3 Biological Treatments for Wastewater

Biological treatment is used as secondary treatment in most wastewater treatment plants. In general, studies have shown that biological removal methods can be effective against estrogens. Estrogenic hormones degrade over time (approximately 11 days), making them easier to remove from the environment than contaminants that do not degrade such as heavy metals [110]. Smallscale testing and biodegradation modules have suggested that existing biological treatment methods can remove over 90% of natural and synthetic estrogens from wastewater. This can be done using the activated sludge process, or by using a membrane bioreactor that has nitrification/denitrification capabilities [110]. While biological methods show a high removal efficiency for a variety of CECs, removal efficiencies decrease during periods of increased influent concentrations due to seasonal variations. Additionally, removal efficiencies can vary between contaminants in a CEC category (ex. higher removal of one heavy metal than another) and can vary for a specific contaminant depending on process conditions. The removal efficiencies of different biological removal methods can be seen in Table 1.4.

Removal Methods	Heavy Metals	Estrogens	PPCPs
Activated Sludge Process	6–99%	75–99%	70–99%
Biological Nutrient Removal	6–99%	95%	80%
Membrane Bioreactors	64–92%	75–99%	90%
Biological Filtration/Trickling	22-71%	-	90%
Filter			
Algae	50-90%	-	>50%

Table 1.4: Removal Efficiencies of Biological Methods for Common CECs [6, 111-125]

1.4.3.1 Activated Sludge Process

The activated sludge process (ASP) is the most common secondary treatment. During ASP, the effluent from primary treatment enters an aeration tank where it is mixed with oxygen and bacteria rich sludge and allowed to sit for several hours. During this time, the bacteria break down the organic matter creating more sludge. The resulting bacteria-rich sludge is reused and mixed with the next batch of sewage. From the aeration tank, the sewage passes into a second settling tank to remove excess bacteria [16]. This process has the potential for CEC removal of up to 99% for certain CECs [111].

Large scale testing in Canada has shown that conventional secondary biological treatment systems can remove 17 β -estradiol (E2) as well as estrone from municipal wastewater. Water treatment plants that used activated sludge had removal efficiencies ranging from 75 to 98%, reducing E2 levels from 15.6 ng/L to 1.8 ng/L without further treatment. However, the removal of estrogen varied greatly, with removal varying from 98% to having a larger concentration in the effluent than the influent. Additionally, while treatments were able to remove most of the estrogen, traces lingered for at least 26 days in bioreactors. This study also suggested that treatment plants
with denitrifying bacteria have better E2 removal than those that did not, however this link is not understood and could simply be due to a larger diversity in microbiota [112]. ASP has also proved to be efficient for the removal of many PPCPs, with over 85% removal for 55 PPCPs [113]. The removal efficiencies for prominent PPCPs is particularly promising with 99% removal measured for ibuprofen, 95% for caffeine and 70% for Trisoclan [111].

Heavy metals can be removed through ASP as well, however the removal efficiencies vary greatly depending on the pH, temperature, initial concentration, and heavy metal being targeted. A study by AjayKumar et al. explored the effect of these parameters on cadmium, copper, nickel, and zinc adsorption. The authors found that removal efficiency varied between 6 and 99%. The highest removal efficiencies were observed at basic pH with long contact times [6]. The remaining heavy metals contaminate the sludge and thus an adequate disposal method needs to be implemented. One common disposal method for this sludge is to spread it on the ground. This is problematic as a portion of metals contained in the sludge remain mobile and will return to the environment through leaching. For metals such as copper and zinc, 40% returns to the environment [126].

1.4.3.2 Biological Nutrient Removal Plants

Biological nutrient removal (BNR) is used to remove nutrients such as nitrogen and phosphorus but can also remove CECs using nitrification and denitrification. Nitrification takes place first, converting ammonia into nitrate. The nitrate is then removed from the solution by microorganisms and converted into nitrogen gas during denitrification. These plants can have different configurations, however, they all rely on this same working principle, recirculating the sludge through the system [127].

This system is effective for the removal of estrogens and PPCPs. Natural estrogens are degraded in both the nitrifying and denitrifying tanks, however synthetic estrogen (EE2) is only degraded in the nitrifying tank. Overall, BNR has an estrogen removal efficiency of 95% [114]. When BNR is used in combination with disinfection, it can remove up to 80% of PCPPs (55 different ones including antibiotics, analgesics, antiepileptics, antilipidemics, antihypertensives, antiseptics and stimulants) from municipal wastewater [115]. Additionally the sludge from these plants can remove heavy metals from solution through biosorption just as in the activated sludge process [116].

1.4.3.3 Membrane Bioreactor

Membrane bioreactors (MBR) offer sewage treatment plants the option to operate with longer retention times on a smaller area of land. They integrate biological degradation with membrane filtration and efficiently remove both organic and inorganic contaminants. A study conducted by Anderson et al. showed that the degradation rates for E2 in traditional activated sludge and bioreactor sludge did not differ. However, MBR system showed little to no degradation of synthetic EE2, which is much more persistent [117].

Membrane bioreactors are capable of heavy metal removal with a slightly higher efficiency than the activated sludge process. This is due to the membrane and will vary depending on pore size. They generally have removal efficiencies ranging from 64 to 92% depending on the metal [118]. Additionally, this method shows promise for the removal of some PPCPS. In a study performed by Kim et al., the removal of 99 PPCPs by MBR was studied. It was found that 23 of the 99 PPCPs (including included anti-inflammatory, antibiotic and antifungal agents) were removed at levels above 90% [119].

1.4.3.4 Biological Filter Systems/Trickling filter

Biological filter systems are composed of porous media that remove contaminants from solutions. They function through two mechanisms: straining of large particles and adsorption of smaller particles. There are generally multiple layers of filter media (e.g., sand and silt clay) covered by a biofilm [120].

Sand filtration media have a large variability in their ability to remove PCPs. A study by Reungoat et al. demonstrated removal efficiencies ranging between 20% to 85% [121]. A biological filter system can also be built with granular activated carbon. This allows for the dual processes of efficient adsorption and filtering. With a contact time of less than 20 min, a granular activated carbon system was able to remove 21 PCP with above 90% removal efficiency, some of which are normally very poorly removed [121].

A trickling filter is a specific kind of biofilter, constructed using stones, used for secondary wastewater treatment [128]. The removal efficiencies of trickling filters vary greatly for heavy metal removal. One study found efficiencies from 22 to 71% for copper removal [122]. The characteristics of the effluent itself is an important factor for the removal efficiency [122].

1.4.3.5 Algae

Micro algae are microscopic photosynthetic organisms which uptake contaminants as they grow [120]. Algae can then be removed and recycled into fertilizer, depending on the contaminants present. This is a simple process that avoids the production of unusable sludge. However, it can be difficult to harvest the algae once it is fully grown. Several methods have been used to immobilize the algae such as encasement in alginate beads or immobilization in filters. This process can be done by a single microalgae pond or by sequential ponds with different species of micro and macro algae in each, targeting different nutrients [129]. The removal rate will vary largely depending on the setup and algae chosen [129].

This process can be performed with the presence of bacteria. Bacteria generally require aeration, which is provided by microalgae. In this case, the algae and the bacteria work together to rid the water of contaminants [120]. Many different live algae species can be used to remove heavy metals from wastewater. Both marine and freshwater algae have been tested for their bioaccumulation of metals. A study performed by Hamdy investigated the use or 4 different species of algae (3 brown, 1 red) for the removal of chromium, cobalt, nickel, copper, and cadmium. Removal varied depending on metal and algae, however it was above 80% for all metals except cobalt [123]. Further, dried algae can also be used as an adsorbent for heavy metals. It has previously been used to remove cadmium, lead, mercury, arsenic, cobalt, zinc, nickel, and copper from solutions [124, 130]. Removal efficiencies vary depending on the dried algae used and the heavy metal being targeted; however, removal efficiencies were generally over 80%, with only nickel, zinc and cadmium showing lower adsorbance with certain strains of algae [124, 130]. Algae can also be effective for the removal of certain PPCPs, particularly pharmaceuticals. Removal efficiencies ranged from>90% to negligible for 45 pharmaceuticals tested with 23 being over 50% [125].

