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Superabsorbent Hydrogels for Heavy Metal Removal

Tanzil Ur Rehman, Luqman Ali Shah, Noor Saeed Khattak, Abbas Khan, Noor Rehman and Sultan Alam

Abstract

The superabsorbent hydrogels (SAHs) are 3D polymer networks having hydrophilic nature, which can swell, absorb, and hold incredible amount of water in aqueous medium showing better sorption ability. The sorption ability enables SAH to absorb organic pollutants, dyes, and heavy metal ions (HMI) from wastewater. Therefore, SAHs have recently got considerable interest from the researchers to be used for wastewater treatment. In order to know the swelling property and to understand the wastewater treatment in general and heavy metal ion removal from industrial effluent in particular, this chapter describes the removal of heavy metal ions from wastewater in details. Thus this chapter will enable us to understand the theoretical and experimental part regarding the removal of heavy metal ions by SAH from wastewater. It also highlights the parameters of adsorption process such as effect of initial concentration of heavy metal ions, effect of external stimuli (pH), effect of temperature on the removal of heavy metal ions, and dosage studies. The synthesis of SAH and its use for removal of heavy metal ions from wastewater as well as recycling, selectivity, and effectiveness are also discussed in detail.

Keywords: superabsorbent hydrogels, swelling ability, sensitivity, heavy metal ions, wastewater treatment

1. Introduction

Recent advancement in industrialization, industrial waste, and effluents has direct impact on water bodies and causes water pollution. This phenomenon not only affects the plants and animals but also has alarming impact on drinking water for human beings and causes severe health issues [1]. The largest water pollution sources are organic pollutants, dyes, and inorganic heavy metals [2]. The industries which are declared as the main source of these water pollutants include pharmaceuticals [3], textiles [4], dyeing and metallurgical industries [5], etc. However, the removal of these organic pollutants and heavy metal ions from the polluted water is a challenging task for researchers, as most of the industries lack the technology and facilities to treat the wastewater before entering into the main streams. For this purpose various chemical, physical, and biological methods were used for wastewater treatment which includes filtration [6], advanced oxidation [7, 8], flocculation and coagulation [9], catalysis [10–13], photo and chemical degradation [14, 15], and adsorption [16]. Due to low cost and easy operation, adsorption is the most appropriate and reasonable choice for the removal of organic pollutants and inorganic

heavy metal ions from wastewater. Many traditional materials can be used for the removal of these pollutants from wastewater as an adsorbent like rice husk charcoal [17], saw dust [18], activated alumina, silica gels, activated carbon, and nut shells [19]. However, the limitation of traditional adsorbents demanded the introduction of novel materials with low cost, biocompatibility, biodegradability, easy synthesis, simple regeneration, and recycling with good efficiency. Thus, the introduction of SAHs makes possible the solution of aforementioned limitations. SAHs are the polymeric materials having 3D cross-linked polymer network (chemical or physical cross-linked) having the capability to absorb a large amount of water in its network, which is thousand times more than its dry state [20]. The dry state of SAHs is because of collapsing and dominance of hydrophobic interactions of the polymer chains, which strongly depend on the nature and composition of the materials. But, when the dry SAH is in contact with water or any other solution (aqueous medium), it expands significantly to a considerable large size while retaining the water inside the 3D network. The better objectives to synthesize the SAH are to once absorb the water and then maintain the water inside the gels for a long time [21].

The swelling ability of these SAHs is due to the presence of physical and electrostatic interactions among polymer chains and water molecules. The presence of hydrophilic groups on polymer chains makes the network hydrophilic and sensitive toward environmental temperature [22]. The ionic groups like sulfonic ($-\text{SO}_3\text{H}$), amines ($-\text{NH}_2$), carboxyl ($-\text{COOH}$), and hydroxyl ($-\text{OH}$) [23] within the network are also responsible for the swelling of polymer networks by undergoing ionization. It generates the electrostatic repulsions and increases the osmotic pressure within the polymer network and increases the size of SAHs. Thus taking the advantage of this swelling ability, SAHs can be successfully applied for the removal of heavy metal ions from wastewater.

The two main processes involved in the removal of heavy metal ions from wastewater by SAHs are the diffusion and electrostatic attractions. The diffusion process causes the penetration of ions inside the SAH network through concentration gradient, while the ionizable groups set up an electrostatic attraction with heavy metal ions and remove them from the aqueous medium by attraction mechanism as shown in **Figure 1**.

