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2-Acrylamide-2-Methylpropane Sulfonic Acid Hydrogels; Preparation, Characterization, and Removal of Heavy Metals Pb^{2+} and Cu^{2+} from Wastewater

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Abstract:

The aim of the study was the preparation and characterization of 2-Acrylamide-2-methylpropane sulfonic acid (*AMPS*) hydrogel with the intent to remove Lead (Pb^{2+}) and Copper (Cu^{2+}) heavy metals from wastewater. *AMPS* hydrogels were prepared by the free radical polymerization method at 70℃ for six hours. Potassium persulfate (*KPS*) was used as an initiator, and *N,N′*-Methylene-*bis*-acrylamide as a crosslinking agent. The swelling properties of hydrogels were studied in diverse conditions, such as temperature, ion strength, and *pH*. *NaOH* neutralized *AMPS* in 50%, 65%, and 75% *w/w*. *AMPS* monomer showed absorption by *UV* spectrophotometer at 229 *nm*. After neutralization, absorption was established at 203, 213, and 200 *nm* for 50%, 65%, and 75% *w/w* solution, respectively. This study showed a robust, complex formation between SO_3^- and Na^+. The maximum swelling of *AMPS* hydrogels was determined as 16000% in 65% *w/w NaOH* and *pH*=7. The swelling behavior of hydrogels was studied at 25°*C*, 50°*C*, and 75°*C*. The maximum swelling was 220%, which was seen at 75°*C*. To evaluate the effect of ionic strength on hydrogel swelling, *NaCl* and *KCl* were used in different *mol* concentrations. In this research, the swelling properties in 0.00001*M* were more than 0.001*M*. *FT-IR* and *TGA* were used to characterize the structural and thermal properties. Atomic Absorption spectroscopy was performed to evaluate the removal of the heavy metals (Cu^{2+} and Pb^{2+}) in wastewater. Morphologic investigation was studied by the Scanning electron microscopy (*SEM*) micrographs.

Keywords: Bifunctional Hydrogel; Swelling Properties; Atomic Absorption; Water Remediation; Neutralization; Scanning Electron Microscopy

INTRODUCTION

Reuse of water and the need for this universal solvent (water) is increasing daily. However, water resources are limited, and it is soon understood that they must not be adequate for today's population. In this regard, we need to contemplate a method to reuse water. On the other hand, industrial wastes and effluents are considered dangerous if not removed from toxic and hazardous substances and cause problems for the environment and life cycle. To solve this problem, using hydrogels having functional groups is appropriate [1].

Hydrogel is a three-dimensional, *3D* network of hydrophilic polymers that can swell in water and hold a large amount of water while reserving structure because of each polymer chain's chemical or physical crosslinking. Recently, many studies have been performed on the effect of *pH* and temperature on the swelling behavior of hydrogels. Hydrogels show different behavior with environmental stimuli. Determination of the swelling behavior of hydrogels has many applications regarding their usage in medicine and industry, such as drug delivery systems, tissue engineering, artificial muscle production, agriculture, removal of heavy metal ions, and sensors [2-6]. Hydrogels are polymers with functional groups such as SO_3H^-, COO^-, *OH*, and NH_2 [2-6]. Hydrogels are vital in water purification, agriculture, medical sciences, and drug deliveries [7].

2-Acrylamide-2-Methylpropane sulfonic acid (*AMPS*) is an anionic vinyl monomer. Its structure has three functional groups: SO_3, NH_2, and $C=O$ [8, 9]. Hydroxyethyl and hydroxypropyl are two derivatives of *AMPS* hydrogel. These biocompatible derivatives have non-immunogenic characteristics, so they are used in various industries, especially in drug delivery systems. *AMPS* monomer is water soluble. *AMPS* monomers are stable in saline solution systems because of sulfonic groups. They are stable in media variability of temperature and show resistance to hydrolysis by acid and base. *AMPS* products are not expensive. Therefore, using these products is applicable and instrumental in the hydrogel research area [10].

Liu *et al.* studied the swelling properties of *AMPS* and methyl acrylamide hydrogels [9]. They showed a significant difference between the calculated swelling in water and the theory of swelling equilibrium prediction [10, 11]. Okay *et al.* prepared Acrylamide (*AAm*) and *AMPS* hydrogels and examined their swelling in aqueous, organic, and ionic solutions. While prior studies were based on the physical properties of hydrogels, Okay found relations between the formation mechanism and the swelling behavior of *AAm* and *AMPS* hydrogels [11, 12]. Hazer *et al.* studied the swelling behavior of polyacrylamidoxime-co-*AMPS* and poly(acrylonitrile-co-*AMPS*) hydrogels. They characterized their structural and thermal behaviors by using *FT-IR* and *TGA* methods [13]. Soykan *et al.* prepared copolymer-metal (copper, nickel, and cobalt) complexes and synthesized poly(crotonic acid-co-*AMPS*) polymers [14]. Cavus *et al.* prepared poly(*AMPS*-co-itaconic acid) and a homopolymer of *AMPS*. They applied these homopolymers to remove metal ions (Pb^{2+}, Cu^{2+}, and Cd^{2+}) from water [15].

This study prepared *AMPS* hydrogels by the free radical polymerization method for six hours at 70°*C* with potassium persulfate (*KPS*) as an initiator and *N,N'* methylene-*bis*-acrylamide as a crosslinker. The swelling properties of *AMPS*-prepared hydrogels were studied in diverse conditions, such as *pH*, temperature, and ionic strength. *FT-IR* and *TGA* were used to show the synthesized gels' structural behavior and thermal properties. As an application of these hydrogels, we studied the removal of heavy metal ions, Cu^{2+}, and Pb^{2+} in wastewater by Atomic Absorption Spectroscopy (*AAS*). Adsorption of Cu^{2+}, and Pb^{2+} with *AMPS* hydrogel and morphologic investigation was studied by the Scanning electron microscopy *SEM* micrographs.