1.4.4 Adsorption

Adsorption is a very effective way to remove contaminants from wastewater and is performed through the addition of an adsorbent. Adsorption is the attraction between the outer surface of the sorbent and the sorbate. This leads to an accumulation of the sorbate on the surface of the sorbent. Adsorption is considered to be one of the best removal methods for contaminants in low quantities [131]. Adsorbents can be made from a variety of materials including petrochemicals, natural monomers, and various carbon sources. The removal efficiencies for various adsorbents can be seen in Table 1.5.

Removal Methods	Heavy Metals	Estrogens	PPCPs
Activated Carbon	99%	90%	90%
Biochar	33–69%	99%	99%
Manganese Oxide	Up to 1800 mg/g	82%	90%
Agricultural Waste Adsorbents	99%	90%	60–99%

Table 1.5: Removal Efficiencies of Adsorption Methods for Common CECs [7, 132-141]

1.4.4.1 Activated Carbon

Adsorbents are generally activated through one of two methods: physically or chemically. Feedstocks with large amounts of carbon are activated physically to become activated carbon, one of the most commonly used adsorbents [142]. First, feedstocks are carbonized at medium temperatures under inert atmospheres. The product of this process has a porous structure. Thereafter, the porous material is then activated at high temperatures with water vapour or carbon dioxide causing gasification, which produces a structure with developed pores that are easily accessible [142]. The adsorbent is generally applied in a packed bed filter, which can be powdered or granular [108]. The method of activated carbon addition (loose or filter bed) can also have an important effect on the removal efficiency [87]. Loose carbon can be added to wastewater as a powder and must later be removed from solution. When activated carbon is fixed in a filter bed, water is passed through the filter, removing the need for later removal. It is effective at adsorbing heavy metals, estrogens, and PPCPs.

Activated carbon can remove most heavy metals from solution and has a removal efficiency of above 99%. Despite this high level of performance, there are serval issues with the process including the high cost of activated carbon and the fact that activated carbon cannot be regenerated [7].

Activated carbon has a removal efficiency of over 90% for a wide range of PPCPs, including estrogen if a sufficient dose of activated carbon is used [132]. However, the mixture and quality of the wastewater have a large effect on the removal efficiencies. A study by Snyder et al.

showed that hydrophilic compounds tend to be removed faster than hydrophobic ones, and organic materials could easily block the pores of activated carbon, lowering removal efficiencies [67].

1.4.4.2 Biochar

Biochar is a carbonaceous, porous material created by heating biomass in a limited oxygen environment. It can be used as a sorbent, similar to activated carbon. Biochar can be an effective adsorbent for heavy metals with removal capacities ranging between 0.3 mg/m to 147 mg/g for metals such as chromium, cadmium, nickel, lead and copper. This adsorption capacity is dependent on the feedstock, method of preparation and the heavy metal [143]. Biochar is also an effective sorbent for estrogens. A study by Ahmed et al. showed that biochar was able to lower concentrations of both E2 and EE2 below detectable limits in under 42 hours [133]. Biochar is also an effective sorbent for PPCPs. It can to achieve up to 99% removal for a variety of chemicals, such as carbamazepine and caffeine, and can sustain this removal efficiency for up to 22 weeks [134].

In addition to being used in water treatment directly, biochar can be incorporated into agricultural soils. This slows the release of contaminants that may have been applied to the soil via animal manure and helps to prevent the contamination of natural water ways [37], helping to minimize what has to be removed by water treatment. This method can also be effective at minimizing contaminants entering crops grown with wastewater. Another study showed that plantain peel biochar reduced cadmium and zinc concentrations in potato tuber flesh by 69% and 33% respectively [135].

1.4.4.3 Manganese Oxide

Manganese oxide is a sorbent that can be incorporated into bioreactors. Up flow bioreactors are systems in which wastewater is pumped upwards into a tank through a porous matrix that typically houses bacteria. These matrices can be replaced by adsorbents such as granulated activated carbon or manganese oxide. De Rudder et al. found that up flow bioreactors with a modified matrix of manganese oxide could remove around 82% of synthetic estrogen and did not become saturated after 40 days. This led researchers to conclude that it was degrading EE2 and shows a promising ability for regeneration [136]. Additionally, manganese oxide shows promise for the removal of heavy metals, with removal capacities up to 1800 mg/g. It offers a high removal

efficiency, fast adsorption and selectivity towards heavy metal ions [137] as well as adsorbance at low concentrations of contaminants with small amounts of adsorbent [137]. Finally, manganese oxide can be used as a catalyst in ozonation reactions for the degradation of pharmaceuticals. This mixture has been shown to be effective at removing up to 90% total organic carbon (TOC) for a range of common pharmaceuticals [138].

1.4.5 Biosorption

Generally, biosorption is an adsorption method performed using bio-sorbents. These are biological materials that have been chemically activated to promote adsorption. The chemical used will depend on the nature of the material they are treating, but some commonly known treatments include alkali and alkaline Na₂S solutions for human hairs, and anionic surfactant to treat tea leave wastes [142].

There are several advantages to biosorption including high removal efficiency at low contaminant concentration, low cost, minimal detrimental effects on the environment [7], minimization of sludge and regeneration of bio sorbents. However, this is still a relatively new process and there are still several disadvantages such as early saturation of the adsorbent and limited potential for material improvement [7].

1.4.5.1 Agricultural Wastes (AW) based Adsorbents

Since activated carbon is extremely costly, other alternatives such as adsorbents made from agricultural wastes are gaining in popularity. Agricultural wastes generally consist of the parts of the plants that are high in cellulose, hemicellulose, and lignin. These molecules have a high content of functional groups that attract heavy metals such as hydroxyl groups [7]. The functional groups will either replace metals in solution with hydrogens or will form complexes with ions to remove them from a solution [7]. Agricultural wastes have a high affinity for heavy metals, require very little processing and are relatively low cost [7].

The feedstocks for the adsorbents are low value and low cost, thus reducing the price to manufacture the adsorbents. These feedstocks include sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, and neem bark, all of which have previously been used for the removal of heavy metals. The overall cost of the final product is influenced by the level of processing required, the local availability of the wastes and the amount of the final product

required. For this reason, though products with higher sorption capacities tend to cost more per unit, they may lead to a lower overall cost [139].

The sorbents are added to solutions, mixed for a period of time, and allowed to settle out of solution. Despite promising studies that demonstrate that high levels of heavy metal removal are possible (over 99%), there are major drawbacks [139] such as their sensitivity to the charge and size of ions. Therefore, an adsorbent that is highly effective with copper may be ineffective at adsorbing lead. Additionally, the pH of the wastewater solution must be adjusted to achieve maximized adsorption, and large doses of adsorbents are often required to remove acceptable amounts of heavy metals from solution, increasing the cost and complexity of the process [139]. The factors affecting the adsorbance are the pre-treatment, the materials used (amount of cellulose, lignin, etc.), and the method of addition (mixing, time period, amount added) [7].

Due to the diversity of agricultural waste bio-adsorbents and the diversity of processes for use reported in the literature, the mechanism for adsorption is unknown, although several have been proposed. These mechanisms include ion exchange, complexation and chelation, diffusion through the cell wall and membrane, precipitation and surface adsorption. The most likely scenario is that several of these mechanisms are occurring simultaneously and that the mechanism of removal will vary depending on the adsorbent and the heavy metal [7].

Typically, agricultural wastes for biosorption are thought of as crop residues, however wastes can come from animals as well. Chicken feathers are an animal agricultural waste that have shown great promise in adsorption. Chicken feathers make up 4–6% of the weight of an adult chicken and are a huge by-product of the chicken industry, making it low value and low cost [142]. This agricultural adsorbent has been used to adsorb zinc and copper with adsorption varying depending on feather treatment, initial concentration and metal used but zinc removal reached 0.18 mmol/g while copper removal reached 0.14 mmol/g [142].

Agricultural waste based adsorbents have also shown promise for the removal of pharmaceuticals such as anti-inflammatories and antibiotics (60–99% removal) [140] and estrogens (90% removal) [141], however this field requires more research into the feasibility of their application [140].