The hydrogels are responsive toward the external stimuli including pH [25], temperature [10, 11], intensity of light [26, 27], pressure fluctuation, etc. These stimuli in turn bring a volume phase transition with reversible property in aqueous medium [28].

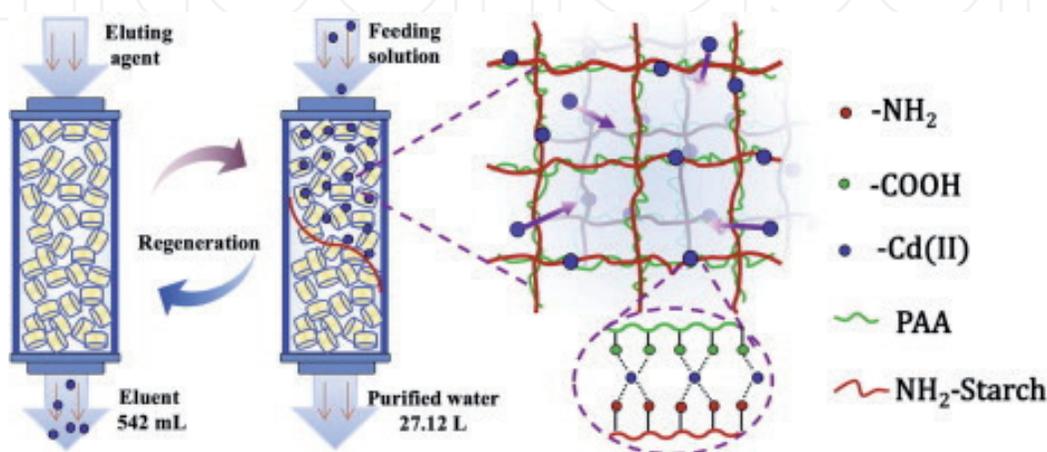


Figure 1. Sorption mechanism, interaction, and regeneration of hydrogel network with heavy metal ions and removal process [24].

2. Synthesis of SAHs

Different polymerization methods are used for the synthesis of SAHs, i.e., grafting, free radical, suspension, etc.; among them the free radical polymerization process is widely used. It is a single-step synthesis process which requires monomers (cationic, anionic, and neutral), cross-linkers, free radical initiators, and accelerators. Accelerators are required for the generation of free radicals from initiators. This is done by heat or using accelerating agents like N,N,N',N'-tetramethylethylenediamine (TEMED), NaSO₃, etc. Currently, our group synthesized SAH based on acrylic acid (AAc) and acrylamide (AAM) with different compositions having good thermal and mechanical properties by thermal free radical polymerization process [29]. Liu et al. [30] prepared a novel chitosan-g-poly(acrylic acid)/sodium humate SAH via grafting polymerization process using N,N'-methylenebisacrylamide (MBA) as a cross-linking agent and ammonium persulfate (APS) as an initiator. Similarly, Thakur and Arotiba [31] synthesized poly acrylic acid (p(AA)) grafted on sodium alginate (SA-cl-PAA) superabsorbent hydrogel. The grafted hydrogels were synthesized while grafting acrylic acid (AA) monomer on polymer sodium alginate in the presence of N,N' methylenebisacrylamide (MBA) as cross-linking agent and potassium persulfate (KPS) as an initiator. The proposed mechanism of the reaction was reported by the author and shown in **Figure 2**. The selection of synthesis process is strongly related with the final application of materials.

A copolymer series of SAHs was synthesized and characterized by Mohana Raju and Padmanabha Raju [32] based on monomers acrylamide (AAM), sodium acrylate (SA), and calcium acrylate (CA) p(AAM-co-SA-co-CA) in the presence of MBA as a cross-linker and APS (initiator) and stirrer for 2 h at 80°C.