Experimental SECTION

1.1. Materials

The chemical materials used in this study are 2-acrylamide-2-methylpropane sulfonic acid (*AMPS)* with 99% purity, potassium persulfate (*KPS*) (99% purity), Pb^{2+}, and Cu^{2+}. Compounds were purchased from Merck Company. Methylene-*bis*-acrylamide (*MBA*, 99% purity) and Sodium hydroxide (*NaOH*) were purchased from Sigma Company.

2.2. Preparation of Hydrogel

To prepare *AMPS* hydrogel, we solved 0.001*mol* of *AMPS* in 65% *w/w* of *NaOH* solution. 0.00001*mol* of the *MBA* cross-linker and 1% of the initiator *KPS* were added. *NaOH* with different concentrations was used to prepare the neutralized hydrogel product. This mixture was poured into the same size and diameter tubes and placed in an oven for six hours at 70°*C*. Finally, the gels were removed from the tubes and cut into equal portions. After weighing, these portions were placed in distilled water for 24 hours, weighed again, exposed to laboratory temperature for 24 hours, and then weighed. This time, for 24 hours, they were placed inside the oven at 50°*C*. The swelling of dried hydrogels was studied in different *pH*, *NaCl*, and *KCl* concentrations.

2.3. Characterization Experiments

***FT-IR* Measurements:** The hydrogel disks were prepared by grinding in *KBr* and compressing the mixture. A Perkin Elmer spectrophotometer recorded *FT-IR* spectra of the gels with a resolution of 4 cm^{-1} and averaged over 32 scans.

***UV* Spectroscopy:** A 200-700 *nm* double-beam *UV* spectrophotometer was used to show the complexation between *AMPS* and *NaOH* in different percentages (30, 50, 65, and 75*% w/w*).

***TG* Analysis:** Thermogravimetric analysis (*TGA*) of the hydrogels was carried out on a Perkin Elmer Pyris with a nitrogen flow rate of 20 *ml/min* and a temperature range of 10*°C* to 700*°C*.

Scanning Electron Microscopy (*SEM*) analysis

Two *mg* of the samples used in the analysis were covered with Au and a vacuum evaporator.Morphologies of the sample were determined by using a *Jeol JSM*-6060*LV* model *SEM*.

Atomic Absorption Spectroscopy: The analytical Jena model removed Cu^{2+} and Pb^{2+} ions in 20, 50, and 100 *ppm* concentrations. For this, the hydrogel was put into each solution, and adsorption was measured by atomic absorption (*AA*) spectroscopy at different times.

2.4. Swelling Studies:

The swellings of the prepared samples were measured in deionized water and various buffers, with *pH*=2-12 and different temperatures in a temperature-controlled bath. The samples were periodically separated from the superficial water or buffer solution, weighed, and replaced in identical vials. The swelling of the hydrogels was obtained from the equation (1):

$$S = W\text{-}W_0/W_0 \qquad (1)$$

Where W_0 denotes the weight of the dry hydrogel, and W is the weight of the swollen hydrogel.

2.5. Diffusion at Different pH:

The Fickian kinetic model was used for the initial swelling to determine the nature of water diffusion into hydrogels (this model is valid just for the first 60*%* swelling), equation (2) [16-18]:

$$F = \frac{M_t}{M_\infty} = kt^n, \qquad (2)$$

Where M_t and M_∞ are the total water absorbed at that t and time equilibrium, respectively, with M_∞ determined by a gravimetric method, k is a swelling coefficient correlated with the polymeric network structures, and n is an exponent characteristic of the swelling, which represents solvent diffusion modes inside hydrogels [19-21].

2.6 Adsorption:

The cupric ion and lead adsorption capacities of the *AMPS* hydrogel were determined using an aqueous solution containing Cu^{2+} and pb^{2+}. The procedure was started by adding 0.1 *gr* of *AMPS* hydrogel to the 100 *mL* Erlenmeyer stock solution.

The initial metal ion concentration was 125 *ppm* for kinetic studies, and increasing Cu^{2+} concentrations were evaluated for the binding isotherms.

The equilibrium binding capacity of the *AMPS* hydrogels (Q, $g_{AMPS}/\ g_{Cu}{}^{2+}$) was estimated by the following equation;

$$Q = \frac{(C_o - C_e)}{m} \times V \qquad (4)$$

C_o and C_e are the Cu^{2+} metal ion concentrations in the aqueous solution ($g\ Cu^{2+}/L$) before and after bindings. m is the hydrogel mass (g_{AMPS}), and V is the total solution volume (Liter).

The differential and integral representations of the pseudo-first and second-order binding kinetics equations can be written as follows.