1.4.5.2 Biopolymers

Biopolymers are polymers that occur naturally in the environment. These polymers include proteins such as chitin and chitosan, as well as polysaccharides such as starch [17] and also include agricultural waste-based adsorbents. Biopolymers can be used for the removal of many CECs such as heavy metals. A study performed by Rana et al. investigated the use of chemically modified chitosan sourced from crab shells. Chitosan was found to be a good adsorbent for zinc, cadmium, cobalt, nickel, manganese and iron. One hundred percent removal was measured when solutions were allowed to sit for over 24 hrs and sufficient chitosan was used (5 g chitosan for 100 mg/L metal solutions) [144]. Other heavy metal biopolymer adsorbents include cellulose and hemicellulose adsorbents, with some having adsorption of over 200 mg/g [145]. Additionally, some protein biopolymers, such as the elastin ones studied by Kostal et al. to remove cadmium, are reusable. These polymers can adsorb cadmium ions and then release the ions if a trigger (such as a salt) is added to cause the aggregation of proteins. The proteins can be regenerated and reused [146], making them an eco-friendly and efficient option for the removal of cadmium.

Biopolymers can also be used for the removal of estrogens. Activated carbon encapsulated in alginate beads were used to remove ethinylestradiol from solution. At pH 3, with a dose of 10 g/L and stirring of 100 rpm, 84% removal was achieved [147]. A study performed by Li et al. used chitosan/Al2O3-HA composite beads to form an adsorbent for estrogen. This composite material was reusable and had a removal capacity of 39.78 mg/g for estradiol [148].

Adsorbents and bio-sorbents can be used as "as needed" adsorbents or can be packed into filter beds. The same is true of hydrogels. Hydrogels are chemically modified polymer networks which allows for a certain extent of customization. Hydrogels can be modified to target contaminants that the wastewater plant has a low removal efficiency for. This allows them to be more adaptable to a variety of situations.

1.5 Hydrogels

Hydrogels are 3D, physically or chemically crosslinked networks that can absorb up to thousands of times their own weight when they are immersed in water. They are an interesting class of polymers that have uses which vary from water retention in agriculture to their use in baby diapers and feminine hygiene products [149]. They can also be tailored for water remediation as they can adsorb contaminants such as heavy metals [8], motor oil [150] and diesel fuel [151].

Hydrogels are a diverse group of materials and can be classified by their monomers, their structure, or the way in which they react to their environment. The structure of a hydrogel is one of the determining factors in its swelling ability. The structure is dependent on the porosity of the hydrogel and on the shape of these pores. Non-porous hydrogels (NPH) are basic 3D crosslinked networks. They have small, irregular, collapsed pores, producing a lower exposed surface area than other structures, leading slow swelling dynamics [152]. Superabsorbent hydrogels (SAP) have a higher porosity than non-porous hydrogels. This porosity can be induced by the reaction of the components or by using foaming agents which are often acid induced, such as sodium bicarbonate. A higher porosity leads to more rapid swelling dynamics. SAP porosity is not uniform, and some cells collapse, leading to a lower surface area and slower swelling dynamics than super porous hydrogels (SPH). SPH have a high porosity and uniform pores. This is created by using a foaming agent and a foam stabilizer during synthesis. The higher, uniform porosity increases the surface area and allows for rapid swelling dynamics [152].

Smart hydrogels are hydrogels that react to changes in their environment. Some factors that can trigger a change include pH, temperature, and pressure. The triggers illicit an immediate reaction, usually the expansion or contraction of the gel [149]. The chemical composition of the hydrogel has a large effect on its swelling capacity. The chemical composition includes the chemical backbone, monomers and crosslinkers. These components can be synthetic or natural. Synthetic monomers are derived from petrochemical products and are generally long or short-chain hydrocarbons that are highly modifiable, allowing them to have a large range in properties [8]. Additionally, thanks to their known structure, synthetic monomers can be very accurately modified to target specific properties such as high swelling capacity and rapid swelling dynamics while retaining a high stability. However, synthetic hydrogels may be toxic and have low biocompatibility leading to a limitation on their applications [152].

Natural monomers are derived from plant or animal-based sources. The two main categories of natural monomers are carbohydrates and proteins. Carbohydrates are long, repeating chains, such as starch, which yield more predictable properties than the protein alternatives [9]. Protein hydrogels can be made from animal proteins such as gelatin and chitin or plant-based proteins such as zein or canola protein [8, 149]. Protein chains are not uniform and lead to a much larger variability in the properties that are expressed. Natural hydrogels have high biocompatibility and are generally non-toxic. Their applications include agriculture, biomedical engineering, and

soil remediation. While some components of bio-based hydrogels are natural, they can still contain synthetic components, generally as a crosslinker [152]. A recently published paper outlines the synthesis of a hydrogel from 100% bio-based components including starch, citric acid and itaconic acid [9].

While hydrogels are currently popular in the medical and personal care industries, they demonstrate great potential for environmental remediation, particularly in soil and water remediation as they can be used as an adsorbent and have shown an affinity for many CECs. Hydrogels have previously proved to have chelating abilities. The chelation ability of a hydrogel is dependent on the chemical composition, as different groups are available to form bonds. Additionally, the ion being targeted has an effect on the ion chelating ability. Metal ions will have charges generally varying from 1 to 3, this, coupled with the size of the ion will either increase or decreases the ion chelating ability. A polyacrylic acid hydrogel with a zein protein backbone reported on by Ni et al., achieved a copper ion removal capacity of 208 mg/g at pH 4.5 with an initial ion concentration of 1500 mg/L [8]. Additionally, as reported in literature, hydrogels have an affinity for copper, zinc, chromium, lead and nickel ions among others [27]. This allows hydrogels to remove heavy metals from solution. The fully bio-based hydrogel reported by Duquette et al. demonstrated the ability to remove copper, nickel and zinc from solutions with initial concentrations ranging from 10 to 200 mg/L. Removal (mg/g) ranged from 2.3 mg/g to 49.3 mg/g and was influenced by the heavy metal and initial concentration of the solution [9].

In a study performed by Borisenkov et al., a bio-based hydrogel made from a hybrid of citrus pectin and oak lignin showed a moderate ability to adsorb estrogen. Increasing amounts of lignin increased the estrogen adsorbance ability. Another form of lignin, wheat lignin, was also tested; however, it achieved lower levels of estrogen adsorbance, suggesting that the structure of the lignin was an essential variable. Overall this study demonstrated a bio-based hydrogel's potential as an adsorbent for estrogen [153]. Additionally, modified chitosan hydrogels have been used for the adsorbance of a common anti-inflammatory drug (diclofenac sodium). In laboratory conditions, this hydrogel was able to remove 100% of the contaminant within 5 hours, making it a promising option for similar pharmaceuticals [154].

Many hydrogels used for the removal of contaminants such as heavy metals are reusable. Heavy metals can be removed from wastewater using hydrogels and then removed from the hydrogel using acid hydrolysis [155]. Hydrogels soaked in acid baths release the heavy metals into the supernatant [156]. This can be used as a recovery method for valuable heavy metal ions. The hydrogels can then be re-used to remove more heavy metal from wastewater. In some cases, the acid hydrolysis treatment actually increases the hydrogels heavy metal removal capacity [155].

Thanks to the wide diversity of hydrogels, they can be tailored to fit a specific need. In this case the industry lacks a simple, low-cost system that can remove a wide range of contaminants at low concentrations, from wastewater while still being environmentally friendly. The use of waste products from agriculture and food industries, such as canola protein, can greatly reduce the environmental impact and price of feedstocks and therefore the final product. Hydrogels can be used in the same way as other adsorbents, avoiding complex operation and have previously been shown to have the ability to remove a range of pollutants. Furthermore, hydrogels can be added as a powder or as a solid block, which can be formed in a mold of any shape. This offers a wide range of possibilities when incorporating hydrogels into the existing water treatment system.

Connecting Statement

The literature review in chapter 1 presented a variety of techniques for the removal of contaminants from wastewater, particularly using membrane filtration or adsorbents such as hydrogels. In chapter 2, the synthesis of an acrylic acid/acrylamide hydrogel is reported on and its effectiveness as a heavy metal adsorbent is investigated. Additionally, the effect of the use of a foaming agent and a foam stabilizer during synthesis on the final structure and properties of the hydrogels is investigated. The three structures are systematically compared to determine which hydrogel shows the most promise as an adsorbent for heavy metals in wastewater.