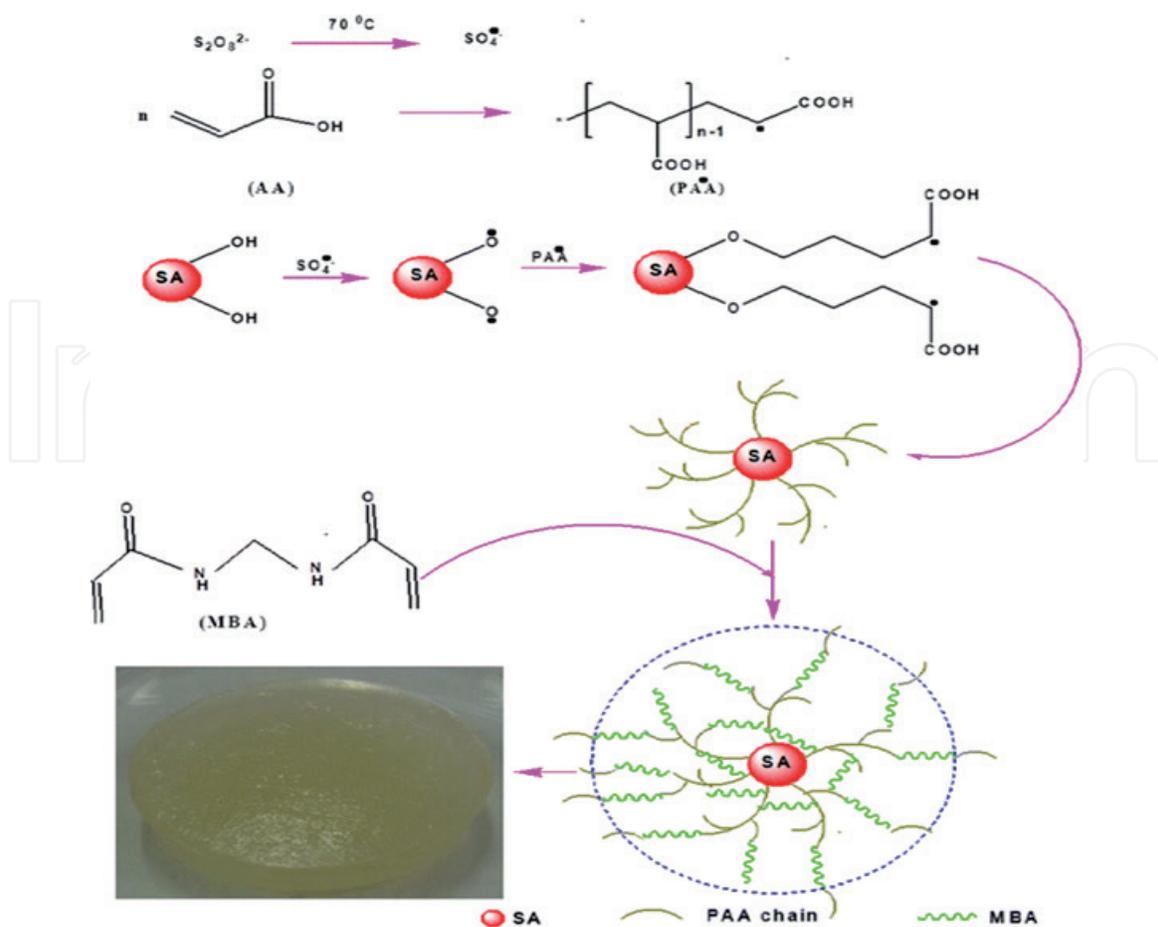


Figure 2.
Proposed mechanism for the formation of a SA-cl-PAA hydrogel network.

3. Properties of SAHs

The SAHs show unique properties which are associated with the structural changes of their network. This makes the hydrogels versatile for various applications. Reversible swelling and deswelling transition is the most important property shown by SAHs. It occurs due to the hydrophilic nature of polymer chains, which is the presence of hydrophilic groups in SAHs and enables them to interact with water. So, the penetration or uptake of water molecules inside the polymer network causes expanding or swelling of SAHs. The absorption property of SAHs toward water can be evaluated from the swelling ratio (Eq. (1)) and depends on the temperature of the medium. The SAHs composed of thermosensitive monomers like N-isopropylacrylamide (NIPAm), acrylamide (AAM), vinylcaprolactam, etc. show reversible swelling properties with temperature of the medium. At above and below the lower critical solution temperature (LCST), these SAHs behave differently. The temperature-sensitive hydrogel system was reported for the removal of metal-extractant complex at temperature below LCST, followed by desorption from p(NIPAM) network at temperature higher than LCST. The model system for this study was Cu^{2+} as a heavy metal ion, sodium n-dodecyl benzene sulfonate (SDBS), and p(NIPA) hydrogel, while a novel proposed temperature-swing solid-phase extraction (TS-SPE) technique has been introduced effectively [33]. The mechanism can be best seen in **Figure 3**.

