



Advancements in Hydrogel-Based Adsorbents for Heavy Metal Removal: An Overview

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Abstract

The environment and public health face a significant risk from increasing levels of heavy metals in wastewater resulting from industrial activities. Researchers are exploring new techniques for eliminating these pollutants by the production of potential hydrogel materials that can provide a comprehensive analysis of recent advancements in the utilization of these hydrogels for the adsorption of heavy metals from aqueous solutions. Heavy metal pollution poses a significant threat to ecosystems and human health, necessitating effective remediation strategies. Hydrogels, with their unique physicochemical properties, have emerged as promising materials for heavy metal adsorption due to their high-water retention capacity, tunable porosity, and the active functional groups. This review discusses the significance of hydrogels as effective adsorbents for removing heavy metals and the impact of reaction conditions on their adsorption efficiency. Furthermore, it explores the principles of adsorption mechanisms involved, such as ion exchange, chelation, and electrostatic interactions, which are critically evaluated in terms of adsorption capacity, selectivity, and recovery.

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1. Introduction

Environmental contamination by heavy metals has become a serious pollution problem and public health issue in recent years. This was ascribed to the continuous discharging of heavy metals into water streams. Consequently, human exposure has significantly grown with their exponential expansion across a range of industrial, agricultural, household, and technological applications [1]. Heavy metals tend to accumulate instead of biodegrade. As such, the continuous exposure to toxic metal, such as Zinc (Zn), Manganese (Mn), Copper (Cu), Lead (Pb), Cadmium (Cd), and Nickel, can harm human organs including the brain, kidneys, nose, skin, gastrointestinal tract, and lungs [2]. In addition, heavy metals can be detoxified by an organism enclosing the active ions in a protein or storing them in an insoluble state in intracellular granules for later excretion in the organism's waste. In general, certain metals can be divided into two categories i.e., essential and non-

essential elements. Essential metals are important to many physiological and biochemical processes because they are necessary for our life. While Non-essential metals do not play a significant role in the body, but they can still be harmful by impacting the levels of essential elements in the body and potentially causing toxicity[3]. Meanwhile, some of them are considered as co-factors for certain enzymes, micronutrients, osmotic pressure regulators, and molecules' stability. However, most of them have no known biological role in living organisms and are hazardous when produced in excess dose [4]. Various wastewater treatment techniques have been developed for the removal of heavy metals such as chemical precipitation, ion exchange, liquid-liquid extraction, resins, coagulation, flotation, hyper-filtration, oxidation, bio-sorption, and adsorption [5]. However, each of these traditional treatment methods has its disadvantages that eliminate its usage, such as the high cost,

complexity, chemical usage, and poor efficiency. For example, electrolysis techniques usually have higher costs for operation [6]. Meanwhile, the adsorption process was one of the common and suitable technique for the removal of heavy metal from wastewater due to simplicity, flexibility, cost-effective and the superior efficiency of the adsorption process that make it suitable for the removal of various organic pollutant [7]. Consequently, the efforts have pushed forward for the developing of suitable adsorbents with acceptable specifications such as biochar loaded manganese dioxide [8], the green adsorbent prepared from Eucalyptus Camaldulensis [9], Cellulose/ chitin beads [10], adsorption heavy metal by active Carbon[11], polymer-based adsorbents of polypyrrole-polyaniline[12]. Recently, hydrogels have attracted wide attention due to their unique properties such as the high porosity, large surface area, hydrophilicity, and the existence of various active functional groups such $-\text{COOH}$, $-\text{NH}_2$, $-\text{SO}_3\text{H}$ and $-\text{OH}$ [13]. In 2018, Tian and colleagues developed a hydrogel made from lignin that includes $-\text{NH}_2$ groups. This hydrogel has an adsorption capacity of 385 mg. g^{-1} for Co^{2+} and 290 mg. g^{-1} for Cu^{2+} [14]. Similarly, Li et al. (2016) developed a lignosulfonate-modified graphene hydrogel (LS-GH) with R-C=O , R-OH , and R-COOH groups, which exhibited an adsorption capacity of 1210 mg. g^{-1} for Pb^{2+} [15].

The main objective of this review focuses on the use of hydrogel as an efficient adsorbent for heavy metals. The selection of hydrogel as an effective adsorbent was ascribed to its unique properties such as the high swelling capacity, good porosity, low cost, ease of usage, and high adsorption capacity. The influence of reaction parameters on efficiency of adsorption process were discussed. Furthermore, the fundamentals of adsorption mechanisms were estimated in terms of adsorption capacity, selectivity, and recovery.