Chapter 2 The Effect of Foaming Additives on Acrylic Acid/Acrylamide Hydrogels

2.1 Abstract

The physical and chemical properties of hydrogels are greatly dictated by their composition. In this study, modifications were brought to the macroscopic structure of hydrogels using foaming additives, and their effects on the swelling capacity and heavy metal adsorption were investigated. The hydrogels synthesized with a foaming agent and a foam stabilizer (257 g/g), with a foaming agent without foam stabilizer (195 g/g), or without any additives (182 g/g), demonstrated a significant difference in swelling capacities. The study compared the ion removal capacity for copper (II), cadmium (II), and nickel (II) under competitive and non-competitive conditions. The use of a foaming agent significantly increased the ion removal capacity of the hydrogels, from 54 to 93 mg/g cadmium, from 75 mg/g to 104 mg/g copper and from 48 mg/g to 80 mg/g nickel. Under competitive conditions, the hydrogels preferentially removed cadmium> copper> nickel. However, maximum removal decreased for individual heavy metals under competitive conditions (ex from 104 mg/g to 32 mg/g copper). This study systematically addresses the knowledge gap of how changes in the porosity of the macrostructure of acrylic acid/acrylamide hydrogels, brought on by the use of foaming additives, affects their swelling properties and their heavy metal ion removal.

2.2 Introduction

Heavy metals occur naturally in the earth's crust and have a detrimental effect on human health [4]. Human activity has increased the quantity of heavy metals released into the environment. Industrial pollution, generated by various industries including agriculture, mining, and construction, is a leading source of heavy metal ions [1, 2]. Heavy metal contamination in soil can be as high as 100,000 mg/kg [4]. The wastewater, or runoff water, from these sources contains the heavy metals and enters the water table through streams and rivers where it can come into contact with the general population if it enters groundwater. Common examples of heavy metals include cadmium, copper, lead, nickel, and zinc [3]. The maximum contaminant level in drinking

water is 0.005 mg/L cadmium and 1.3 mg/L for copper [58]. The maximum tolerable soil contamination concentration of cadmium is 4 mg/kg while for nickel its 107 mg/kg [56]. The production of nickel-cadmium batteries is a major source of both metals [157] while cadmium is also released by pesticides and cigarette smoke [2]. Additionally copper is released by pesticide production and metal piping [4]. Heavy metals are toxic and can cause damage at low concentrations, in most cases, the threshold is under 0.1 ppm [4]. They accumulate in the body and can disrupt organ and gland function causing health problems such as organ damage, cancer, and neurological damage [4, 157-159]. Due to the adverse health effects, minimizing an individual's contact with heavy metals is essential. To do so, a possible approach is to remove them from water sources using adsorbents.

Adsorbents can be used to remove heavy metals from water. One of the most common adsorbents is activated carbon however, it can be expensive to manufacture (US\$4–12/kg depending on carbon source) [160]. Low-cost adsorbents such as chitosan (US\$ 15.43/kg) [161], zeolites (US\$ 0.03–0.12/kg) [162], peat moss (US\$ 0.023/kg) [163] and lignin (US \$ 61/t) [164] have all proved to be efficient adsorbents for a variety of heavy metals (cadmium, lead, chromium, etc.) [165]. In certain cases, such as with agricultural waste adsorbents, the adsorbent must be chemically treated to activate it, thus leading to a higher environmental impact [166]. Some chemical activation methods include treatments with acids and bases [166] or the use of photo-initiated chemical vapour deposition [167]. Hydrogels are a category of adsorbent that can be used for the removal of a wide variety of heavy metals [11].

Hydrogels are 3D chemically or physically crosslinked polymeric networks that can absorb hundreds of times their weight in water. They have previously been used for soil and water remediation, namely for the removal of diesel fuel [151], motor oil [150], and a variety of heavy metals such as copper [8, 9], zinc, and nickel [9, 11].

Hydrogels can be synthesized from many different monomers, both synthetic and biobased, the most prominent including acrylic acid and acrylamide. Certain polyacrylamide hydrogels are reusable, going through several contaminant removal and regeneration cycles without a significant loss of effectiveness [11]. Additionally, acrylic acid/acrylamide hydrogels have demonstrated large swelling capacity and significant ion removal over a range of concentrations for a variety of heavy metals [168].

Acrylic acid and acrylamide can be used as monomers when synthesizing hydrogels of differing porosity. The porosity and the shape of the pores are determining factors of a hydrogel's structure and swelling ability. There are three categories of hydrogel structures: (1) non-porous hydrogels, (2) superabsorbent hydrogels, and (3) super-porous hydrogels. Previous generations of superabsorbent and super porous hydrogels were prepared in various ways, including freezedrying [12]. Modern versions are typically prepared using the gas blowing technique (acid-induced decomposition of a foaming agent) and by the use of a foam stabilizer [169]. Non-porous hydrogels are synthesized without any additives, and superabsorbent hydrogels are synthesized using only a foaming agent [13]. Non-porous hydrogels are solid and rigid with no porous network. The average pore size is under 10 nm, and they are non-continuous. They generally have a slow swelling rate [14]. Superabsorbent hydrogels typically form a solid, flexible, unstable foam [14]. They have a micro to macroporous pore structure and pore sizes ranging from 10 nm - 1µm. The swelling rate of superabsorbent hydrogels depends on the porosity of the individual sample [14]. Super porous hydrogels form a solid, flexible, stable foam with an open-cell structure and pore sizing over 1µm [14]. They have a rapid swelling rate, and previous acrylic acid/acrylamide hydrogels produced using the gas blowing technique have reported swelling capacities of 159 g/g [170] and 194 g/g [171]. In this study, the hydrogels will be referred to by their additives. The hydrogel without any additives will be referred to as the base hydrogel (BH), the hydrogel with a foaming agent as the foaming agent hydrogel (FAH), and the hydrogel with both a foaming agent and a foam stabilizer as the foaming agent, foam stabilized hydrogel (FAFSH).

Previous research work on the synthesis of acrylic acid/acrylamide super porous hydrogels focused on the effect of crosslinker and foaming agent concentration, as well as their mechanical properties. This work reports, for the first time, a systematic comparison of the properties of three hydrogel structures synthesized using the same monomers. The impact of the porosity of the hydrogels on the swelling ratio, and the adsorption of heavy metals (copper (II), nickel (II), and cadmium (II)) under competitive and non-competitive conditions has been studied.

2.3 Materials and Methods

2.3.1 Materials

Acrylic acid (AA) (99% purity), acrylamide (AM) (99% purity), N, N'methylenebisacrylamide (NMBA) (99% of purity), Pluronic F127, ammonium persulfate (APS) (98% purity), N,N,N', N'-tetramethylethylenediamine (TEMED) (99% purity), sodium hydroxide (NaOH) (98% purity), sodium bicarbonate (NaHCO₃) (99% purity), copper sulfate (99% purity), nickel chloride (98% purity) and cadmium chloride (99.99% purity) were purchased from Sigma-Aldrich Co. LLC, USA. Ethanol (purity of 95%) and nitric acid (86% purity) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Distilled water (DW) with a resistance of 18 megaohms/cm² was used in all preparations and tests.

2.3.2 Hydrogel Synthesis

In a typical experiment, 5 g AM was dissolved in 10 ml DW and mixed with 5 ml AA. The pH of the solution was adjusted to 5.5 using 5M aqueous NaOH. The pH-adjusted solution was then used to make 1 of 3 structures:

- the base hydrogel (BH): 0.05 g NMBA was added to the AA/AM pH adjusted solution and stirred at 300 rpm and 70 °C in an oil bath for at least 10 minutes or until dissolved. Afterward, 2 ml of a 10 (w/v) % APS solution was added and stirred for 1 minute. Finally, the stir bar was removed, and 2 ml TEMED was added to the solution and stirred quickly with a spatula. The reaction was allowed to proceed for 5 minutes at 70 °C, and the hydrogel was dried.
- 2. The foaming agent hydrogel (FAH): 0.05 g NMBA was added to the AA/AM pH-adjusted solution and stirred at 300 rpm and 70 °C in an oil bath for at least 10 minutes or until dissolved. Afterward, 2 ml of a 10 (w/v) % ammonium persulphate solution was added and stirred for 1 minute. Following this, 0.5 g of foaming agent (NaHCO₃) was added to the solution and mixed for 20 seconds. Finally, the stir bar was removed, and 2 ml TEMED was added to the solution and stirred quickly with a spatula. The reaction was allowed to proceed for 5 minutes at 70 °C, and the hydrogel was dried.
- 3. The foaming agent and foam stabilizer hydrogel (FAFSH): 0.05 g NMBA and 1 g of foam stabilizer (Pluronic F127) were added to the AA/AM pH adjusted solution and stirred at 300 rpm and 70 °C [149] in an oil bath for at least 10 minutes or until dissolved. Afterward, 2 ml of a 10 (w/v) % ammonium persulphate solution was added and stirred for 1 minute. Following this, 0.5 g of NaHCO₃ was added to the solution and mixed for 20 seconds. Finally, the stir bar was removed, and 2 ml TEMED was added to the solution and stirred quickly with a spatula. The reaction was allowed to proceed for 5 minutes at 70 °C, and the hydrogel was dried.