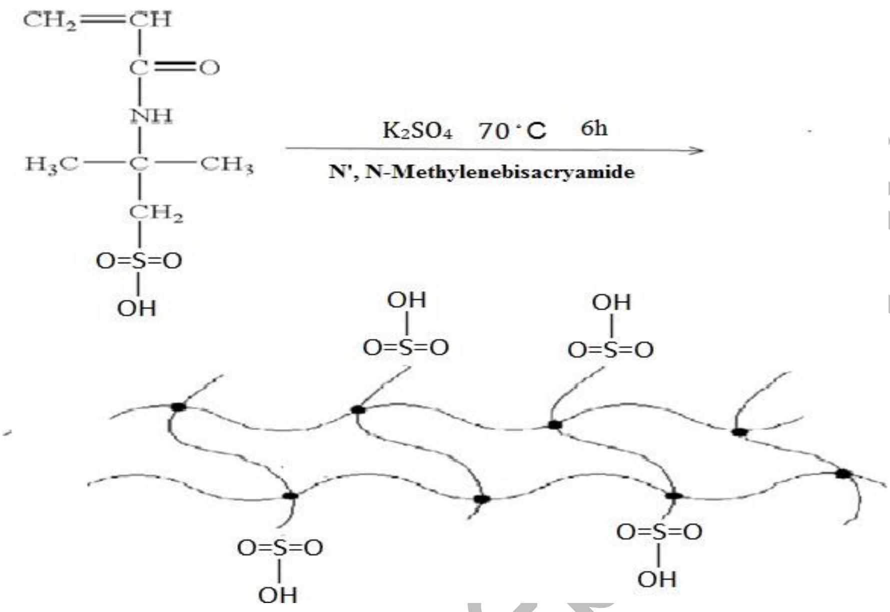
First-order $$\frac{dQ}{dt} = k_1(Q_e - Q_t) \qquad Q_t = Q_e(1 - e^{-k_1 t}) \qquad (5)$$

Second-order $$\frac{dQ}{dt} = k_2(Q_e - Q_t)^2 \qquad Q_t = \frac{t}{A + Bt} \qquad A = \frac{1}{k_2 Q_e^2} \qquad B = \frac{1}{Q_e} \qquad (6)$$

In these equations, Q_t (*mg/g*) and Q_e (*mg/g*) are the amounts of adsorption at time t (*min*) and equilibrium. k_1 (*1/min*) and k_2 (*1/mg, g/min*) are pseudo-first and pseudo-second-order rate constants, respectively [18].

RESULTS AND DISCUSSION

AMPS hydrogels were prepared using potassium persulfate as an initiator and *N,N′* methylene-*bis*-acrylamide as a crosslinker at 70*°C* and six hours by free radical polymerization. *65% w/w NaOH* neutralized *AMPS*. The mechanism of hydrogel preparation has been shown in Scheme 1.

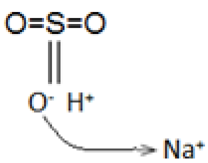


Scheme 1. The mechanism of preparation reaction of hydrogel

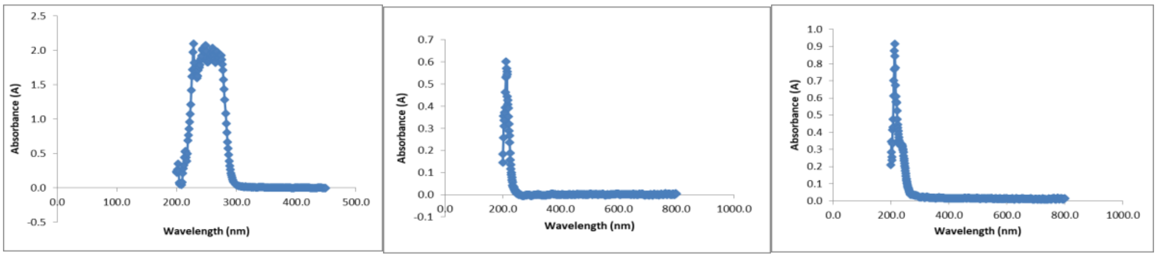
3.1. UV-VIS ANALYSIS:

UV-Vis spectrophotometry was used to show the swelling behavior of *AMPS* hydrogel neutralized by 50*%*, 65*%*, and 75*% w/w NaOH* and its neutralized properties (Figure 1).

According to the results, the maximum absorption (*A*) magnitude was as follows: *A*=2.098 for pure *AMPS* at 229 *nm*, *A*=0.634 for 50*%* neutralized *AMPS* at 203 *nm*, *A*=0.916 for 65*%* neutralized *AMPS* at 213 *nm* and *A*=0.900 for 75*%* neutralized *AMPS* at 200 *nm*, which indicates a potent complex between Na^+ ions and the sulfonic groups (shows as $SO_3^-Na^+$, Scheme 2) [22, 23].



Scheme 2. The functional group of *AMPS* hydrogel



A B C

FIGURE 1. ***UV-SPECTROSCOPY* OF *AMPS*** A) ***AMPS* MONOMER WITH 50%*W/W NAOH* ;** B) ***AMPS* WITH 65% *W/W NAOH*;** C) ***AMPS* WITH 75% *W/W NAOH***

3.2. *FT-IR* ANALYSIS OF *AMPS* HYDROGEL:

To investigate the structural behavior of prepared hydrogel, we used *FT-IR* spectroscopy. Figure 2 shows the *FT-IR* spectroscopy of *AMPS* hydrogel in 65% *NaOH w/w*. In this figure, two peaks at 3300 cm^{-1} to 3500 cm^{-1} are assigned to the vibration of the *N-H* and *O-H* bands. The peak at 1666 cm^{-1} is attributed to the amide carbonyl group. The peak at 1594 cm^{-1} is assigned to the *N-H* banding. The prominent peak of characterization of *AMPS* at 1220 cm^{-1} is attributed to the sulfonic acid groups [6, 24-26].

