Removal of Some Heavy Metals from their Aqueous Solutions using 2-Acrylamido-2-Methyl-1-Propane Sulfonic Acid/Polyvinyl Alcohol Copolymer Hydrogels Prepared by Gamma Irradiation

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ABSTRACT

2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and Poly vinyl alcohol (PVA) were used to synthesis a series of functional copolymer hydrogels by means of ?-radiations induced copolymerization and crosslinking. Factors affecting the hydrogel preparation were optimized. The prepared hydrogels were characterized by studying their swelling characteristics. The possibility of using the prepared hydrogel in the field of water treatment was evaluated by investigating their ability to recover some heavy metal ions from their aqueous solutions. The prepared hydrogel showed a promising capability to chelate metal ions such as: Cu²⁺, Mn²⁺ and Ni²⁺ from their aqueous solutions. The obtained data show that the chelating ability of the prepared hydrogels increases by increasing the AMPS content in the hydrogel as well as the increment in the pH of the solution and the metal ion concentration. The prepared hydrogel was able to remove as much as 230 mg of Ni, 160 mg of Mn and 140 mg of Cu per gram of dry gel at the optimum conditions. The prepared PVA/AMPS copolymer hydrogels are chemically stable enough to be reused for at least 5 times with the same efficiency.

Keywords: Radiation/ hydrogel/ copolymerization/ metal ions/ removal.

INTRODUCTION

In the last decades, the remarkable increase of heavy metal contaminants is one of the most important problems threatening our world. Many serious environmental problems are posed due to the toxicity of the heavy metals to different life forms(1). Heavy metals are metabolic poisons, enzyme inhibitors and cause mental retardation and semi- permanent brain damage(2). Heavy metals are classified as persistent environmental toxic substances because they cannot be rendered harmless by chemical or biological remediation processes(3). The removal of toxic and polluting metal ions from industrial effluents, water supplies, as well as mine waters is an important challenge to avoid one of the major causes of water and soil pollution.

Numerous research efforts are being done to develop methods to remove heavy metal ions, particularly in waste streams of hydro-metallurgy and related industries, and to subsequently reuse them. These techniques include filtration, chemical precipitation, neutralization, chelating ion-exchange and adsorption(4, 5). Among these techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. Toxic metal ion removal using chelating polymers would be of great importance in environmental applications(6-8).

Fast, efficient and selective complexion of the chelating polymer, towards specific metal ions, are characterizing parameters can be tailored via controlling the type and the amount of the integrated
within the chelating polymer structure. Recently, many scientists have prepared and studied many kinds of chelating polymers containing various ligands and have used these resins for the removal and recovery of heavy metal ions from industrial wastewater as well as the recovery of some precious metal ions such as uranium and vanadium from sea water\(^9,10\).

Chelating polymeric hydrogels accomplish some advantages over insoluble polymer beads and membranes as well as water soluble polymers. Instead of toxic solvents, water is used for synthesis. Unlike insoluble polymer beads and membranes that suffer from low surface area to volume ratios, the high swelling ability ensure the incorporation of every single functional group in the complexation process. A large number of polymers incorporating a variety of metal-chelating ligands such as poly ethyleneimine, amidoxime, acrylamide and amino acids have been used to prepare chelating polymers and their adsorption and analytical properties were investigated\(^11\text{-}13\). Poly(vinyl alcohol) (PVA) is a nontoxic water-soluble synthetic polymer, which is widely used in industrial, biochemical and medical applications because of its compatibility with the living body\(^14\). The incorporation of PVA in certain hydrogel ensure its excellent water retention properties\(^15\). 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) comprises strongly ionizable sulfonate group which acquire its hydrogel high chelating ability\(^16,17\).

In this work, it is aimed to develop a good chelating hydrogel composed of (AMPS) and (PVA) using ionizing radiation for initiation and copolymerization. The factors governing the complete copolymerization process will be optimized and the prepared hydrogel will be characterized. The chelating ability of the prepared hydrogels will be estimated by studying their affinity towards different metal ions and the parameters affecting their efficiency will be investigated.

**EXPERIMENTAL**

**Materials:**

2-Acrylamido-2-methyl -1-propane sulfonic acid (AMPS) of purity 99.9% (Merck, Germany) and poly vinyl alcohol (PVA) were used as received. Other reagents namely; metal chlorides and the components of the citrate and phosphate buffers were analytical grade and purchased from El-Nasr Co. for Chemical Industries, Egypt and used as received without further purification.