Hydrogels were dried using one of two methods: freeze-drying or oven drying. To prepare hydrogels for the drying process, they were cut into small pieces and then rinsed with a 50/50 solution of ethanol and distilled water until the solution ran clear. After the rinsing process, hydrogels that were freeze-dried were frozen at -15 °C for 16 hours. The hydrogels were freeze-dried (Labconco, FreeZone 2.5) under vacuum at -46 °C for 48 hours. After the rinsing process, hydrogels that were oven-dried were immersed in ethanol for 24 hours. The samples were then put in an oven (Precision Scientific, Thelco Laboratory Oven) for 72 hours at 70 °C [149]. After drying, all hydrogels were ground into a powder (particle size < 4 mm) using a Black & Decker CBG110SC Grinder (and stored in a desiccator.

2.3.3 Morphology

The macroscopic structure of the hydrogels was observed using images of the hydrogel taken before the drying process. The morphologies of the original and regenerated hydrogels were studied using a scanning electron microscope (SEM) (SU3500, Hitachi High-Technologies Co., Tokyo, Japan) at 1000x magnification at an acceleration voltage of 10 kV, beam current of 140 μ A and a working distance of 5700 μ m.

2.3.4 Surface Area

The BET (Brunauer, Emmett, and Teller) surface area, BJH (Barret, Joyner, and Halenda) adsorption cumulative surface area, and single point surface area data were obtained with BET surface area analysis performed by a nitrogen adsorption-desorption apparatus (TriStar 3000, Micromeritics Co., USA). Each sample weighed approximately 1 g and had been degassed for 20 hours at 120 °C prior to the test.

2.3.5 Thermal Properties

A thermogravimetric analyzer (TGA Q50, TA Instruments, New Castle, DE, USA) was used to determine the thermal properties of the original and regenerated hydrogels. Samples weighing 5 ± 1 mg were heated from 25 °C up to 600 °C at a rate of 5 °C min⁻¹. The analyses were carried out under a stream of nitrogen at a flow rate of 60 ml min⁻¹ and were performed in duplicate.

2.3.6 Swelling Measurements

The swelling tests were performed with six replicates as follows: nylon tea bags were initially weighed (m_1) . The tea bags were immersed in water for 2 h, after which they were removed and hung in the air for 10 min to remove the excess water. They were weighed again, and this wet bag weight was recorded (m_2) . After drying the bags in an oven at 70 °C until constant weight, they were weighed again (m_3) . Finally, they were loaded with \approx 50 mg of dry hydrogel, which was recorded as the weight of the loaded bag (m_4) . The loaded tea bags were placed in excess distilled water and allowed to swell, removing them (at 0.25, 0.5, 1, 24, and 48 hrs) for weight measurements (m_x) . The bags were hung for 10 minutes to allow excess water to drip off before weighing.

The weight ratio of absorbed water to the original hydrogel sample (q (g/g)) is calculated using Eq. (1).

$$q = \frac{m_x - m_4 - (m_2 - m_1)}{m_4 - m_3} \qquad (1)$$

The swelling ability of the hydrogels was tested in varying pH (2, 4, 6, 8, 10, 12) and in salt solutions containing 100 mg/L NaCl using this same tea bag method with 6 replicates.

2.3.7 Regeneration of Hydrogels

To observe the effect of a 24-hour distilled water wash on the swelling properties of the hydrogels, samples of the three structures were swollen in distilled water for 24 hours and then dried in an oven at 70 °C [149] until constant mass was reached (72 hours). The hydrogels were then ground into a powder and used to test the swelling ability of regenerated hydrogels, denoted by the letter *R* (RBH, RFAH, RFAFSH) using the tea bag method with 50 mg of powdered sample in distilled water, salt solution (100 mg/L NaCl), and at varying pH (2, 4, 6, 8, 10, 12). Samples were swollen for 24 hours, and then the mass was recorded.

2.3.8 Reusability of Hydrogels

The reusability of the oven dried FAFSH AA/AM hydrogel was tested using the tea bag method with 50 mg of powdered sample in distilled water using 6 replicates. Samples were

repeatedly swollen for 24 hours and then dried at 70 °C for 24 hours until the swelling ability remained relatively constant.

2.3.9 Metal Binding Tests

The metal binding ability of the hydrogels (original and regenerated) was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Thermo 6500 Dual View, Thermo Fisher Scientific, US). The metals tested were copper, nickel, and zinc. NIST traceable standards were used to prepare the calibration curves for each metal. Trace metal grade nitric acid (4 vol%) was used for all dilutions. The calibration curve had a range from 0 to 100 mg/L. The standard bracketing technique was used to correct for drift over time. In addition, 2 quality control points, at 0 and 10 ppm, were used to ensure the quality of the data.

For the metal adsorption tests, \approx 50 mg of hydrogel powder was placed in a 50 ml aqueous solution of an individual metal (approximately 100 ppm), distilled water, or all three metals (approximately 33 ppm each) and left at room temperature without agitation for 24 h. Additionally, distilled water blanks and metal solution blanks were prepared, to perform a spike recovery study. After completing the process, the hydrogels, the blanks and the spikes were filtered using vacuum filtration followed by a second filtration using 1.0 µm DigiFilters (SCP science, Montreal). The volume of the remaining supernatant was recorded after the first filtration. The remaining solutions were analyzed using ICP-OES with a 50/50 dilution with 4% Vol trace metal grade nitric acid. The sorption tests were performed in triplicate.

The initial concentration of the supernatants was determined using the spike for each metal solution, and the metal's removal was calculated using Eq 2:

$$Removal = \frac{(C_1V_1 - C_2V_2)}{m} \quad (2)$$

Where C_1 is the initial concentration of the ion solution, V_1 is 50 ml, C_2 is the concentration after 24 hours of hydrogel adsorption, V_2 is the volume measured after hydrogel removal, and *m* is the dry mass of the hydrogel.

2.4 Results and Discussion

2.4.1 Mechanism and foam structure

The hydrogels were synthesized by copolymerization of acrylic acid and acrylamide in the presence of NMBA, a crosslinker. The proposed mechanism for copolymerization is shown in Figure 2.1[172-174]. As seen in the figure, the foaming agent and foam stabilizer used in some formulations are not part of the final hydrogel structure.



Figure 2.1: Mechanism of synthesis of acrylic acid/acrylamide hydrogel [172-174]

APS and TEMED were used as initiators. Under heating, ammonium persulphate decomposed into ammonium and persulphate ions. The TEMED was added to increase the speed of sulfate anion-radicals formation [175]. The hydrogens from the functional groups of the acrylic acid or acrylamide were attracted to the anion radical and formed macroradicals. Thereafter, the macroradicals initiated polymerization, creating the copolymer [172]. Due to the presence of a crosslinker, the copolymer formed a three-dimensional crosslinked structure. The blowing agent

reacted with acid in solution and released carbon dioxide, which caused the formation of bubbles. These bubbles were stabilized by Pluronic F-127 when the FAFSH was synthesized [171].

The volume to mass ratio of acrylic acid to acrylamide in the final network was fixed at 50/50 based on swelling results taken from another study [173].

The difference in macroporous structure was evident when observing the hydrogels before the drying process (Figure 2.2). The BH sample had no foam structure. The hydrogel was flat and clear, with minimal bubbles caused by air escaping during synthesis. The FAH had an unstable foam structure. Many of the pores generated by the foaming agent collapsed during synthesis. The FAFSH sample was a stiff, stable foam. The foam stabilizer supported the foam structure during synthesis, which allowed the rigid hydrogel foam to form. These results were consistent with the literature [13].