Thakur et al. studied the absorbency and swelling of water by the dried hydrogel samples in aqueous solution at different pH values at room temperature. The % swelling was found to be 41,298% which is quite a greater value. The % swelling of the investigated samples was calculated by Eq. (1):

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_s is swollen and W_d is dry weight of the SAH sample.

The SAHs consist of various different positive and negative functional groups as an active site also causes swelling and deswelling transitions by undergoing the ionization of active sites with respect to change in the pH of the medium. For example, $-\text{OH}$ and $-\text{COOH}$ groups in the network of the hydrogels undergo protonation and deprotonation at low and high pH of the medium, respectively. At high pH ($\text{pH} > \text{pKa}$ of monomer used), the deprotonation causes the surface to become negatively charged, and an electrostatic repulsions occur, which in turn expands/

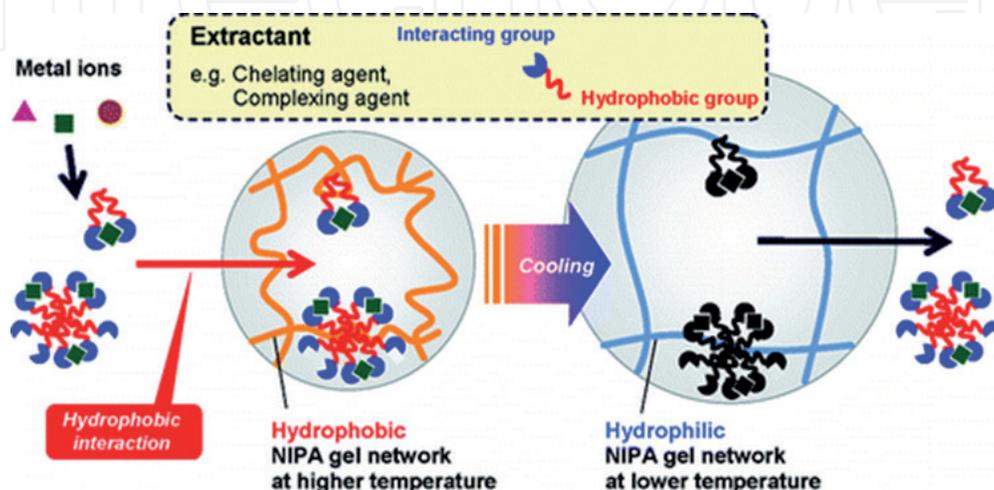


Figure 3. Extraction of metal-extractant complex onto p(NIPAM) hydrogel by TS-SPE technique [33].

swells the SAH network. Similarly, the process becomes reversed where the low pH of the medium causes the protonation of active sites, resulting in the disappearance of surface charge and the collapse of SAH network. The same results but with opposite trends can be observed for basic groups like —NH_2 functional groups. The major application of pH-responsive hydrogels is used in drug delivery, removal of organic pollutants, dyes, and heavy metal ions from polluted and toxic water. In this chapter we are compiling the importance of SAHs in the removal of heavy metal ions from wastewater.

4. Removal of heavy metal ions by SAHs

The heavy metal ions are important and can be used up to certain permissible limit. But, when the concentration of these metal ions increases, then these become toxic and produce a huge number of disease in both terrestrial and aquatic animals. The accumulation of heavy metal ions in water bodies for a long time acts as a pollutant and undergoes in living bodies through different food chains. Therefore, the removal of these toxic heavy metal ions from wastewater is important and a hot area for researchers to work in. Various traditional adsorbents are used for the removal of these impurities from water. However, in the present the synthesis of SAHs has been increasing due to its easy synthesis route, better performance, selectivity, and recyclability with good efficiency toward absorption of heavy metal ions. A general sketch for entrapment of heavy metal ions by SAHs through swelling mechanism is presented in **Figure 4**.