**Preparation of AMPS/PVA copolymer hydrogels :**

AMPS/PVA hydrogels were obtained by radiation-induced homo/ copolymerization of mixtures of different compositions using \(^{60}\)Co gamma rays at a dose rate of 4.0 kGy/h using Canadian gamma cell, Nordion 2.2, established by National Center for Radiation Research and Technology, NCRRRT, Atomic Energy Authority, AEA, Cairo, Egypt. All samples were washed in excess water to remove the unreacted component and the soluble homo/copolymer then air dried at room temperature.

**Gel determination :**

The dried hydrogel polymer networks were soaked in water for 24h at 80°C in order to extract the insoluble part. The gelled parts was taken out, then dried and weighed. This extraction cycle was repeated till the weight became constant. The gel percent in the hydrogel was determined from the following equation:

\[
Gel(\%) = \frac{W_e}{W_d} \times 100
\]

Where \(W_d\) and \(W_e\) represent the weights of the dry hydrogel and the gelled part after extraction, respectively.
Swelling study:

The obtained crosslinked gels were soaked in buffer solutions of different pH’s; ranged from pH 1 to pH 7 at 37°C. The swelling percent ($S\%$) was determined from the following equation:

$$S(\%) = \frac{W_s - W_o}{W_o} \times 100$$

Where $W_s$ and $W_o$ are the weights of the swollen and the dry hydrogel, respectively.

Preparation of Buffer Solutions of Different pH’s:

(Citric acid/trisodium citrate) and (sodium dihydrogen phosphate/ disodium hydrogen phosphate) were used to prepare buffer solutions of pH values ranged from 3–5 and 6–7, respectively \(^{18}\). HCl was used to prepare solutions of pH values which ranged from 1–2.

Metal uptake measurement:

Batch adsorption experiments were carried out by soaking a fixed weight of the prepared hydrogel with 100 ml aqueous metal ion solutions of various concentration, pH values, and time intervals. The concentration of metal ions was detected by Plasma Optical Emission-Mass Spectrometer (POEMS III); Thermo Jarrell Ash, USA. The amount of metal ions adsorbed was calculated as follows:

$$E\ (mg/l) = \frac{C_i - C_f}{W} \times 10$$

Where $W$ is the weight of the dry hydrogel in grams, $C_i$ and $C_f$ are the initial and remaining concentrations of metal ions in mg/l. The total uncertainly for all experiments ranged from 3-5%.

Recovery and regeneration experiments:

Recovery of adsorbed metal ions and regeneration of adsorbent are a key process in wastewater treatment. To achieve these two purposes and to assess the practical utility of the adsorbent, the PVA/AMPS–metal hydrogels were stirred with 100 mL of 0.1 M HNO$_3$ (2M) at 50°C for 2 h to desorb the metal ions. Thereafter, the hydrogels were neutralized with dilute NaOH, washed with deionized water and again subjected to chelation processes.

Results and discussions:

The Hydrogels proposed to be used as metal chelating agents must possesses a remarkable crosslinking level at which the developed hydrogel can stand against its dissolution. In this respect, AMPS/PVA copolymer hydrogels were synthesized by means of \(\gamma\)-irradiation as a high energy source for copolymerization and crosslinking. The preparation conditions will be optimized to ensure the production of insoluble polymeric material with good physical properties that can be used for the removal of metal ions from their aqueous solutions.

Preparation of AMPS/PVA hydrogel:

The effect of the feed solution composition and concentration as well as the irradiation dose on the gelation degree of AMPS/PVA copolymer hydrogel were investigated and shown in Table (1). The presented data revealed the clear dependence of the gelation process on the reaction parameters. It is obvious that the increase in either reactant concentration or total irradiation leads to a significant
improvement of the gel content. Also, the increase in the AMPS content in the feed solution increases the gelation degree.