Figure 2.2: a) base hydrogel b) foaming agent hydrogel c) foaming agent, foam stabilized hydrogel

2.4.2 SEM

When using SEM to examine the six structures, the pores of the original hydrogel structures were apparent. As seen in Figure 2.3, these pores were not present in the regenerated samples. This suggested that the 24-hour distilled water wash altered the surface of the hydrogel by removing the pores. Small (<50 μ m), uniform pores were present on the surface of the BH samples. This showed that while the macrostructure was not porous, the pores were still present at a microscopic level. Pores of varying sizes (> 50 μ m) were present on the FAH samples. Additionally, there were fewer pores present on the FAH samples than the BH samples and they had a greater variation in

shape. The FAFSH samples had a rough surface and many pores varying in both size and shape. There was a larger quantity of pores present in the FAFSH samples than the FAH samples.



Figure 2.3: SEM images 50 µm scale a) BH b) FAH c) FAFSH d) RBH e) RFAH f) RFAFSH

A previous study found that the swelling capacity of hydrogels was affected by the internal pore structure rather than the surface pore structure. Minor changes in surface pore structure had a minimal effect on swelling capacity [176]. This explained why the hydrogels with the largest number of pores (BH and FAFSH) had a significant difference in swelling capacity. All three of the regenerated hydrogel samples had no surface pores. This suggests that the swelling and drying process used was responsible for the smoothing of all surface pores in the regenerated samples.

2.4.3 Surface Area

Powdered samples were used for surface area tests, the results of which are shown in table 2.1. Due to the low surface area of the samples, some measurements could not be performed as they were below the detection limit. From the BET surface area measurements, the regenerated samples had a very low surface area. RFAH and RFAFSH samples had very low surface area values, and the instrument could not obtain a measure for the RBH sample. The RFAFSH sample had a slightly higher surface area. The low surface area measurements support the SEM data, which showed that the regenerated samples did not have surface pores.

Sample	Swelling Capacity (g/g)	BET Surface Area (m ² /g)	Adsorption Average Pore Width (Å)	t-Plot micropore volume (cm ³ /g)
BH	182	0.0436	40.29	0.000035
FAH	195	0.0223	NA	0.000038
FAFSH	257	0.0276	NA	0.000032
RBH	219	NA	NA	NA
RFAH	204	0.001	6168.16	NA
RFAFSH	285	0.002	NA	NA

Table 2.1: BET Results

By contrast, the original samples had higher surface areas. The BH sample had the highest surface area. This supports the SEM data as many pores were visible on the BH samples. The FAH and FAFSH samples had similar surface areas, but the FAFSH sample's surface area value was slightly higher. This is due to the larger size and higher number of pores visible on the FAFSH samples when compared to the FAH SEM samples. When comparing the BH surface area to the FAH and FAFSH surface areas, it is obvious that while using a foaming agent did change the foam structure of the hydrogel, it did not significantly increase the porosity at a microscopic level, it simply changes the shape of the pores. This was surprising as previous literature reports that use of a foaming agent increases the porosity, and therefore surface area, of AA/AM hydrogels [14].

2.4.4 Thermal Properties

The TGA curves obtained for the BH, FAH, FAFSH, RBH, RFAH, and RFAFSH samples were nearly identical as they were composed of the same monomers. Additionally, the differences in physical structures did not greatly affect the thermal stability of the hydrogels. As seen in Figure 2.4, the FAH and FAFSH curves are identical, indicating that the use of a foam stabilizer did not affect the thermal stability. However, the BH curve drops below the other two curves at 200°C, indicating that the use of a foaming agent does slightly increase the thermal stability.



Figure 2.4: TGA results for original BH, FAH and FSFSH

From 25 °C to 140 °C, there was a loss in mass attributed to water and ethanol evaporation. From 140 to 225 °C, there was a mass loss due to the vaporization of acrylic acid. At over 225 °C, the network began to break down. After 450 °C, the remnants of the network were mainly ash, and there was little change in mass. As seen in Figure 2.5, the derivative mass of the original and regenerated FAFSH samples was similar. This indicated that there is not a significant difference between the two samples.



Figure 2.5: Derivative mass of FAFSH and R FAFSH

2.4.5 Swelling Ability

The hydrogel synthesis procedure was adapted from Adnan et al. [170] and Shu King et al. [171]. Oven drying was explored as it is a common way of drying hydrogels. It was compared to freeze-drying as this method tends to preserve the pore structure of dried material. Varying initiator and crosslinker concentrations were tested to determine the effect on swelling ability (Table 2.2).

SAMPLE	STRUCTURE	DRYING METHOD	INITIATOR (VOL%)	CROSSLINKER (VOL%)	FOAM STABILIZER (WT%)	FOAMING AGENT (WT%)
1	BH	Oven	20	0.5	0	0
2	FAH	Oven	20	0.5	0	5
3	FAFSH	Oven	20	0.5	10	5
4	FAFSH	Oven	10	0.5	10	5
5	FAFSH	Oven	20	1.5	10	5
6	FAFSH	Oven	20	2.5	10	5
7	FAFSH	Freeze-dried	10	0.5	10	5
8	FAFSH	Freeze-dried	20	0.5	10	5

Table 2.2: Hydrogel Formulations

The final swelling capacity was affected by several factors, including the concentration of reactants and drying method. The present work focused on the effect of four parameters: crosslinker content, initiator content, drying method, and hydrogel structure. As seen in Figure 2.6, decreasing the crosslinker content increased the swelling capacity. This was consistent with the findings of Chavda et al., who found that an increase in crosslinker led to increased crosslinking density and lower swelling capacity in super porous hydrogels [177]. However, when a crosslinker content below 0.5 wt% was used, the hydrogel was unable to form. A crosslinker concentration of 0.5 wt% NMBA was chosen as it demonstrated the highest swelling capacity at 210 g/g. Similar hydrogels reported swelling capacities of 159 g/g [170] or 194 g/g [171], however they were synthesized using 2.5% NMBA. A higher swelling capacity was achieved for the hydrogel synthesized in this paper by using less crosslinker.



Figure 2.6: Swelling capacity of oven dried, foaming agent, foam stabilized hydrogels with 20 wt% initiator (standard deviation error bars)

The drying method and initiator concentration had a significant effect on the final swelling capacity. The two drying methods used were oven drying at 70 °C and freeze-drying at -46 °C. As seen in Figure 2.7, freeze-drying produced a slightly higher swelling capacity when both 10 and 20 wt% initiator were used. This was attributed to the fact that freeze-drying preserved the porous structure. Oven drying allowed the shrinkage and collapse of the pores [178].



Figure 2.7: Swelling capacity of foaming agent, foam stabilized hydrogels with varying initiator content and drying methods (standard deviation error bars)

However, the freeze-dried samples do not have a significantly higher swelling capacity. Because the swelling capacity of the oven-dried and freeze-dried samples are almost identical and that the freeze-drying process is expensive [178], oven drying was selected as the drying method.

As seen in Figure 2.7, when the initiator concentration was reduced from 20 (wt or vol)% to 10 (wt or vol)%, the swelling capacity decreased (from 220 g/g to 181 g/g). This was observed for both freeze-dried and oven-dried samples. Due to the higher swelling capacity, 20 (wt or vol)% initiator was selected. While 20 (wt or vol)% is a very high value for initiator content, it is consistent with previous papers reporting on super porous hydrogels [170, 171]. A very fast rate of reaction is required in order to preserve the porous structure of the hydrogels. As seen in figure 2.7, when less initiator is used the rate of reaction is not sufficient and the final swelling capacity is reduced.

As seen in Figure 2.8, all three structures experienced rapid swelling in the first 15 minutes (288 g/gh-472 g/gh). The swelling rate then reduced over time up to two hours, and a slow swelling rate was observed from 2 to 24 hours. The FAFSH experienced the fastest initial swelling rate, which led to the highest swelling capacity at 15 minutes. This rapid swelling capacity is a characteristic of super-porous hydrogels [14, 170, 171].



Figure 2.8: Swelling dynamics of acrylic acid/acrylamide hydrogel structures (standard deviation error bars)

In addition to affecting swelling dynamics, the structure affected the final swelling capacity. As shown in Table 2.3, FAFSH had the highest 48 hr swelling capacity at 256 g/g, whereas the FAH samples swelled to 195 g/g and the BH samples to 182 g/g. The difference between these swelling abilities was deemed to be significant (p= 2.22×10^{-9}) using a single factor ANOVA (α =0.05). The swelling capacity of the FAFSH samples was higher than 159 g/g [170] or 194 g/g [171], which had previously been reported for the synthesis of similar hydrogels using a foaming agent and foam stabilizer.