SAH network consists of various functional groups (both positive and negative) as an active site for entrapping and removing of metal ions from the medium. Thus the researchers choose to test and work on the removal of these heavy metals from wastewater by incorporating opposite charge density on the network. The sorption process will be more if opposite charge exists on SAH network to that of heavy metal ions. As the charge nature on SAHs depends on the nature (cationic, anionic, and neutral) of monomers used for the synthesis process. So, for efficient removal of heavy metal ions, the hydrogels must have negative active sites for electrostatic interactions. In most of cases, the SAHs contain —OH , —COOH , and $\text{—SO}_3\text{H}$ functional groups as an active site for electrostatic interactions. Similarly, in some cases the sorption mechanism follows the ion exchange route for the removal of metal ions, and the salt group ($\text{—COO}^- \text{Na}^+$) exchanges the heavy metal ions between the

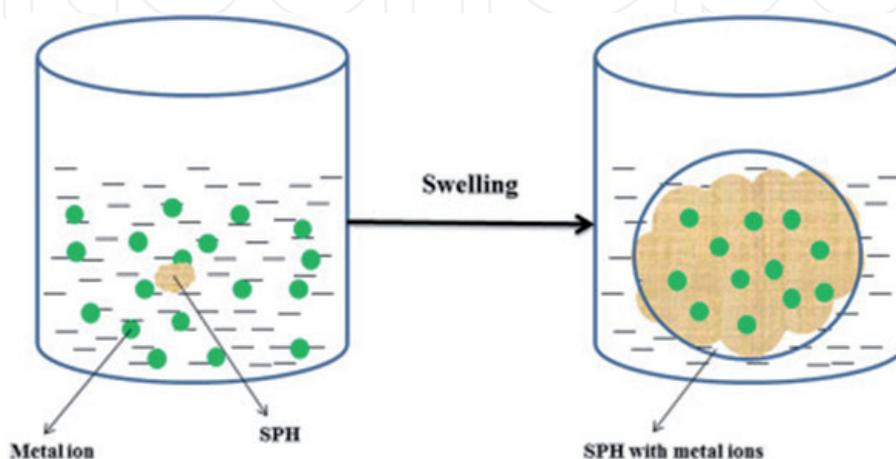


Figure 4. Swelling and sorption process of SAHs toward heavy metal ions [29].

SAH network and that of wastewater. The heavy metal ion removal capacities of SAHs can be calculated by following Eq. (2):

$$\text{Removal capacity (mg/g)} = \frac{(C_o - C_f) \times V}{m_{\text{SAH}}} \quad (2)$$

where C_o and C_f are the initial and final concentrations (mg/L) of heavy metal ions, V is the volume of the solution (L), and m_{SAH} is the mass (g) of superabsorbent hydrogels used as an absorbent.