AMPS is a synthetic monomer with a vinyl group. The presence of the vinyl group in AMPS assists its radiation polymerization and crosslinking. On these bases it is possible to understand that the increase of AMPS concentration in the reaction medium would result in the increment of homopolymerization and crosslinking\(^{(19)}\). Meanwhile, the increase in the gelation degree as a result of the increase in the reactants concentration could be referred to the increase in the viscosity of reaction medium as well as the increase in the number of the radiation reactive vinyl groups. Such condition reduces the mobility of PVA segments and as a result increases the probability of the recombination of the macro-radicals as well as crosslinking and self bridging of the PAMPS which allow the production of much perfect network of higher crosslinking density. In the same manner, the increase in the irradiation dose results in the increment in the number of the formed free radical which in turn increase the probability of recombination and enhance the degree of crosslinking.

Table (1): Effect of preparation conditions on the gelation content of AMPS/PVA copolymer hydrogel

<table>
<thead>
<tr>
<th>AMPS content (wt%)</th>
<th>Total concn. (wt%)</th>
<th>Irradiation dose (kGy)</th>
<th>Gel content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>10</td>
<td>10</td>
<td>56</td>
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<td></td>
<td>20</td>
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<tr>
<td>70</td>
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<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Swelling Characteristics of AMPS/PVA copolymer hydrogels:

Figure 1 shows the effect of preparation conditions namely; AMPS content in the feed solution and irradiation dose, on the equilibrium swelling as a characteristic property of the prepared polymeric hydrogel. In general, it is clear that the increase in AMPS content increases the swelling ability of the prepared hydrogel. The increase in the AMPS content in the reaction medium would increase the hydrophilicity of the prepared hydrogel because of the high hydrophilic character of the sulfonic group. On the other hand, the increase in the irradiation dose increases the crosslinking density. The increment in the degree of crosslinking reduces the free volume available for swelling by increasing the tightness of the network structure.
Figure 1: Effect of AMPS content in the feed solution composition on the equilibrium swelling in double distilled water of AMPS/PVA copolymer hydrogel prepared at different irradiation dose (\(\gamma\)) 20 and (\(\gamma\) )30 kGy.

On the other hand, Figure 2 shows the pH dependent swelling of AMPS/PVA copolymer hydrogels as a function of AMPS content in the feed solution composition. The data show that all of the examined hydrogel possesses sensitivity towards the change in the pH of the swelling medium. The swelling ability of the prepared hydrogel dramatically increases at pH value around pH 1.0, which is the \(pK_a\) value of sulfonic groups\(^{(20, 21)}\). At pH values higher than the \(pK_a\) value, the swelling degree increased due to the ionization of the sulfonic groups and broken the hydrogen bonding. The increase in the AMPS content in the hydrogel leads to the increment in the ionized groups and consequently increases the electrostatic repulsion, which results in the expansion of the network structure.

On the other hand, as soon as the pH value of the swelling medium exceeds pH 2 to reach the pH values ranged from pH 3 to pH 5, a clear decrement in equilibrium swelling was observed. Upon further increase in the pH value of the swelling medium (pH 6 – pH 7), an extra decrement in the swelling equilibrium was observed. The drastic decrease in the swelling at pH values higher than pH 2 may be attributed to electrostatic shielding takes place as a result of the change in the ionic strength accompanied by changing the medium from an aqueous HCl solution to 0.2 M citrate buffer solutions. The last reduction in the equilibrium swelling is also accompanied by changing the buffer solution type from 0.2 M citrate to 0.2 M phosphate which is also attributed to the change in ionic strength resulting from the difference in the ionization degree between citrate and phosphate salts\(^{(22)}\).
Metal chelation Properties of AMPS/PVA copolymer hydrogel

Effect of hydrogel composition:

The chelation of AMPS/PVA hydrogels of different compositions was investigated towards Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$ by the batch equilibration method. The results show a slight dependence of metal ion uptake on the copolymer hydrogel composition are given in Figure 3. The data shows that the amount of metal ion uptake slightly increases with increasing AMPS content. It is also clear that all of the affinity of hydrogels under investigation towards the metal ions of interest was in the following order Ni$^{2+}$$>$Mn$^{2+}$$>$ Cu$^{2+}$. These results are in a very good agreement with relative size and crystal field radii of these hexa-coordinated metal ions.$^{(32)}$
Effect of the medium pH:

pH is a critical parameter that can affect the chelating ability of the prepared hydrogel by influencing its swelling ability, formation of metal ions as well as the interaction between the hydrogel and the metal ions. Figure 4 shows the adsorption capacity of the prepared AMPS/PVA copolymer hydrogel towards Cu$^{2+}$, Mn$^{2+}$, and Ni$^{2+}$ ions as the function of the pH value of the surrounding medium with the initial metal concentration of 1000 ppm. It is clear that there is a slight increase in metal adsorption amount when pH was raised from pH 3 to pH 7 thereafter leveling off takes place. These adsorption trends could probably be affected by the competitive interaction between metal and hydrogen ions with the active sites located within the prepared hydrogel \(^{24, 25}\). At lower pH, an excess of hydrogen ions can compete effectively with metal ions for binding sites, resulting in a lower level of metal uptake. It is well known that at the pH-value higher than 7, the metal ions might precipitate, the presence of alkaline ions help to form the hydroxyl complexes \(^{25}\).