Table 2.3: 24 h swelling capacity of hydrogel structure

Hydrogel Structure	Swelling Capacity \pm standard deviation (g/g)	
ВН	182 ±6	
FAH	195±11	
FAFSH	257 ± 17	

These swelling results are lower than those reported by other novel acrylic acid/acrylamide hydrogels or composite acrylic acid hydrogels (Table 2.4). However, they demonstrate that swelling capacity can be improved with the use of foam additives.

Table 2.4: Swelling capacity of several novel acrylic acid hydrogels

Hydrogel	Swelling Capacity
poly (acrylic acid-co-acrylamide)	Up to 600 g/g [179]
/bentonite/ kaolin composite hydrogel	
Poly (acrylic acid-co-acrylamide) hydrogel	Up to 70 000 % [180]
pH sensitive poly(acrylamide-co-acrylic acid)	Over 3000 % [181]
acrylamide–acrylic acid hydrogel	Up to 1040 % [182]

2.4.5.1 Effect of Regeneration

The synthesis process for most hydrogels includes a rinse in distilled water to remove unreacted components that contaminate the network. However, this step affected the structure of the original hydrogels and was therefore not included in the original procedure. Samples were swollen continuously for 24 hours and then oven-dried to study the effect of the wash. As seen in Figure 2.9, the regenerated hydrogels had a higher swelling capacity than the original hydrogels.



Figure 2.9: Original and regenerated hydrogel swelling capacity in distilled water (24 h) (standard deviation error bars)

This difference was found to be significant (p=0.000612) using a single factor ANOVA (α = 0.05). This improvement was most likely due to small amounts of unreacted monomers present in the original hydrogel samples. Hydrogels are generally rinsed in distilled water for 24 hours before the final drying process [9, 179]. This step removes unreacted monomers, leaving only the hydrogel network that can absorb water, which results in a higher swelling capacity. This is consistent with other research conducted on the gel fraction of hydrogels. When they are soaked in distilled water for 24 hours, the non-crosslinked parts of the matrix dissolve [183]. When the hydrogel is dried it weights a fraction of the start mass. When this hydrogel is swollen again the swelling capacity is retained but the start mass is decreased (fraction of initial start mass) so the hydrogel has a comparatively higher swelling capacity.

2.4.5.2 Effect of pH

The swelling capacity of a hydrogel is affected by the properties of the liquid it is immersed in, including ionic strength, temperature, and pH. As pH increases or decreases from neutral, the swelling capacity of the hydrogel usually decreases [149, 184]. As seen in Figure 2.10, the hydrogels had the highest swelling capacity in distilled water. The swelling capacity was slightly reduced at pH 4, 6, 8 and 10, and drastically reduced at pH 2 and 12. This is because highly acidic or basic conditions change the charge of functional groups.



Figure 2.10: Swelling capacity of oven dried hydrogels at varying pH (standard deviation error bars)

At acidic pH, carboxylate ions became protonated, which changed their charge [185]. This caused the network to shrink due to increased hydrogen bonding and new physical interactions. The shrinkage of the network decreased the swelling ability [185]. Additionally, changes in the charge of functional groups reduced the hydrogel's internal repulsion and decreased the hydrogel's swelling capacity. At medium pH, some carboxylate groups became ionized which broke the hydrogen bonds and caused repulsion between the negatively charged groups, thus increasing the swelling ability of the hydrogel [185]. At very basic pH, charge screening decreased the swelling ability. This resulted from excess Na⁺ ions that prevented proper anion-anion (OH⁻ & OH⁻) repulsion in the hydrogel [185].

The regenerated hydrogels showed high swelling capacities in basic pH. As shown in Figure 2.11, the regenerated hydrogels had the highest swelling capacity at pH 8 rather than pH 5.6. Additionally, the regenerated FAFSH outperformed the BH and FAH samples by a much higher margin at pH 6 and 8 than the original samples. Finally, the regenerated samples showed higher swelling capacities than the original samples at all pHs, making them a better option for absorption in environments with varying pH.



Figure 2.11: Swelling capacity of regenerated oven dried hydrogels at varying pH (standard deviation error bars)

2.4.5.3 Effect of NaCl on Swelling Ability

As previously stated, the swelling capacity of hydrogels was affected by the ionic strength of the solution [184]. Increasing the ionic strength of the solution (by using a 100 ppm salt solution) typically results in a decrease in swelling capacity when compared to swelling in distilled water. This is due to the "charge screening effect," in which the increased cations in solution decrease anion-anion repulsion [186]. However, as seen in Figure 2.12, the swelling capacity of all samples was not significantly affected by the 100 mg/L NaCl solution.



Figure 2.12: Swelling capacity of oven-dried hydrogel in distilled water or a salt solution (standard deviation error bars)

This result is similar to Mirdarikvande et al. [186]. They observed that ionic strength depends on the salt concentration and the ions that make up the salt. In their study, the NaCl solutions did not significantly affect the swelling capacity of poly-alginate-based hydrogels [186], supporting the non-significant effect of the NaCl solution on the swelling capacity of the six samples.

2.4.6 Reusability

Reuse of a polymer that maintains its properties is more desirable than the synthesis of a new polymer. As seen in Figure 2.13, the swelling capacity of the three structures either increased or stayed constant over cycles 1–3. After cycle 3, the swelling capacity decreased until cycle 6, after which it remained stable. The FAFSH showed the most considerable reduction in swelling capacity. However, its swelling capacity remained high, plateauing around 80% of initial swelling. The hydrogel shows a constant swelling capacity suggesting that the material remains stable even after multiple swelling cycles. This indicates that it would be suitable for long term use.



Figure 2.13: Reusability of oven-dried hydrogels (standard deviation error bars)

2.4.7 Heavy Metal Adsorption

Heavy metal adsorption was measured using the original and regenerated hydrogels in solutions of copper (II), cadmium (II) and nickel (II) ions. These ions were chosen as they are among the most commonly found in wastewater [28] and are often used for heavy metal adsorption tests in the literature [9, 27, 180]. The data were then analyzed using multiple two-factor ANOVAs (α =0.05) with three replicates. It was determined that there was no statistical difference in the ion removal capacity of the original and the regenerated samples (p=0.973). However, the removal was affected by the hydrogel structure (p= 8.55x10⁻¹¹) and the heavy metal ion (p=4.677x10⁻¹²). As can be seen in Figure 2.14, under non-competitive conditions, the removal capacities of the FAH and FSFSH hydrogels were not statistically (ANOVA with α =0.05) different and were significantly larger than the removal of the BH hydrogel (p= 8.55x10⁻¹¹). The initial concentration of ion solutions were 105 ppm (Cu), 109 ppm (Cd) and 99 ppm (Ni). This variation was due to human and equipment error. The variation between the expected and the actual results for the spikes were 5%, 9% and -1% respectively. The FAFSH samples had a removal capacity of 103.7 mg/g +/- 1.9 mg/g copper (II), 92.3 mg/g +/- 9.3 mg/g cadmium (II), and 73.2 mg/g +/- 12.6 mg/g nickel (II).



Figure 2.14: Heavy metal removal under non-competitive conditions (24 h) (standard deviation error bars)

Under competitive conditions, the structures and ions' type also affected the removal. The removal of the FAH and FAFSH were not significantly different (ANOVA with α =0.05), but the BH had a significantly lower removal capacity (p= 6.44 x 10⁻⁷). As shown in Figure 2.15, the order

of preference for removal of the hydrogel was Cd> Cu> Ni. The removal capacity for individual ions was decreased under competitive conditions. Both copper and cadmium, having a higher removal than nickel, is consistent with previous literature [187-191]. Cadmium had the highest initial concentration, which can explain the highest adsorption by the hydrogels.





Heavy metals are removed from solution through ion chelation. Functional groups such as carboxyl, amide, imidazole and pyridine can participate in chelation reactions [192, 193]. The carboxyl and amide functional groups in acrylic acid and acrylamide are capable of forming complexes with the divalent ions [192-195] such as those used in the experiments.

The removal capacity of the hydrogel was affected by many factors, including the initial concentration of the ion solution, the pH of the solution, the ions present, and the length of time the experiment is run [196]. Therefore, it can be challenging to compare ion removal capacity as the start conditions must be similar in order to make a valid comparison. In this study, the initial concentration of the ion solution was approximately 100 ppm, the pH was around 5, and the ion solutions were in contact with the hydrogels for 24 hours.