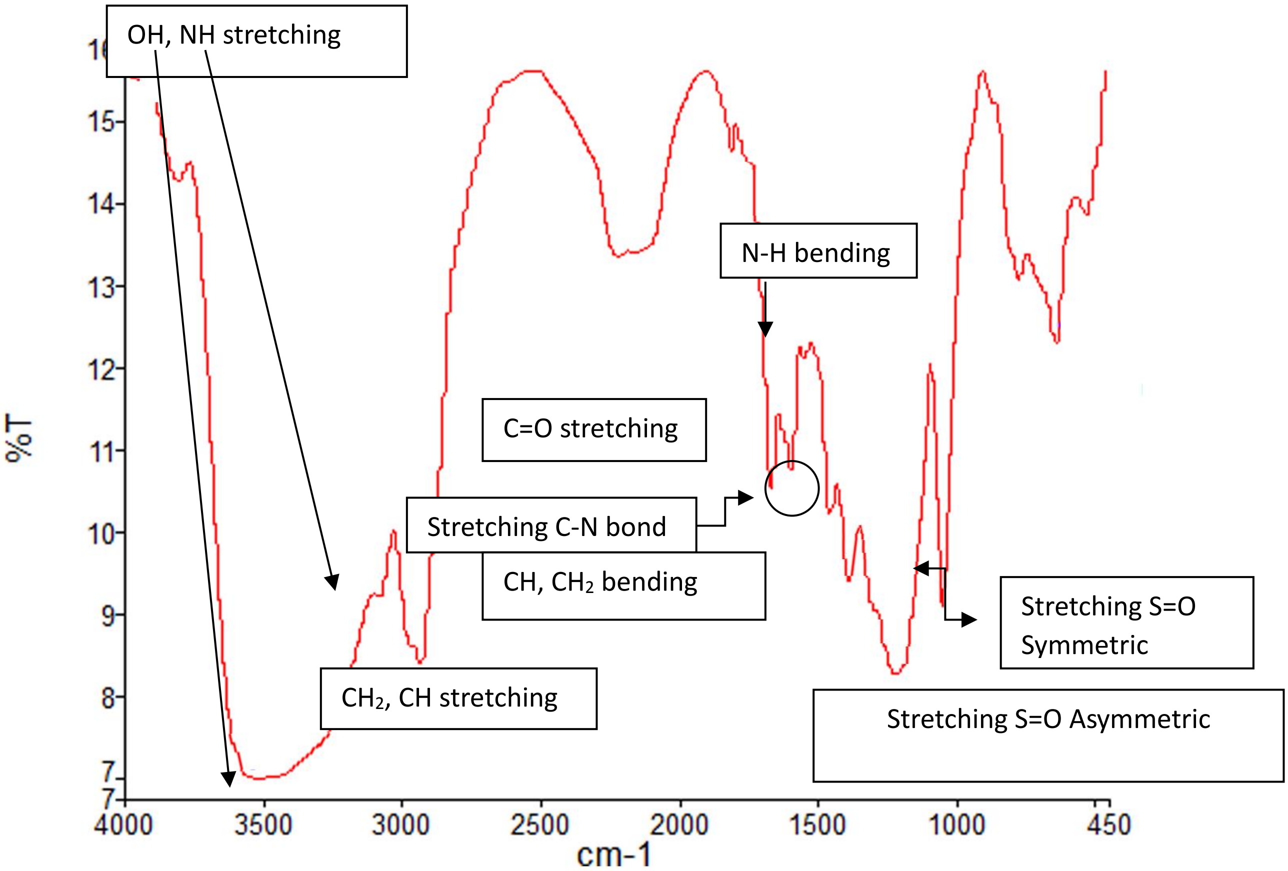


Figure 2. *FT-IR* spectrum of *AMPS* hydrogel neutralized by 65*% NaOH*

3.3. THERMAL BEHAVIOR OF *AMPS* HYDROGEL:

TGA was used to investigate the thermal properties of prepared *AMPS* hydrogel. Figure 3 shows the thermal resistance of *AMPS* hydrogel in a nitrogen atmosphere. According to it, the water in the hydrogel evaporates up to 100°*C*. Mass deficiency of 11*%* from 100°*C* to 180°*C* can be attributed to the loss of surface water penetrated inside the hydrogel or to the probable separation of -*HO* and -HN_2 inside the molecules. The maximum degradation temperature of *AMPS* hydrogel (*NaOH* 65*%*) is 358°*C*, which destroyed about 55*%* of the material (from 300°*C* up to 400°*C*) [6, 26-31]. Degradation step can be ascribed to the sulfonation or amide group or backbone degradation