2. Sources of Heavy Metal Contamination in the Environment

Excessive contact to heavy metals in soil can be caused by a variety of factors, including air pollution, sewage irrigation, industrial solid waste, and the use of fertilizers and pesticides. The composition of surface earth has 5% of sedimentary rocks whereas 95% of it is made up of igneous rocks. In general, shales contain large amounts of Pb, Cu, Zn, Mn, and Cd, whereas basaltic igneous rocks are rich in heavy metals like Cu, Cd, Ni, and cobalt (Co). Rocks can get directly contaminated with heavy metals by a variety of natural processes, such as erosion, leaching,

surface winds, biogenic processes, meteoric processes, and volcanic eruptions. Heavy metals accumulate in the soil as a result of the gradual disruption of the heavy metals geochemical cycle caused by human activities. Recent advancements in the agricultural sector brought about by urbanization and industrialization have virtually reduced the amount of metal pollution in the soil. Anthropogenic activities including mining and smelting, fossil fuels usage for energy, clearing garbage from cities, applying pesticides, irrigating sewage, and applying fertilizer all contribute to the buildup of heavy metals in agricultural soil environments[16]. Table 1 presents the sources of some heavy metals and their effects on human health. [17]

3. Toxicity of Heavy Metals: -

Accumulation of harmful heavy metals in different tissues can negatively affect the health of animals and interfere with their regular bodily functions. The toxicity of heavy metals can greatly reduce the survival and reproductive abilities of organisms. Certain heavy metals have been found to be extremely cancer-causing, mutation-inducing, and causing birth defects, with the severity depending on the species, amount, and duration of exposure [18]. Heavy metals have been shown to impact various cellular structures and elements within biological systems, including the cell membrane, mitochondria, lysosomes, endoplasmic reticulum, nuclei, and certain enzymes involved in metabolism, detoxification, and repair processes. Metal ions have been observed to engage with cellular components like DNA and nuclear proteins, resulting in DNA damage and structural alterations that could potentially influence cell cycle regulation, cancer development, or cell death[19].

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Table1.The sources of some heavy metals and their effects on human health [17]

Metal	Sources	Effects on Human
Arsenic	Atmospheric deposition, mining activities, pesticide use, rock sedimentation, and smelting processes.	Potential health issues include brain damage, heart and lung problems, eye inflammation, skin irritation, and skin cancer.
Antimony	Sources of coal combustion, mining, smelting, soil erosion, and volcanic eruption.	Cancer, heart diseases, conjunctivitis, skin inflammation, liver issues, nasal ulcers, and respiratory illnesses.
Beryllium	Burning coal and oil, along with volcanic ash	Various health issues such as allergic reactions, berylliosis, cancer, heart diseases, and lung diseases.
Cadmium	Fertilizer, mining, pesticide, plastic, refining, welding.	Bone disease, coughing, emphysema, headache, hypertension, itai-itai, kidney diseases, lung and prostate cancer, lymphocytosis, microcytic hypochromic anemia, testicular atrophy, and vomiting are mentioned.
Chromium	Dyeing, electroplating, paints production, steel fabrication, tanning, textile.	Bronchopneumonia, chronic bronchitis, diarrhea, emphysema, headaches, skin irritation, respiratory tract itching, liver diseases, lung cancer, nausea, kidney failure, reproductive toxicity, and vomiting.
Copper	Activities such as copper polishing, mining, painting, plating, and printing.	stomachs pain, low red blood cell count, digestive issues, head pain, harm to liver and kidneys, disruptions in metabolism, and feelings of nausea and vomiting.
Mercury	Batteries, burning coal, geothermal processes, mining operations, paint manufacturing, paper production, volcanic eruptions, and the natural weathering of rocks.	Cognitive impairment, vision and hearing loss, reduced fertility, memory loss, confusion, speech difficulties, stomach discomfort, gum inflammation, kidney issues, weakened immune system, and lung swelling.
Lead	Coal burning, electroplating, battery production, mining, and the manufacturing of paint and pigments.	Anorexia, long-term kidney disease, nerve damage, hypertension, excessive activity, sleeplessness, cognitive impairments, decreased ability to conceive, kidney damage, increased risk for Alzheimer's disease, decreased ability to focus
Nickel	Electroplating, working with non-ferrous metals, applying paints, and porcelain enameling.	Heart problems, chest discomfort, skin inflammation, feeling lightheaded, persistent cough and difficulty breathing, head pain, kidney issues, lung and nasal cancer, and feeling sick to the stomach.
Zinc	Brass production, mining, oil processing, and plumbing.	Ataxia, depression, stomach pain, blood in urine, jaundice, erectile dysfunction, kidney and liver problems, fatigue, eye macula deterioration, metal fume fever, and prostate problems. cancer, seizures, vomiting