Effect of initial solution concentration:

The effect of the metal ion concentration on the chelating ability of the prepared hydrogels is an important parameter to estimate the efficiency of the hydrogel as a chelating material at low pollution levels. Figure (5) shows a sharp increase in adsorption capacity at low initial concentrations.
Figure 5: Effect of metal ion initial feed solution concentration on the capacity of the AMPS/PVA copolymer hydrogel towards (? ) Cu, (†) Mn and (?) Ni.

up to 100 ppm then it tends to level off at higher concentrations. At initial step the adsorption capacity increases 15 folds as the solution concentration increases from 5 to 100 ppm. Whereas, less than 50% increment in the adsorption capacity as the feed solution concentration increased to 250 ppm. Such difference in the adsorption trend reveals the variety in the adsorption interactions that involves physical and chemical mechanisms.

The prepared hydrogel shows higher chelating ability at low metal ion concentration which indicates that the adsorption takes place by the electrostatic attraction (physical adsorption). On the other hand, at high metal ion concentrations, the adsorption is relatively low which indicates that the adsorption takes place by the chelating interaction (chemical adsorption). Langmuir isotherm is one of the most commonly isotherms used to evaluate the sorption capacity of the chelating material. From the linear form of this isotherm, equations can be written as follows:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \left[ \frac{a_L}{K_L} \right] C_e
\]

Where \( q_e \) is the amount of metal adsorbed at equilibrium (mg/g) and \( K_L \) and \( a_L \) are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively.

Figure 6: Plot of \((C_e/q_e)\) against \(C_e\) for AMPS/PVA copolymer hydrogel towards (? ) Cu, (?) Mn and (?) Ni.
The linear plot of \((C_e/q_e)\) against \(C_e\), Fig. 6, for the metal ions under investigation shows that the adsorption data are well fitted by Langmuir isotherm model \((r^2 > 0.99)\). The Langmuir constants were evaluated and reported in Table 2. The ratio \([K_L/a_L]\) from the table is known as the capacity factor, which is the maximum adsorption capacity of the hydrogel toward particular metal ion.

Table (2): Langmuir Model

<table>
<thead>
<tr>
<th></th>
<th>Langmuir equation</th>
<th>Langmuir parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slop</td>
<td>Intercept</td>
</tr>
<tr>
<td>Cu</td>
<td>0.019</td>
<td>2.50</td>
</tr>
<tr>
<td>Ni</td>
<td>0.012</td>
<td>0.94</td>
</tr>
<tr>
<td>Mn</td>
<td>0.015</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Adsorption kinetics:

The rapid interaction of metal ions with the adsorbent is very favorable for the feasible processes. The effect of contact time on the adsorption capacity of the prepared AMPS/PVA copolymer hydrogel towards Cu, Mn, and Ni ions was shown in Figure 7. The amount of the absorbed metal ions increased sharply during the first 60 min and then slows down. Numerous researchers thought that the decrease of free chelating site resulted from polymer chains shrinkage takes place as a result of the adsorption occurring at the polymer surface. So the cations were difficult to diffuse toward the adsorption sites located in the bulk of the hydrogel. In other words, at the beginning of the process, the adsorption occurs on the polymer surface, so, a fast adsorption rate was found \((27, 28)\). After that; the adsorption takes place at the inner surface of the polymer, so, the adsorption rate was slow due to the pore diffusion of metal ions into the polymer matrix i.e. intraparticular diffusion or chemical reaction (chelating or ion-exchange) would be the rate limiting step of sorption kinetics.