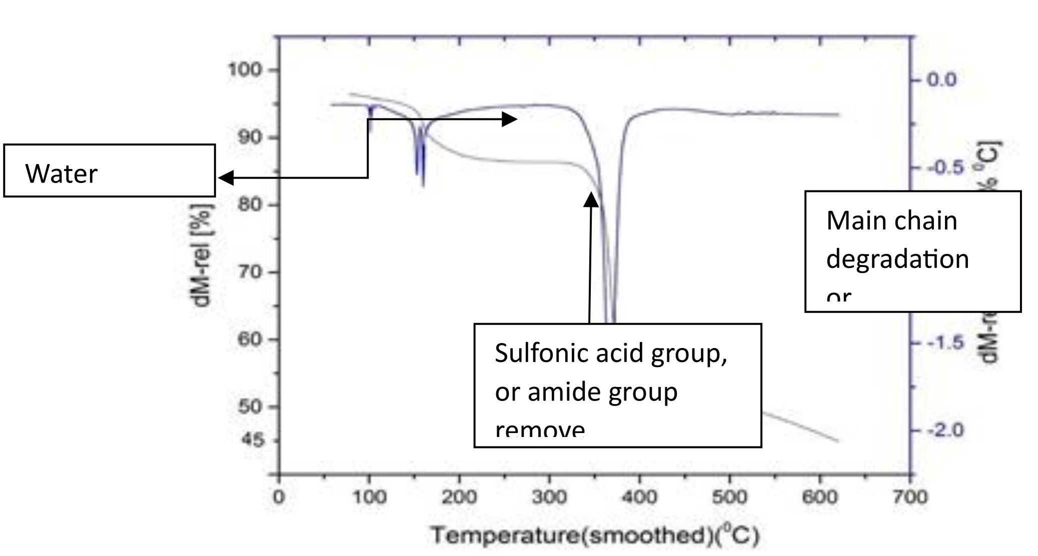


Figure 3. *TGA* thermogram of *AMPS* hydrogel

3.4. Swelling Studies

The Effect of Sodium Hydroxide on Swelling

Figure 4 shows the swelling behavior of *AMPS-Na* at different concentrations of *NaOH* (10% - 100%). The maximum swelling was obtained at a concentration of 65% *NaOH*. At low *NaOH*, homopolymer chains of *AMPS* rarely convert to *AMPS-Na* (low ionic responsive). At high *NaOH*, sulfonic groups Na^+ in hydrogel chains lead to low swelling as the Steric effect. 65% *NaOH* is the optimum in which the ionic responsibility increases, so swelling increases [32-34].

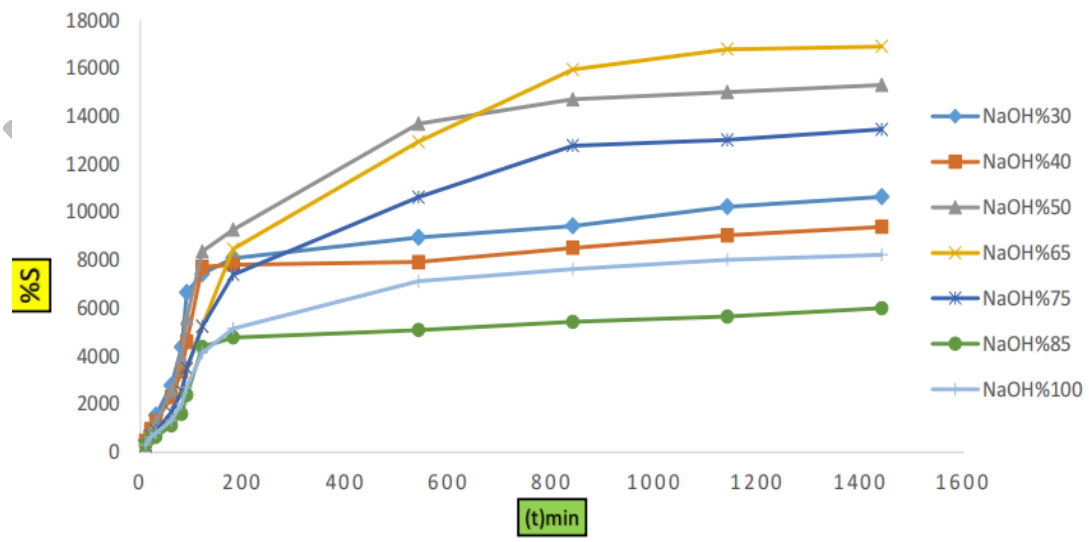


Figure 4. The swelling behavior of *AMPS* hydrogel at different concentrations of *NaOH*

The Effect of *pH* on Swelling

To study the swelling behavior of *AMPS* hydrogel in 65% *NaOH*, three different media with *pH*=1, 7, and 12 were chosen. The results are shown in Figure 5. The maximum swelling ratio of *AMPS* hydrogel was 16000% obtained in *pH*=7. In *pH*=1 and *pH*=12, the swelling ratio was 14000% and 5000%, respectively. A significant decrease in the swelling ratio *pH*=12 occurred due to the Steric effect caused by Na^+ heads and Basic media. In acidic media with *pH*=1, an ion mutation and competition between ions (Na^+, OH^-, Cl^-, and H^+) occurs, and swelling increases significantly. However, the swelling ratio is less than the solution with *pH*=7 [31-34].

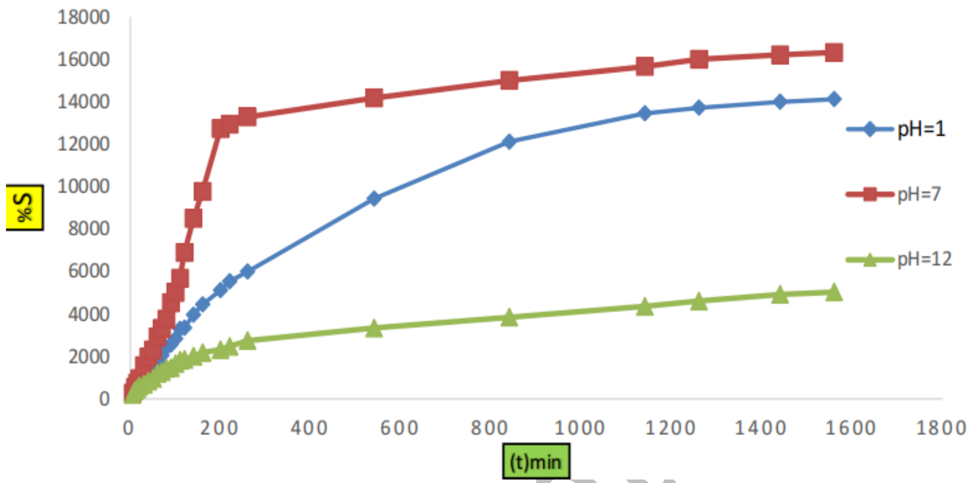


Figure 5. The swelling behavior of *AMPS* hydrogel at different pH and 65% *NaOH*

The Effect of Temperature on Swelling

Figure 6 shows the swelling behavior of *AMPS* hydrogel in 65% *NaOH* and *pH*=7 at different temperatures. The maximum swelling of 220% is related to 75ºC, and its minimum of 130% occurred at 25ºC. Inter and intra-molecular bonds are weakened, molecular complexes are broken, and the hydrogen bonds between hydrogel and solvent (physical bond) are also broken with increasing temperature, so the pores inside the hydrogel and, therefore, the swelling increase.