5. Hydrogels

The history of hydrogel was referred to the year 1960 when Wichterle and Lim firstly reported the hydrogel of poly (2-hydroxethyl methacrylate) (PHEMA), applied it to the contact lens market, showcasing the modern hydrogel's capacity to absorb moisture while reiterating its network structure.[20]. Hydrogels are defined as three-dimensional cross-linked polymer networks with a high capacity for absorbing huge quantities of water or fluids. [21]. They are highly crystalline and insoluble in water, allowing easy regeneration due to being constructed from chemically cross-linked polymers. However, the main drawbacks of hydrogel are its limiting mechanical and thermal properties, non-biodegradability, unproductive monomers, and the use of harmful cross linkers. Modification the properties of hydrogels is possible by mixing them with natural and/or artificial polymers with predetermined characteristics such as biodegradation, solubility, crystallinity, and biological activities.[22]. Furthermore, to create a stronger hydrogel, the amount of crosslinking and swelling ratio must be balanced [23]. The crosslinking helps to maintain the network structure and regulate water absorption [24]. Gibas and Janik (2010) described the swelling functionality of hydrogels, which is a complicated process consisting of three stages. Firstly, the hydrogel matrix is water-loving due to the hydrophilic groups in its structure. Secondly, the hydrophobic groups react with water to form secondary bound water. As such, both primary and secondary bound water contribute to the total bound water. Thirdly, the physical and chemical crosslinks is considering as a controlling step for the osmotic driving force of the network towards infinite dilution. Consequently, additional water is absorbed and when the equilibrium swelling is reached the free water will be able to fills the spaces between the network or chains and the center of the larger pores [25].

Several factors influence the ability of hydrogels to remove heavy metals, including pH, concentration of metal ions, complexing ability of metal ions, ionic radius, hydration energy, structure of the hydrogel, amount of swelling, uptake time, experimental conditions, and the presence of functional groups within the hydrogel. These features affect how hydrogels interact with heavy metal ions.[26]. By using the following formulas, the adsorption capacity and percentage of removal efficiency can be calculated [27].

$$\text{Adsorption Capacity (Qe)} = \frac{(C_0 - C_e) * V}{m} \quad \dots (1)$$

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad \dots (2)$$

In the adsorption experiment, C_0 and C_e represent the initial and final concentrations of heavy metal ions, respectively, before and after the experiment. V is the volume of the metal ion used, and m is the weight of the dried hydrogel employed. It is well known that hydrogels can be either natural or synthetic. The synthetic hydrogels have a long service life, extraordinary absorption capacity, and strong gel strength. The developable structures make it capable of achieving customizable degradability and functionality. Hydrogels can be manufactured from entirely synthetic components. Additionally, it exhibits stability in severe conditions and great temperature variations [28]. Different published works were successful to create many cross-linking hydrogels-based adsorbent for heavy metals removal. Chowdhury et al. (2021) reported the adsorption capacity of the fabricated hydrogel of poly acrylic acid (AAc), acrylamide (AAm), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), (AAm-AAc-AMPS) for the removal of some heavy metal's ions such as Fe^{3+} , Cr^{3+} from an aqueous solution with higher adsorption capacity of 210 mg/g and 129 mg/g respectively. For both cases the (AAM-AAc) showed slightly higher adsorption capacity in comparable to (AAm-AAc-AMPS) due to the higher amount of AAC which has higher functional groups of COOH bind with Fe^{3+} . The mechanism of adsorption was ascribed to the electrostatic interactions, coordination bond formation, and diffusion process [29]. In a study by Mishra and colleagues in 2021, it was found that polyacrylic acid hydrogel cross-linked with allyl sorbitol(AS), allyl mannitol(AM), or allyl pentaerythritol (AP) was effective in removing Cu(II) and Ni(II) ions. The highest removal efficiencies for copper were 81.8%, 81.6%, and 86.8% with AS, AM, and AP cross-linkers, respectively. For nickel ions, the maximum removal efficiencies were 96.8%, 96.6%, and 99.0% [30]. Ozay, et. al., (2009) emphasized the significance of utilizing magnetic adsorbents for eliminating heavy metals from water sources. These adsorbents can be easily removed using a magnetic field after absorbing pollutants. They used magnetic-sensitive hydrogels containing 2-acrylamido-2-methyl-1-propane sulfonic acid to extract heavy metal ions in the sequence: Cd(II) > Pb(II) > Co(II) > Cu(II) > Ni(II) > Fe(II) > Cr(III) [31]. Wang et al., (2013) fabricated a hydrogel of Ioponite and polyvinyl pyrrolidone by in situ polymerization with nano-clays assistance for the removal of Cu (II). The results revealed high porous structure with higher surface area consequently higher adsorption capacity [32]. Table 2 present more published work for various types of hydrogel applied for heavy metals removal.

Table 2: Various hydrogels have different abilities to swell, contain functional groups, and remove contaminants.