The effect of charge nature on hydrogels toward the removal of heavy metal ions was demonstrated previously by our group [12]. The synthesis of anionic [poly(methacrylic acid) (P(MAA))], neutral [poly(acrylamide) (P(AAm))], and cationic [poly(3-acrylamidopropyltrimethyl ammonium chloride) (P(APTMAcI))] hydrogels was carried out to study the effect of charge nature on the removal of heavy metal ions. The prepared hydrogels have the potential to remove heavy metal ions selectively in the following orders such as P(MAA) > P(AAm) > P(APTMAcI). Güçlü et al. [34] reported the synthesis of starch-graft-acrylic acid/montmorillonite (S-g-AA/MMT) superabsorbent composite hydrogels. These synthetic materials were used as a superabsorbent for the removal of Cu^{2+} and Pb^{2+} . The removal affinity of Cu^{2+} was found to be greater than Pb^{2+} . Similarly, Zhao and Mitomo [35] synthesized a physically cross-linked CMC-Chitosan hydrogels which were used for Cu^{2+} absorption from wastewater. The absorption of Cu^{2+} ions on hydrogels occurs due to electrostatic attraction between positive metal ions and that —COOH and —NH_2 functional groups, which are the active sites of synthesized hydrogels. The maximum amount of Cu^{2+} ions removed by Chitosan-CMC was 169.5 mg/g. Thus the hydrogels can be used for the removal of Cu^{2+} ions. Yung et al. [36] synthesized SAH of sodium poly(acrylic acid) p(AANa) through single-step cost-effective techniques. This SAH was used to remove Cu^{2+} ions from aqueous solution. It was found that the maximum uptake capacity of Cu^{2+} ions was 243.91 mg/g, which they claim the highest uptake capacity mentioned in literature. Tang et al. [37] developed an interpenetrating network hydrogels for entrapping heavy metal ions. Especially the superabsorbents were reported by the author for efficient removal of Ni^{2+} , Cr^{2+} , and Cd^{2+} from aqueous solution. The study reveals that 102.34 mg/g of Ni^{2+} metal ions were removed, followed by chromium and cadmium divalent ions. The acrylic acid-based monomer SAH was synthesized by Bulut et al. [38] by dissolving AAc monomer in distilled water and then neutralized with NaOH solution, followed by dispersing the clay (bentonite) powder. The reaction was facilitated by adding MBA (as a cross-linker) and APS (as an initiator) into the reaction vessel and leads the reaction for 2 h at 70°C. The sample was reported by the author for the removal of heavy metal ions (Pb^{2+} , Ni^{2+} , Cd^{2+} , and Cu^{2+}) from aqueous medium. The maximum adsorption capacities of the sample as per reported were 1666.67, 270.27, 416.67, and 222.22 mg g^{-1} for Pb(II), Ni(II), Cd(II), and Cu(II) at 25°C, respectively. A novel poly(pyrrole) graft-based magnetic hydrogel nanocomposite (MHN) was reported by Hosseinzadeh and Tabatabai Asl [39]. It was mentioned that the sample is an effective adsorbent for the removal of lethal Cr(VI) ion from aqueous medium. The maximum absorption capacity of this sample was found to be 208 mg/g. Chauhan et al. [40] synthesized polycarboxylated starch-based hydrogels which were applied for the sorption of copper ions. This hydrogel is stimuli responsive in nature for the sorption of Cu^{2+} ions and strongly depends on the 3D network of hydrogels. The polycarboxylated hydrogel works as a chelating agent and causes chelation with Cu^{2+} ions. The 128 mg/g absorption capacity was reported by the author toward Cu^{2+} ions. Novel SAH nanocomposites were reported by Kaşgöz et al. [41] based on acrylamide (AAm)-2-acrylamido-2-methylpropane sulfonic acid (AMPS) sodium

Hydrogel	Maximum adsorption (mg/g) of copper ion	Reference
Starch-graft-acrylic acid/montmorillonite (S-g-AA/MMT)	130.1	[34]
Chitosan-CMC	169.6	[35]
Sodium poly (acrylic acid) p(AANa)	243.9	[36]
Acrylic acid/clay	222.2	[38]
Polycarboxylated starch p(CS)	128	[40]
Acrylamide (AAM)-2-acrylamido-2-methylpropane sulfonic acid (AMPS) sodium salt/clay	81.66	[41]

Table 1.
 Maximum absorption capacity of different hydrogel samples toward Cu^{2+} ions.

salt along with clay and were synthesized through in situ copolymerization process. The synthesized materials were successfully used for removal of heavy metal ions including $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ from the aqueous medium. The absorption capacity of the samples was 1.07, 1.28, and 1.03 mmol/g for $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ ions, respectively. The comparative removal of copper divalent metal ions by different hydrogel samples are tabulated in **Table 1**.

5. Factor affecting the absorption of heavy metal ions by SAHs

The removal ability of SAHs toward heavy metal ions depends on the environmental conditions. The factors which directly affect the sorption of heavy metals ions are discussed in this chapter.

5.1 Effect of pH

The modified polysaccharide superabsorbent (MPSA) hydrogel was synthesized by Guilherme et al. [42] following free radical polymerization protocol by first treating KOH with AAc, followed by addition of known amount of AAm, modified gum arabic (MAG), and 84 mmol sodium persulfate (SPS) as an initiator. The synthesized SAHs were used as an ionic absorbent for the removal of two metal ions. It was found that the swelling of these SAHs is dependent on the pH of the medium. They studied the removal of Cu^{2+} and Pb^{2+} from aqueous medium, and it was found that the removal of heavy metals increases with the increase in pH value from 3 to 5. It is because of the deprotonation of carboxyl groups above the pK_a value (4.0) present in hydrogel network. Thus the basic media generated anionic atmosphere which in turn established an ionic bond with positive metal ions in the medium and favor the process of removal. Another pH-sensitive hydrogels were reported by Peng et al., which were synthesized by grafting acrylic acid (AA) on hemicellulose having xylene. The samples were used for the removal of heavy metal ions like Pb^{2+} , Cd^{2+} , and Zn^{2+} from the medium. The maximum adsorption capacity of the sample for the heavy metal ions was reported by the authors as Pb^{2+} (859 mg/g), Cd^{2+} (495 mg/g), and Zn^{2+} (274 mg/g). It was also reported by the authors that the increase in the uptake capacity of the heavy metal ions from the solution by hydrogels was due to the increase in the pH value of the medium, which is due to the presence of —COOH group. The —COOH group deprotonated into —COO— at high pH value; thus more active sites are available on hydrogel network to remove the positive heavy metal ions and vice versa.