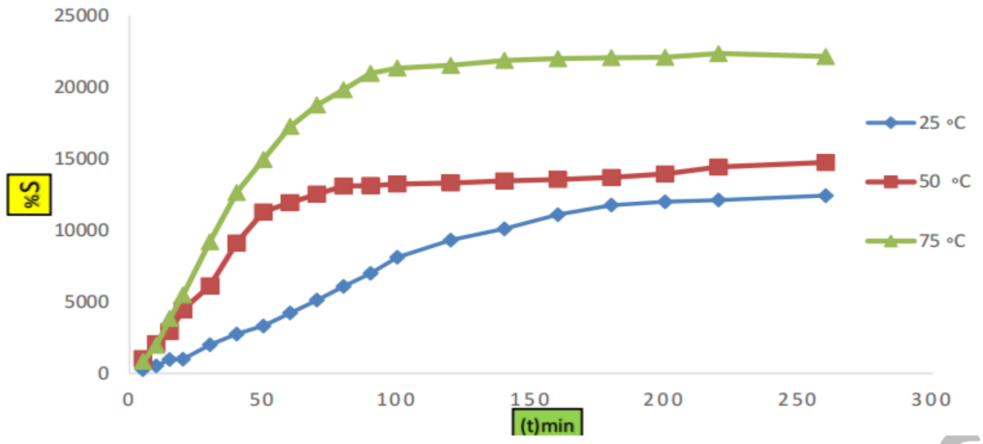
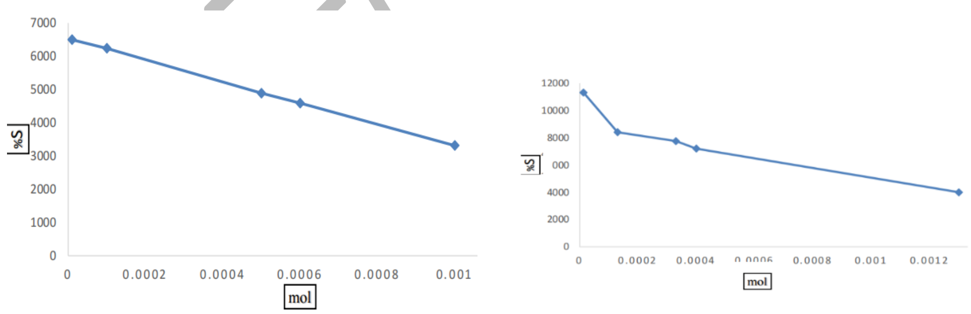


Figure 6. The swelling behavior of *AMPS* hydrogel at different temperatures (65% *NaOH*, *pH*=7)

The Effect of Ionic Strength on Swelling

Here, we studied the swelling of *AMPS* hydrogel at different concentrations of *NaCl* and *KCl*. As shown in Figure 7a, in the presence of *NaCl*, due to the ion repulsion between the media and the hydrogel, and according to the Donan phenomenon, the osmotic pressure of the medium increases with increasing salt concentration, so swelling is reduced. The swelling in 0.00001*M* is about double rather than 0.001*M NaCl* [17-22].

Figure 7b shows the swelling of *AMPS* hydrogel at *pH*=7 in different concentrations of *KCl*. Similar to *NaCl* and for the same reason, the lowest concentration is accompanied by the highest swelling and vice versa. Comparing the changes in *NaCl* and *KCl*, the reason for more swelling in *KCl* can be attributed to a larger radius of K^+ rather than Na^+[28, 31-34].



a) **b)**

Figure 7. Swelling of *AMPS* hydrogels in different molars of **a)** *NaCl*; **b)** *KCl*