Hydrogel type	Swelling capacity	Available functional groups	Removed contaminant	Absorbance capacity or (removal percentage)	Ref.
PVP/AAC copolymer hydrogel	2000%	Carboxylic groups, Carbonyl groups	Fe^{+3} , Cu^{+2} , Mn^{+2}	Fe^{+3} (72%), Cu^{+2} (46%), Mn^{+2} (28%)	[33]
alginate-based porous nanocomposite hydrogels	90%	Carboxylic groups, Amines	Cr (VI) and Cu (II)	Cr (VI) (~133.7 mg/g) and Cu (II) (~87.2 mg/g)	[34]
Hydrogel-rice husk biochar composite	1008%	$COONH_2$, $-OH$, $-NH_2$, $-COOH$, $-SO_3H$	As	(93%)	[35]
Poly (Amidehydrazide) Hydrogel	1414%	amide, C=O	Cu^{+2} Cd^{+2}	85 mg/g 47.6 mg/g	[36]
α - Fe_2O_3 magnetic hydrogel	12.5%	Amine I, Amine II, trimethyl ammonium group	Cr (VI)	(95%)	[37]
Poly (vinyl alcohol) hydrogel	250-195%	hydroxyl and acetate groups	Cu^{+2}	-	[38]
Superabsorbent hydrogels	41,298%	$-OH$, $-COOH$, $-SO_3H$	Cu^{+2}	243.19mg/g	[39]
modifications of p(AAm-co-AAc) hydrogel	=	Carboxylic groups, amine groupe	Cu^{2+} , Ba^{2+} , and Sr^{2+}	13.67, 36.4, and 27.31 mg/g,	[40]
Glucan/chitosan (GL/CS) hydrogels	1566 mg/g	$-OH$, $-NH_2$, $-COOH$,	Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+}	342 mg/g, 232 mg/g, 184 mg/g, 395 mg/g and 269 mg/g	[41]
poly-acrylamide/acrylic acid/vinyl imidazole bromide (PAM/AA/[Vim]Br ₂) hydrogel	40,012%	amide groups, carboxyl anion	Ni^{+2} , Cu^{+2} , Zn^{+2} , and Cr^{+3}	91.8%, 97.2%, 95.6%, and 98.1%.	[42]

5.1. Classification of hydrogel

Hydrogel systems can be classified as neutral, amphoteric (based on their basic and acidic properties), zwitterionic (having both anionic and cationic groups), or based on surface/electrical charge (i.e., anionic or cationic). In addition, the kind of crosslinking establishes whether the hydrogel is physical (such as hydrophobic association, chain aggregation, and hydrogen bonding) or chemical (such as covalent bonding), or contains a dual-network of crosslinks.[43]. Scheme.1 presents more categories describe the classification of hydrogels. The hydrophilic nature in the hydrogel structure supports the creation of a flexible structure, and the generation of stable complex with the active sites located on an extended polymeric chain through the easy diffusion of solute into the three-dimensional framework of gels.[44]. Consequently, the specific surface areas of hydrogel adsorbents would be limited, and this would further block the adsorptive

sites of gels, such as amino, hydroxyl, and carboxyl groups, from being efficiently exposed to metal ions. This would result in a reduction in removal efficiency of the heavy metal ions.[45].

5.2. Synthesis of hydrogels

In order to synthesis hydrogels, it is crucial to include a cross-linking agent to improve the structure. This agent plays a key role in forming new polymeric chains within the hydrogel by facilitating reactions between various polymeric molecules or fibrous proteins. Hydrogels are usually produced by hydrolyzing and condensing specific precursors, resulting in the development of a solid nanostructured network. The majority of research in this area concentrates on physical and chemical cross-linking techniques[47]. Physical hydrogels, also referred to as thermoplastic or supramolecular hydrogels, are reversible solids that offer higher biocompatibility and lower toxicity compared to

chemical crosslinking methods. This is because they do not require external chemical crosslinking agents. However, physical crosslinked hydrogels can be unstable at high temperatures, potentially causing damage to the 3D network. Physical crosslinking involves mechanisms like hydrogen bonding, electrostatic attraction, ionic bonding, polymer entanglement, crystallite formation, and van der Waals forces. On the other hand, chemical crosslinking methods such as co-/graft-polymerization, photo-crosslinking, enzymatic crosslinking, and radiation crosslinking allow for the customization of hydrogels based on specific application requirements [48]. An example of the physical hydrogel preparation is poly (ether ester) multiblock copolymers, which are based on poly (ethylene glycol) (PEG) and poly (butylene terephthalate) (PBT). Lysozyme-containing PEG/PBT films and/or microspheres were prepared using an emulsion technique. The swelling capacity of PEG/PBT films in water reached equilibrium within 3 days. The degree of swelling increased with the rise in PEG content and the molecular weight of the PEG segment [49]. On the other hand, hydrogels obtained by chemical crosslinking exhibit thermal, chemical, and mechanical stability due to the formation of covalent bonding formation [50]. The hydrogels prepared from the copolymerization of various vinylated monomers or macromers is an example of chemical crosslinking such as 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl methacrylate (HPMA), acrylamide (AAm), acrylic acid (AAc), N-isopropylacrylamide (NIPAm), and methoxyl poly (ethylene glycol) (PEG) monoacrylate (mPEGMA or PEGMA), with crosslinkers, such as N,N'-methylenebis(acrylamide) (MBA), ethylene glycol diacrylate (EGDA) and PEG diacrylate (PEGDA) [51].