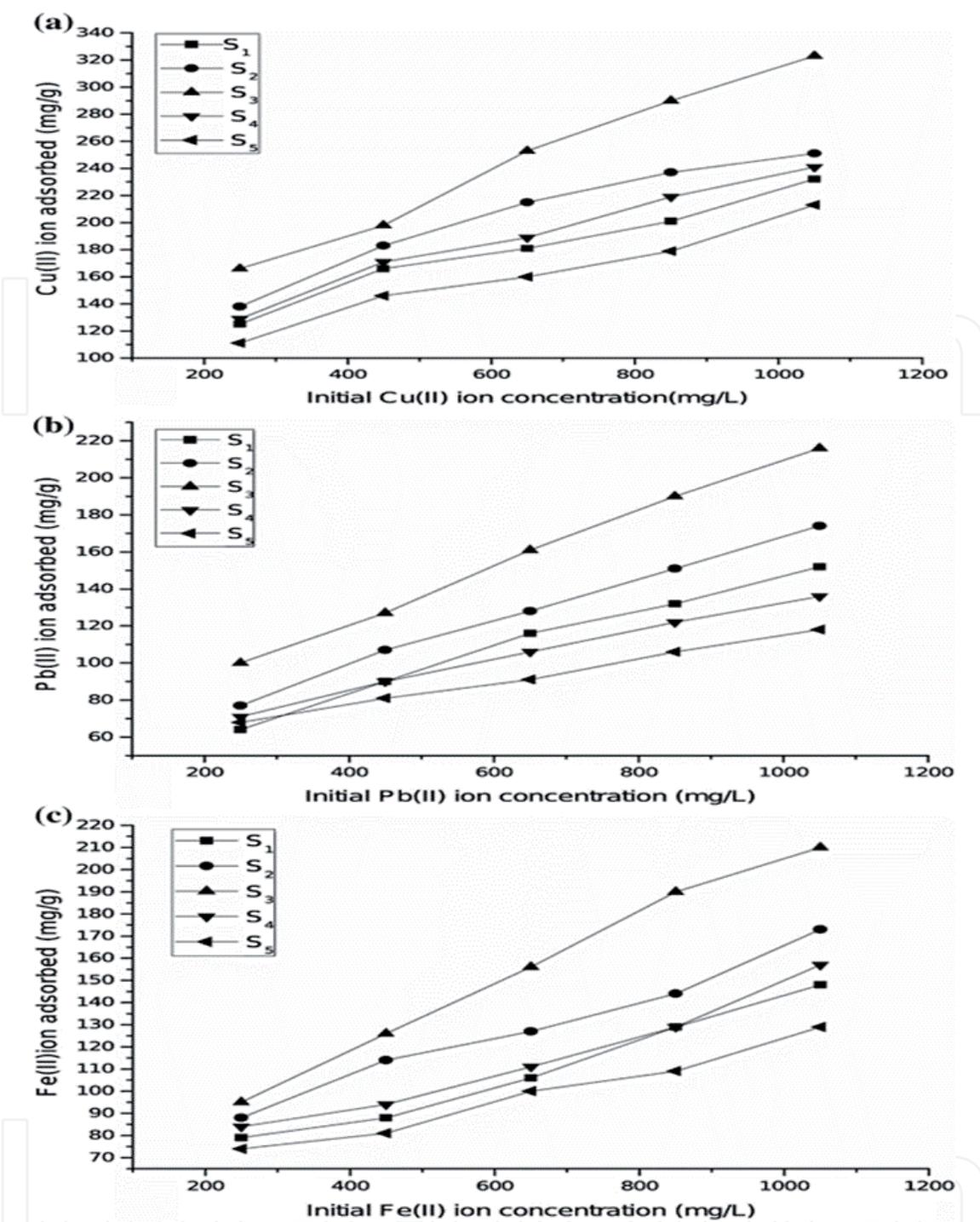


Figure 5.