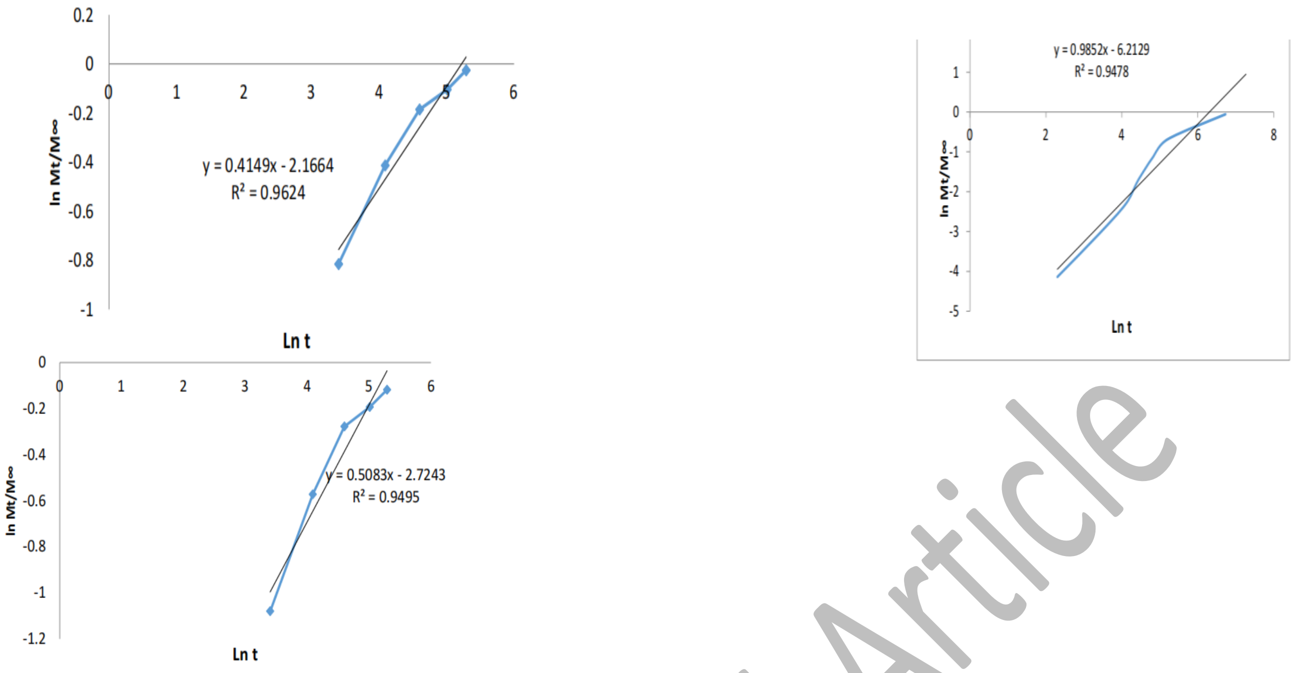
3.5. Hydrogel Diffusion

Due to its essential applications in biomedical, pharmaceutical, environmental, and agricultural engineering, the study of the mechanism of water diffusion in hydrogel swelling has received considerable attention in recent years. Hydrogels play an essential role in biology and the environment in the d removal of pollutants from water. For this, the kinetics of swelling and the type of water diffusion into hydrogels should be carefully studied. Two primary parameters control the kinetics of the hydrogel swelling: the rate of solvent penetration into the hydrogel and the relaxation rate of polymer and solvent. If the penetration rate equals the relaxation rate, then the diffusion is Non-Fickian, with n (equation2) values between 0.5 and 1. In contrast, in Fickian kinetics, diffusion is the rate-determining state, and n is 0.5. Table 1 shows the n values of hydrogel in Fickian and non-Fickian kinetics in different situations.

Table 1- values of *n* in diffusion in the hydrogel

Diffusion of gel	Thin membrane	Cylindrical	Spherical
Fickian	0 .5	0.45	0.43
Non-Fickian	0.5< n<1	0.45<n<1	0.43<n<1

In the following, we studied the type of diffusion into prepared hydrogels at *pH*=2, 7, and 12, respectively (Figure 8), and the results, *k* and *n*, are shown in Table 2.



a b c

Figure 8. Diffusion kinetics diagram of *AMPS* hydrogel in **a)** *pH*=2, **b)** *pH*=7, and **c)** *pH*= 12

Table 2- Diffusion information of hydrogel in different *pH*

pH	*k*	*n*	Type of Diffusion
2	-2.1664	0.4149	Non-Fickian
7	-3.3291	0.645	Non-Fickian
12	-2.7243	0.5083	Non-Fickian

3.6. ATOMIC ABSORPTION ANALYSES OF HYDROGEL

We studied the capability of prepared hydrogels in the adsorption of Cu^{2+} and Pb^{2+} ions by atomic absorption spectroscopy (*AAS*). The $CuSO_4.6H_2O$ and $Pb(NO_3)_2$ were applied in adsorption studies. The aim was to evaluate *AMPS* hydrogels' Cu^{2+} and Pb^{2+} adsorption ability. The assessment of the kinetic and surface adsorption equations was out of our goals in this work. It is performed via interaction between hydrogel's functional groups (*O=S=O*, *N-H*, and *O-H*) and ions. First, the calibration curves were obtained for Cu^{2+} and Pb^{2+} ions in five concentrations, 2, 4, 6, 8, and 10 *ppm*, by putting 0.1 *gr* of hydrogel powder in the ion solution to adsorb Cu^{2+} and Pb^{2+} ions [35-37].

The adsorption process is the binding of solute molecules to the surface of an adsorbent. Adsorption kinetics is a curve (or line) that describes the rate at which a solute is retained or released from an aqueous medium to the solid-phase interface at a given adsorbent dose, temperature, and *pH* [18]

The binding kinetics of Cu^{2+} to the *AMPS* hydrogel is studied and shown in Figure 9. The curves of the integral equals of pseudo-order applied to these data are also shown on the same graph. As a result, kinetic reaction of adsorption of AMPS hydrogel with Cu^{2+} follows the second order reaction.

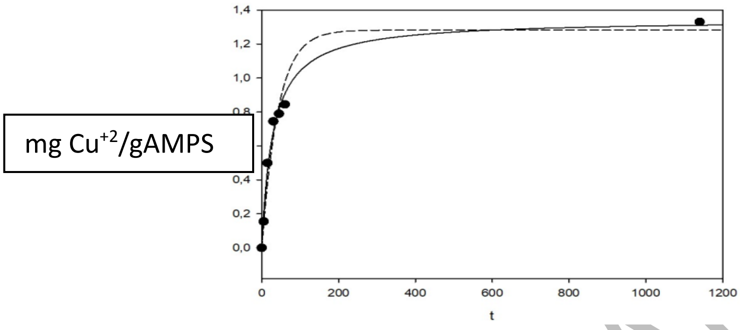


Figure 9. The adsorption kinetics of Cu^{2+} to *AMPS* hydro -pseudo-first-order model fit and; ---- pseudo-second-order model fit.