6. Metal adsorption mechanisms of hydrogels

The hydrogel's mechanism based on metal adsorbents is crucial. Generally, the hydrogel composition and adsorption reaction conditions are main factors affecting the adsorption mechanism for the hydrogels [52]. It was discovered that surface functional groups are closely related to (i) electrostatic interaction, (ii) ion exchange, and (iii) surface complexation (including coordination and/or chelation). Although both the ion exchange and electrostatic interaction are mainly reversible, the adsorbed pollutants can be employed again. On the other hand, a chemical process called surface

complexation takes place at the sorbent's surface where the sorbate forms a chemical link with the sorbent. The specification of metal ions, the surface nature of the hydrogels and their surface charge, all affect how each adsorption mechanism works [53]. Sánchez et al., (2021) reported different designed of hydrogels derived from wood biopolymer hemicellulose and blended with commercial vinyl monomers. These hydrogels were used to remove Cu (II), Cr (VI), and As (V) ions. The study analyzed the absorption capacity of these ions in relation to pH levels and initial ion concentrations in the solutions. The absorption process was carried out in multiple batches, revealing that the poly (GGM-GMA/AMPSH) hydrogel had a maximum removal efficiency of 90 mg/g for Cu (II). Meanwhile the poly(GGM-GMA/APTACl) hydrogel absorbed 69 mg/g and 60 mg/g for Cr(VI) and As(V) respectively [54]. Li et al. (2021) reported the preparation of a sodium lignosulfonate-guar gum composite hydrogel, with highest adsorption capacities of 601 mg/g and 709 mg/g of Cu^{+2} and Co^{+2} respectively. The mechanism study revealed that surface complexation between the lone pair electron of the oxygen atom of COO^- and the unoccupied electron orbitals of Cu^{+2} and Co^{+2} was the controlling step for the adsorbed metals [55]. Godiya et al. designed the egg white / polyethyleneimine hydrogel to quickly extract copper (Cu^{2+}), lead (Pb^{2+}), and cadmium (Cd^{2+}) ions from aqueous solutions. It was discovered that chelating interactions between metal ions and the $-COO^-$, $-O-$, and $-N-$ groups in the hydrogels characterized the main adsorption mechanism. Meanwhile, the critical chelation process is refer to the chelating agent properties, including ring size, ionic diameter, hardness or softness, and the degree of shape ability of the electron contributors and acceptors [56]. Dong et al (2022) suggested adsorption mechanism for the removal of heavy metals using magnetic hydrogels. According to the findings, the hydrogel has individual adsorption capacities for copper, cadmium, lead and cobalt of 206, 178, 168, and 140 mg/g, respectively the author concluded that adsorption process by these hydrogels is a chemisorption process. This means that adsorption could occur through chelation or electrostatic attraction by the existence of two binding sites for the adsorption of divalent metal ions. [57]. Figure 1 describe the adsorption mechanism of hydrogel-based adsorbent for the removal of heavy metals.

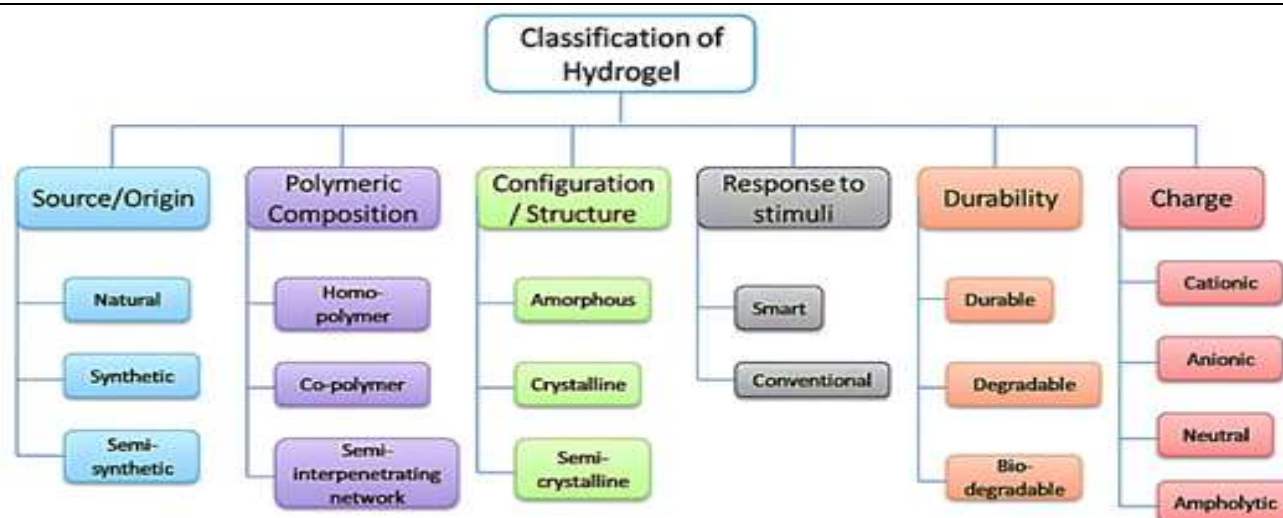


Figure1: Classification of hydrogel based on different properties[46]