A study performed by Yildiz et al. showed that the ion removal capacity of a PVP (poly N-vinyl-2-pyrrolidone) hydrogel increased in more basic start conditions [27]. PVP hydrogels were immersed in 5 ppm metal solutions for 24 hours at pH 2, 5, and 8. The highest removal efficiencies were recorded at pH 8. At pH 5, the recorded removal capacities were 75 mg/g for copper, 32 mg/g for nickel, and 12 mg/g for cadmium. The removal capacity of the PVP hydrogel was increased

by incorporating other monomers into the hydrogel structure. The maximum recorded removal at pH 5 was 130 mg/g copper, 105 mg/g nickel and 40 mg/g cadmium [27]. These measures were higher than, but comparable to, the measures reported in this paper, however cadmium was removed in lower quantities in the Yildiz et al. study. Additionally, a hydrogel with similar monomers to our hydrogel had a maximum ion removal capacity of 121 mg/g and was selective towards copper and zinc over other tested ions [180]. This removal capacity value was higher than the removal capacity reported for the fully bio-based hydrogel synthesized by Duquette et al., whose copper removal was 30.2 mg/g and nickel removal was reported to be 17.6 mg/g at a starting concentration of 100 mg/L [9].

The removal capacities of the AA/AM hydrogel under non-competitive conditions were similar to those reported in the literature for other synthetic hydrogels, and higher than those reported for bio-based hydrogels [9, 27, 180].

2.5 Conclusions

Previous hydrogel studies report on the use of foaming agents and foam stabilizers to increase swelling capacity, however, there has not been a study systematically comparing the effect of structure on multiple properties of hydrogels. This paper reported the effect of a foaming agent and foam stabilizer on the physical properties, swelling capacity and ion removal of acrylic acid/acrylamide hydrogels. There was a significant difference between the swelling capacity of the BH, FAH, and FAFSH hydrogels and the FAFSH samples as the latter had the highest swelling capacity. Additionally, the 24-hour distilled water rinse had a significant, positive effect on the swelling capacity. The distilled water rinse did not alter the chemical composition of the network, but it did change the surface of the hydrogel granules. While the regenerated hydrogel had an increased swelling capacity, it did not have a significantly different ion removal capacity. The FAFSH and FAH did not display a significant difference in their ion removal capacity. However, they both had a significantly higher ion removal capacity than the BH. Under competitive conditions, the order of preference for the removal of ions was Cd> Cu> Ni for all three structures. The increase in porosity of the foam structure increased both the swelling capacity and the ion removal capacity of the acrylic acid/acrylamide hydrogel. This work proves that the use of a foaming agent not only increases the swelling capacity of acrylic acid/acrylamide hydrogels, but also increases their heavy metal removal capacity. Additionally, the use of a rinse to remove

unreacted monomers increased the swelling capacity of the hydrogels while retaining the heavy metal removal capacity. The porous foam structure can be applied to other hydrogels, such as biobased hydrogels, to help enhance swelling capacity and contaminant removal.
Chapter 3

General conclusions and recommendations

3.1 General conclusion

The main objective of this research was to synthesize three different structures of hydrogel by using a foaming agent and a foam stabilizer during synthesis and then to determine which hydrogel had the final properties that resulted in the highest heavy metal adsorption. Detailed descriptions of the conclusions relating to these objectives are listed below:

- I. Synthesis of the three hydrogel structures was successful. The use of a foaming agent and foam stabilizer affect the physical structure of the hydrogels. There was a visible difference in the macroscopic structure of the hydrogels, with the BH forming a translucent hockey puck, the FAH forming a partially collapsed white foam and the FAFSH forming a stiff white foam. Additionally, the SEM images showed a difference in quantity, shape, and size of pores between the three structures and the BET analysis confirmed differences in surface area and porosity. Conversely to what was reported in previous literature, the BH samples had the highest surface area and the most uniform pores.
- II. As evidenced by the SEM and BET, the regeneration step smooths the surface pores of the three structures of hydrogel. No pores are visible on the regenerated samples in the SEM images and the BET surface area measurements decrease to almost below detectable limits.
- III. The FSFSH had a significantly higher swelling capacity than the other two samples in distilled water. The regenerated samples had a higher swelling capacity than the original samples in distilled water. At all pH, the swelling capacity was greatly increased by regeneration. Additionally, the optimum swelling pH for the original samples was 5.6 (distilled water) whereas the optimum swelling pH for the regenerated samples was at pH 8. Finally, the 100 mg/L NaCl solution did not significantly affect the swelling capacity of the hydrogels.
- IV. The regeneration step made no difference in the removal capacities for the hydrogels. Original and regenerated samples had very similar removal capacities. The three structures were all capable of removing heavy metals. Under non-competitive conditions FAH and FAFSH samples had similar removal capacities and BH samples had significantly lower removal rates. Copper and cadmium had the highest removal rates. Under competitive conditions the FAH and FAFSH samples had similar removal capacities and BH samples had significantly lower

removal rates. The hydrogel preferentially removed cadmium> copper> nickel. This hydrogel is a good candidate for use as a heavy metal adsorbent.

3.2 Experimental considerations

There were several experiments where issues were encountered, and the procedure had to be adjusted.

- I. Previous papers stated that the synthesis the FAH and FAFSH hydrogels could be performed at room temperature. This would be beneficial as it would save on cost in the form of energy inputs. However, when synthesis was performed at room temperature no foam was produced when the foaming agent was added. When the synthesis was performed at 70 °C the issue was rectified, and foam was produced.
- II. The use of a cross linker other than NMBA was investigated. Polyethylene glycol diacrylate (PEGDA) was investigated as a crosslinker but ultimately disregarded as the swelling dynamics did not conform with what was expected. The PEGDA hydrogels had slower swelling dynamics and continued to gain mass after 48 hours. However, the swelling capacity at 48 hours was comparable to that achieved with NMBA.
- III. When testing the ion removal capacity of the hydrogel, the removal capacity of the hydrogel is measured indirectly by measuring the ion concentration in the supernatant. Attempts were made to measure the heavy metal present in the hydrogel directly. This was done by degrading the hydrogel in hydrochloric and nitric acid in a hot water bath. The hydrogel did not degrade after several hours. This procedure was abandoned as the lack of degradation meant that 100% recovery of the metal ions in the hydrogel was not guaranteed.
- IV. Some experiments were done aiming to incorporate bio-based monomers (zein protein) into the matrix instead of using acrylamide. There were issues with the solubility of the proteins with the other monomers and the acrylic acid tended to self polymerize, leaving the zein protein was left out of the matrix. The experiments were abandoned but showed potential if the procedure was changed.

3.3 Recommendations and future work

The use of NMBA as a crosslinker severely limits the applications of this hydrogel as NMBA is toxic. For this reason, other crosslinkers should be investigated for use in FAFSHs. One

prime candidate for this is polyethylene glycol diacrylate (PEGDA). PEGDA is another common crosslinker used in hydrogels that is non-toxic. This would allow to widen the range of applications for the hydrogel. Additionally, the concentration of initiator should be investigated. The current initiator content (20 wt%) is very high and not realistic for use in industry. Lower initiator concentrations should be investigated to achieve high swelling capacities at more realistic initiator concentration.

The targeted application for this hydrogel is the removal of heavy metal ions from wastewater. The heavy metal removal has been tested under laboratory conditions in distilled water with only heavy metals in the 2⁺ state, however, this is not realistic. The hydrogels should be tested using a variety of metals with valence states for 1⁺ to 3⁺. It would be interesting to explore if hydrogel prefer metals when they are in a specific valence state (e.g. preferentially remove copper(I) over copper (II)). The hydrogel should also be tested in water that contains other common contaminants to test its interaction with them and to confirm that heavy metal removal is maintained under real-world conditions. Additionally, tests should be done on the hydrogel to quantify any leaching that may be occurring. The goal of the use of the hydrogel was to improve water quality and this cannot be achieved if the hydrogel is leaching toxic monomers into the water source. This may be a reason that the use of the regenerated hydrogel is preferred over the original hydrogel.

Finally, the use of bio-based monomers should be investigated. Hydrogels can be made from synthetic or bio-based monomers. In the case of this thesis synthetic monomers were chosen for their predictable properties. Bio-based monomers are a green alternative. They are non-toxic and generally have a good affinity for heavy metals. Additionally, the use of bio-based polymers whose source is agricultural waste can decrease the cost of the final product. This could be interesting as the use of a foaming agent during synthesis could be applied to already existing biobased hydrogels.

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