In order to interpret the mechanisms of metal adsorption processes, the adsorption data for heavy metals under investigation were analyzed by a regression analysis to fit Langmuir and Freundlich models \((29, 30)\). The linear form of these two isotherms, equations can be written as follows:

\[
\ln \left( 1 - \frac{K_L a_L}{K_L + a_L} \right) = -K_L a_L C_e = -K_L a_L C_e
\]

Where \(K\) is the equilibrium constant, and

\[
F(t) = \frac{C_i - C_e}{C_0 - C_e}
\]

Where \(C_0\), \(C_i\) and \(C_e\) (all in mg/L) represent the concentration of metal ions initially, in aqueous solution, at time \(t\) and at equilibrium, respectively.

Figure 7: Effect of contact time on the adsorption capacity of the prepared AMPS/PVA copolymer hydrogel towards (\(†\) ) Cu, (\(\uparrow\) ) Mn and (\(\downarrow\) ) Ni.
The experimental results shown in Figure 7 can be converted into the plots of \(-\ln (1-F)\) versus \(t\) as shown in Figure 8, and the adsorption rate constants; rate of sorption \((K_s)\) and rate of desorption \((K_d)\) of the chelating hydrogel can be calculated from the slopes and intercepts of the plots as follow:

\[
K_d = k \left( \frac{C_e}{C_0} \right) \quad \text{and} \quad K_s = K - K_d
\]

![Figure 8: Adsorption rate curves of the prepared AMPS/PVA copolymer hydrogel towards (?)Cu, (?) Mn and (?) Ni.](image)

Table 3 shows the values of \(K_s\) and \(K_d\), from which the following can be observed; the highest sorption rates \((K_s)\) were found in case of the reaction with Ni revealing the high affinity of the chelating hydrogel for the adsorption of these metal ions.

**Table (3): Adsorption rate constant of different metals on AMPS/PVA copolymer hydrogel**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(K_s \times 10^{-3}) ((s^{-1}))</th>
<th>(\frac{C_e}{C_0})</th>
<th>(r^2)</th>
<th>(K_d \times 10^{-3}) (s^{-1})</th>
<th>(K_s \times 10^{-3}) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.94</td>
<td>0.847</td>
<td>0.994</td>
<td>0.400</td>
<td>0.008</td>
</tr>
<tr>
<td>Mn</td>
<td>4.99</td>
<td>0.910</td>
<td>0.989</td>
<td>0.719</td>
<td>0.011</td>
</tr>
<tr>
<td>Ni</td>
<td>6.14</td>
<td>0.884</td>
<td>0.986</td>
<td>1.064</td>
<td>0.013</td>
</tr>
</tbody>
</table>

**Regeneration of AMPS/PVA copolymer:**

Currently, emphasis is given on recovery of the adsorbed metal ion rather than simple adsorption and disposal. Regeneration of the chelating hydrogels after metal sorption process without damaging or reducing their absorption capacity is a very important factor for the success of sorption technology development. Recovery of different metal ions adsorbed on AMPS/PVA copolymer hydrogel was carried out by 0.1 M HNO₃ for 2h, at room temperature. The regeneration stability was tested by applying the adsorption and desorption processes several times. The test shows that almost insignificant decrease in the sorption capacity on regeneration as shown in Figure 9.
Figure 9: Effect of regeneration on the efficiency of AMPS/PVA copolymer hydrogel towards (?) Cu, (? )Mn and (?) Ni.

CONCLUSION

2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and poly vinyl alcohol (PVA) were used to prepare chelating polymeric hydrogels by means of ?rays induced copolymerization and crosslinking. Characteristics and some properties of the prepared copolymers were investigated. The possibility of their applications in the removal of some heavy metals was studied. From the obtained results, it can be concluding that: AMPS content is the main effective parameter for the affinity of the copolymer towards different metal ions such as: Ni$^{2+}$, Mn$^{2+}$, and Cu$^{2+}$ from their solutions. The data shows that the affinity of the prepared hydrogels was in the following order Ni$^{2+}$>Mn$^{2+}$>Cu$^{2+}$ and increases by increasing the AMPS content in the hydrogel as well as the increment in the pH of the solution and the metal ion concentration. The prepared AMPS/PVA copolymer hydrogels were also chemically stable enough to be reused for at least 5 times with the same efficiency.

REFERENCES

(7) C. Demirbilek, C. Ö. Dinç; Carbohydr. Polym; 90, 1159, (2012)
(8) C. Demirbilek, C. Ö. Dinç; Carbohydr. Polym; 90, 1159, (2012)

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