7. The effect of reaction parameters on the adsorption of heavy metal ions

7.1. Effect of pH

Generally, several adsorption parameters have significant effects on the adsorption characteristics. The impact of pH level on the heavy metal adsorption capacity is one of the major sorption process parameters. The pH level significantly affects the degree of ionization and protonation of the adsorbent, as well as the surface charges of the adsorbents, consequently influencing the speciation of metal ions. Table 3 summarizes the effect of pH on the adsorption capacity of different hydrogels-based

adsorption. These results show that various heavy metals have varying effects on the maximum amount of adsorption capacity. In order to expand on the impact of pH on the adsorption of heavy metal ions, it is important to note that a higher adsorption capacity was noted as a result of a greater negative surface charge, which strengthens the electrostatic interaction with heavy metal ions and stimulates the adsorption process. Additionally, the treatment of heavy metal ions varies in its adsorption capacity depending on the natural absorbent and adsorbate as a function of pH resulting in an increase or decrease in positive or negative surface charge. [59].

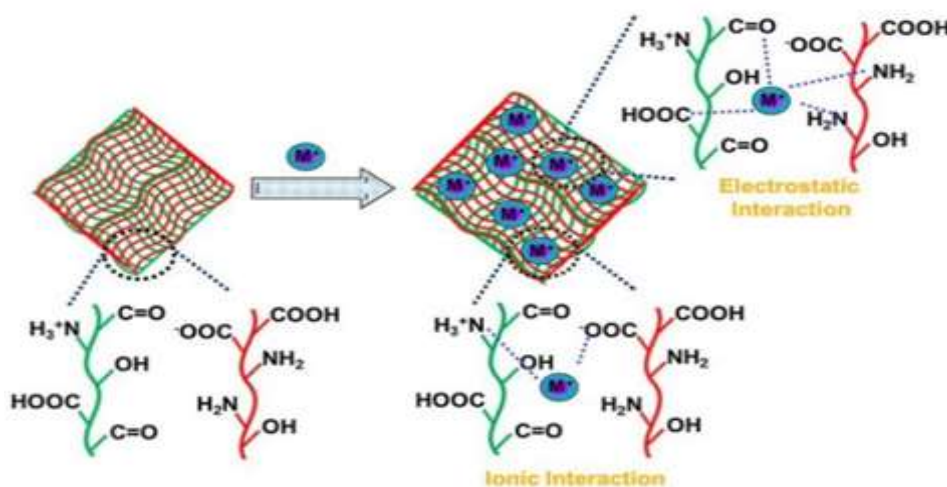


Figure 2: Mechanism of absorbance hydrogel heavy metals[58].

Adsorbent	Heavy metal ions	pH	Maximum adsorption capacity	Ref
Multi walled carbon modified by 3D graphene/polydopamine	Pb (II)	7	271mg/g	[60]
	Cu (II)		224mg/g	
Gum tragacanth/graphene oxide composite hydrogel	Cd^{+2}	6	75%	[61]
	Pd^{+2}		90%	
	Ag^{+}		80%	
Graphene-diatom silica aerogels	Hg^{+2}	6.5	400mg/g	[62]
Highly porous chitosan–gelatin/grapheme oxide (CGGO) monolith	Cu^{+2}	6	88%	[63]
Silica aerogels modified with amino propyl triethoxysilane70%	Cd (II),	8 and	70%	[64]
	Pb (II)	7	100%	
α -FeOOH decorated graphene oxide-carbon nanotubes aerogel	As(V)	5	90%	[65]
PVA/AAc	Cu^{+2}	4.5	13mg/g	[38]
Poly (EGDMA–VIM) hydrogel	Cd^{+2}	3-5	69mg/g	[66]
	Pd^{+2}	3-5	112mg/g	
	Hg^{+2}	3-5	162mg/g	
PAA hydrogel	Pd^{+2}	6.5	113mg/g	[67]
Chitosan Nano fibril	Cd^{+2}	6	140mg/g	[68]
	Cu^{+2}	5.5	169mg/g	
	Pd^{+2}	6.7	61mg/g	

7.2. Effect of temperature

In general, the diffusivity of metal ions within active sites of the adsorbent increase with increasing temperature or with increasing the active sites on the adsorbent surface. With each cases the removal efficiency for the eliminating of heavy metal from wastewater will increase. However, increasing the temperature above the optimum conditions might lower the adsorption capability of heavy metal ions. This decrease in adsorption capacity may be related to the exothermal process of heavy metal ion adsorption onto the hydrogel adsorbent, hence the adsorption at lower temperature would be favorable [69]. Ahmed and Saeed. (2013), studied the impact of temperature on the weight and size of swollen hydrogel beads of commercial poly acrylic acid (PAA) hydrogel beads in relation to both temperature and time. The results proved that temperature change