(a) Variation in the adsorption capacity as function of initial Cu(II) ion concentration using AAc/NaAlg/SH SAHs with the different amount of SH. (b) Variation in the adsorption capacity as function of initial Pb(II) ion concentration using (AAc/NaAlg/SH) SAHs with the different amount of SH. (c) Variation in the adsorption capacity as function of initial Fe(II) ion concentration using (AAc/NaAlg/SH) SAHs with the different amount of SH [43].

5.2 Effect of initial concentration of heavy metal ions

A novel synthesis of SAH consisting of acrylic acid (AA), sodium alginate (SA), and sodium humate (SH) (AAc/SA/SH) to produce poly (AAc-co-NaAlg-co-SH) superabsorbent hydrogels via copolymerization process in the presence of MBA at 70°C for 6 h was reported by Agnihotri and Singhal [43]. These SAHs were used as sorbent for adsorption of heavy metal ions (Cu^{2+} , Pb^{2+} , and Fe^{2+}) and dyes (MB and CV) from aqueous solution. They observed that the adsorption capacity (mg/g) increased with the increasing initial concentration of heavy metal ions, which is

due to force established by the heavy metal ions as a mass transport from liquid to adsorbent surface. The increased trends observed in the adsorption capacity are shown in **Figure 5**.

5.3 Effect of temperature on removal of heavy metal ions

Zendehdel et al. [44] reported about the synthesis of SAH of poly acrylamide-co-acrylic acid (p(AAm-co-AA/Na zeolite)) for the successive removal of heavy metal ions (Pb^{2+} and Cd^{2+}) and studied the effect of temperature (ranging from 285 to 323 K) on the removal of these heavy metal ions from the aqueous solution. They reported that raising temperature from 285 to 303 K, the adsorption of heavy metal ions increased, which indicates that the process is endothermic. However, further increase in temperature up to 323 K, the adsorption of heavy metal ions was decreased, which is due to the desorption of heavy metal ions from the hydrogel network.

5.4 Effect of dosage of adsorbent on the removal of heavy metal ions

The synthesis of a copolymer composed of itaconic acid (IA) and acryl amide (AAm) [p(IA-co-AAm)] has been reported by Sharma and Tiwari [45]. The sample was successfully tested for the removal of Mn^{2+} ions from contaminated water at various environmental conditions. They studied and reported briefly about the effect of adsorbent dose on the removal of Mn^{2+} ions. It was observed that increasing the adsorbent dose ranging from 0.04 to 0.10 g increases the % removal of the Mn^{2+} ions from contaminated wastewater.

6. Conclusion

The industrial growth for manufacturing of goods not only enhances the manufacturing process but also promotes the market for economic development. However, on the other hand, many industries severely contaminated the water bodies with toxic heavy metals and other pollutants. Therefore, the treatment and removal of toxic heavy metals from the wastewater is necessary before going into stream and rivers. The adsorption of heavy metal ions by superabsorbent hydrogels is more popular due to easy operation, low cost, more effectiveness, biodegradable, reusability, and recyclability. The removal of heavy metal ions by these superabsorbent hydrogels is more recent and attracts the interest of the scientists working in this field.

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Abbreviations

AcGGM	acetyl-galacto glucomannan
P(AA)	poly acrylic acid
PEG	poly ethylene glycol
PEDOT	poly(3,4-ethylenedioxythiophene)

P(NIPAM)	poly N-Isopropyl acryl amide
SAHs	superabsorbent hydrogels
MMT	Montmorillonite
AAc	acrylic acid
CMC	carboxyl methyl cellulose
S	starch
g	graft
SA	sodium alginate
AMPS	2-acrylamido2-methylpropane sulfonic acid
APTMACl	3-acrylamidopropyltrimethyl ammonium chloride
AAm	acryl amide
MAG	modified gum arabic
MB	methylene blue
CV	crystal violet
LCST	lower critical solution temperature
IT	itaconic acid
APS	ammonium persulfate
KPS	potassium per sulfate
TS-SPE	temperature-swing solid-phase extraction
MBA	N,N'-methylenebisacrylamide

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