has a significant impact on the weight, diameter, and size of hydrogel beads with maximum swelling ratio as 233.7 at 40°C [70]. Özkahraman et. al. (2021), described the effect of temperature on poly (N-isopropylacrylamide-co-itaconic acid) on the adsorption of Cu (II) and Pb (II). As the temperature got above the LCST, it was found that 40% of the metal ions could be desorbed smoothly without the renewing of temperature-sensitive hydrogels with acid[71]. Zende del et al (2011) investigated the effect of temperature for the removal of heavy metals (Pb²⁺ and Cd²⁺) using SAH of poly acrylamide-co-acrylic acid (p(AAm-co-AA/Na zeolite)) The results revealed an increase in adsorption capacity with an increase in temperature, i.e. from 285 to 303 K indicating an endothermic process. However, above the temperature 323 K, the adsorption capacity was decreased, attributed to the desorption of heavy

metal ions from the hydrogel network[72]. Similarly, Zhang et al (2019) concluded that the enhancement in the adsorption process with increasing temperature as in Fig2 could be ascribed to the

acceleration of the reaction and that the adsorption may occur due to the formation of new vacant active sites on the surface of the hydrogel [73].

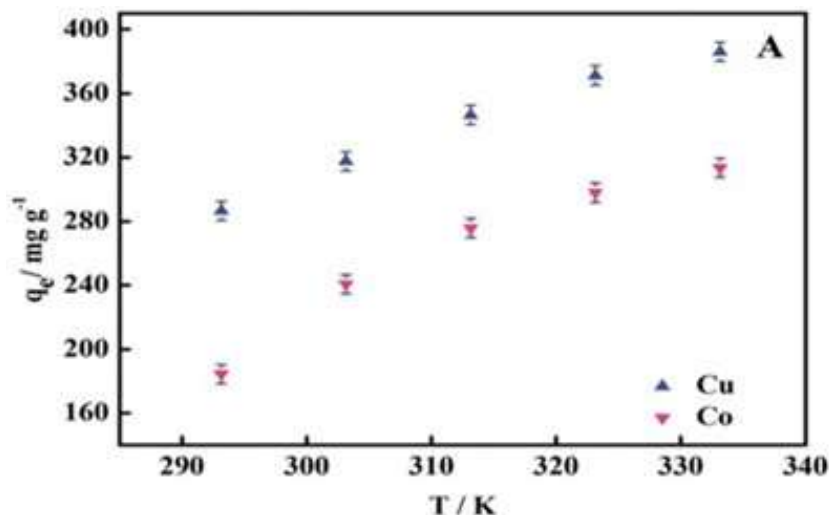


Figure 2: Effect of temperature on removal metal ions.

7.3. Effect of contact time

An increase in contact time permits longer period available for the complexation of metal ions with hydrogel's functional groups. Jiang et al. (2019), reported the preparation of Glucan/chitosan (GL/CS) hydrogels as adsorbents for different heavy metal ions such as Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+} . The results revealed that the adsorption capacity increases rapidly as the adsorption time increases from 0 to 60 minutes reaching adsorption equilibrium after 180 minutes. The maximum adsorption capacities of GL/CS hydrogels for Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+} were 342 mg/g, 232 mg/g, 184 mg/g, 395 mg/g, and 269 mg/g, respectively [74]. Wu et al. (2015) studied the effect of treatment time on the removal of Zn^{2+} and Pb^{2+} ions using sodium alginate/poly (acrylic acid) SA/PAA DN as super adsorbents. The removal capability of the super

adsorbents' metal ion increased rapidly during the first two hours, but gradually decreased as treatment time was increased reaching its saturation point after three hours [75]. In the same field, Tirtom et al. (2021) reported that the adsorption of Cu (II) and Pb (II) ions increased with an increase in contact time due to the large functional groups and porous structure of poly(N-VI-Aam) hydrogels. The intramolecular diffusion occurred after the outer surface saturation, and the adsorbed amounts of lead and copper remained stable after 24 hours. The maximum adsorption capacity values were 262 mg g^{-1} for lead and 53 mg g^{-1} for copper, respectively[76]. Table 4 presents the effect of contact time on the adsorption capacity of heavy metals for various hydrogel.

Table 4 : Adsorption capacity of different hydrogels with different contact time.

Hydrogel	Time	Metals	Capacity	Ref.
Xylan-Rich Hemicelluloses	60 min	Pb ⁺² Cd ⁺² zn ⁺²	859 mg/g 495 mg/g 274 mg/g	[77]
chitosan-based hydrogels	24 hr	Pb (II) Cd (II) Cu (II)	96.6 mg/g 80.5 mg/g 88.94 mg/g	[78]
Polyethylenimine modified graphene oxide hydrogel	48hr	Hg (II), Cd (II) and Pb (II)	97%	[79]
Silica/modified mercaptopropyl trimethoxysilane aerogel	30 min	Cd (II) Pb (II) Cu (II)	85% 99% 80%	[80]
polyaniline (PANI) and <u>graphene oxide</u>	22hr	Hg ⁺²	99%	[81]
polyacrylic acid/polyvinyl	24hr	Ni ²⁺ Co ² Cu ²⁺	150 mg/g 155mg/g 193 mg/g	[82]
chitosan/orange peel	360 min	Cr (VI) Cu (II)	80.43% 82.47%	[83]

The number of collisions between the metal ion and the sorbent increases by an increase in the initial metal ion concentration, which in turn raises the metal gather. Zhang et al. (2017) reported the chemical modification of soybean drug using acrylic acid under the activation of UV source and it was applied for the removal of Zn (II), Fe (III), Cu (II) and Cr (III) ion from aqueous solutions. As initial concentration of metals ions increased, this affected the equilibrium adsorption of metal ions. As such, when the initial concentrations were increased from 23.2, 19.1, 19.3 and 22.1 mg/L to 342.3, 316.1, 315.4 and 321.5 mg/L, the adsorption of Zn⁺², Fe⁺³, Cu⁺², and Cr⁺³ increased from 20.9, 20.7, 19.9 and 10.1 mg/g to 229.9, 118.8, 121.2 and 99.8 mg/g respectively [84]. Chen et al (2020) stated that the enhancement in adsorption process of heavy ions with increasing its ion i.e (Pd²⁺) provides the necessary driving force to overcome mass transfer resistance until the adsorption reached equilibrium. Consequently, the amount of adsorbed pollutant increases from 481 mg g⁻¹ at 293 K to 606 mg g⁻¹ at 313 K, specifying that the adsorption process is endothermic[85]. Similarly, Shah et al., (2018) reported that the effectiveness of acrylic acid and acrylamide (A1M1)

7.4. Effect of metal concentration

hydrogel in absorbing Cd⁺² ions is influenced greatly by the metal dosage used. As the amount of the absorbent increases, the capacity to absorb Cd⁺² ions also increase significantly. Absorption levels reach a plateau when the A1M1 dose falls within the range of 0.1 to 0.2. Within this concentration range, there is no notable change in absorption capacity. Initially, inadequate absorption sites due to low absorbent doses resulted in incomplete absorption of cadmium ions. However, increasing the absorbent dosage creates more absorption sites, leading to a higher absorption capacity [86]. Hence, it can be inferred that the greatest metal concentration corresponds to the highest metal absorption. The bio-sorption capacity of each bio-sorbent increased with the elevation of metal ion concentration. This improvement was attributed to the accelerated driving force the accelerated driving force, which consequently enhanced diffusivity and facilitated a more rapid mass transfer rate.

8. Recovery of Hydrogel

The recovery of the Hydrogel's is considering as one of the most important properties, in addition to its great adsorption efficiency. The importance of

hydrogel recovery ascribed to the ability of repairing itself by removing the heavy metals that has absorbed thus enabling continued reusability. The adsorbent material's capacity for regeneration and reuse is crucial for the practical evaluation of its effective usage. Following each removal cycle, researchers have employed a variety of techniques for the effective desorption of heavy metals from the hydrogel's three-dimensional mesh structure. The desorption of heavy metals will be triggered by variations in the electric field, magnetic field, temperature and pH. Mohammadi et al. (2017) designed an efficient three-dimensional multi-functional hydrogel with a high metal adsorption efficiency and excessive reusability. The author used low concentration of HCl to regenerate the hydrogel after each usage. Five consecutive cycles of adsorption/desorption reuse made a removal ratio of more than 60%. [87]. On the other hand, Zhang, et al., (2021) reported that during the recovery step for magnetic hydrogel, the acidity must be controlled since too much acid can harm the magnetic adsorbent leading to damage hydrogels' binding sites and lowering the adsorption effectiveness.[88]. Contrary, the recovery of magnetic hydrogel with NaCl was described by Tang et al., (2014). The magnetic hydrogel was separated magnetically owing to the special characteristic provided by $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Furthermore, the hydrogel showed excellent reusability with 97% throughout the 20 cycles of treatment.

9. Conclusions

Environmental contamination by heavy metals is a serious pollution problem and public health issue due to continuous discharging into water streams. Human exposure to heavy metals has significantly increased across various applications. Heavy metals can accumulate in the body and harm organs like the brain, kidneys, skin, and lungs. Various wastewater treatment techniques exist for heavy metal removal, with adsorption being a common and effective method. Among various efficient adsorbents hydrogels possess distinctive characteristics such as high porosity and high surface area, which make them appealing for the adsorption of heavy metals. This review emphasizes different types of hydrogels as effective adsorbents for heavy metals removal, underscoring their significant synthesis procedure, swelling capacity, recovery characteristics and the effect of multiple reaction parameters on the adsorption capacity such as effect of pH, temperature, time of reaction, and concentration of metals. The hydrogel is considered as a promising adsorption for heavy metals removal due to the high

surface area, high porosity, high swelling capacity and the efficient functional groups that make them ideal structure for heavy metals removal either by ion exchange or as chelating agent.

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