Moreover, the binding kinetics of Pb^{2+} to the *AMPS* hydrogel is studied and shown in Figure 10. The curves of the integral equals of pseudo-order applied to these data are also shown on the same graph. As a result, kinetic reaction of adsorption of AMPS hydrogel with Pb^{2+} follows the second order reaction**.**

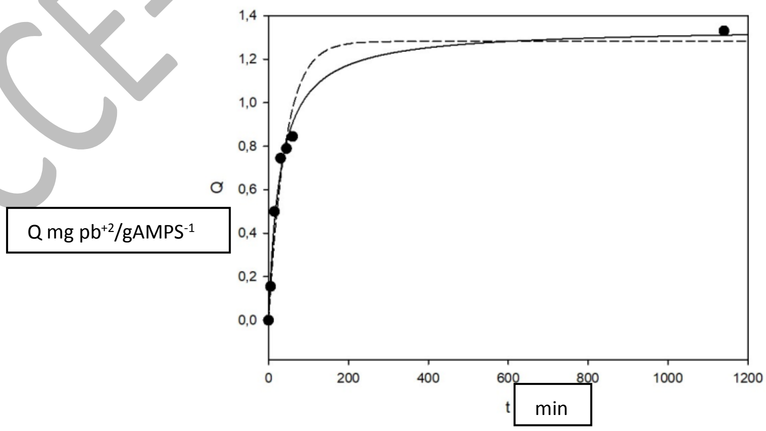
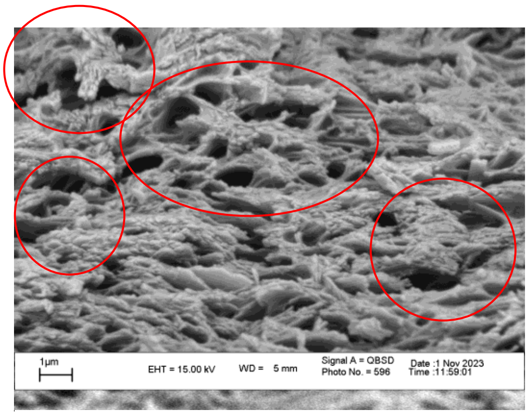


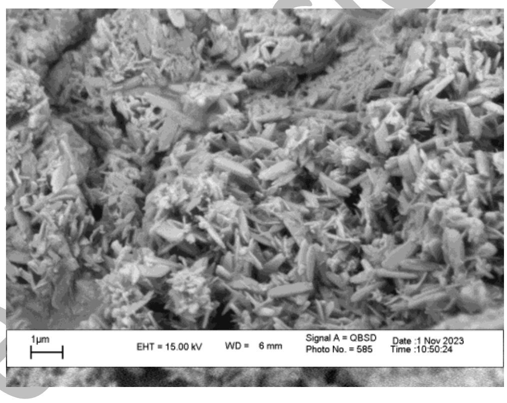
Figure 10. The adsorption kinetics of Pb^{2+} to *AMPS* hydrogel, - - - -; pseudo-first-order model fit and, ----; pseudo-second-order model fit

3.7. Investigation of the Morphology of Hydrogels

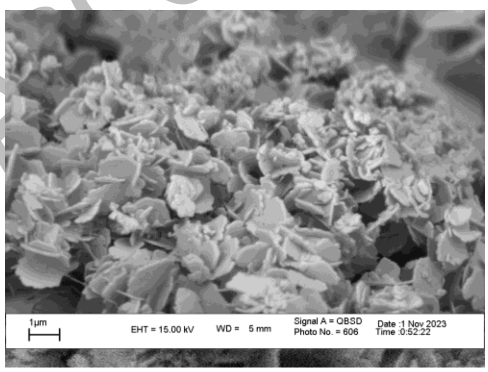
To obtain morphologic properties of *AMPS* hydrogel, *AMPS* hydrogel with Cu^{2+}, and *AMPS* hydrogel with Pb^{2+}, *SEM* micrographs were studied. Considering Fig 11, we claim that the *AMPS* hydrogel can bond to copper and lead ions and remediate wastewater. It had many pores before $Cu^{2+}$and Pb^{2+} absorption, but Cu^{2+} and Pb^{2+} covered nearly all pores after absorption Fig 11[18].



a) *AMPS* hydrogel



b) *AMPS* hydrogel+Cu^{2+}



c) *AMPS* hydrogel+Pb^{2+}

Figure 11. *SEM* micrographs of **a)** *AMPS* hydrogel; **b)** *AMPS* hydrogel with Cu^{2+}; **c)** *AMPS* hydrogel with Pb^{2+}

4. Conclusion

The experimental results showed that prepared hydrogels' swelling behavior depends on *pH*, temperature, and ionic strength. The maximum swelling was obtained in *pH*=7, temperature =75°*C*, and *NaCl* and *KCl* concentration of 0.00001*M*. More swelling in *KCl* can be attributed to the more ionic radius of K^+ concerning Na^+. The kinetic study manifests a non-Fickian behavior, such as polymer relaxation with *n* values between 0.5 and 1.

FT-IR spectroscopy of hydrogels showed an important peak of 1220 cm^{-1} related to the sulfonic acid group. *UV-Vis* determines the swelling of hydrogels neutralized by 50%, 65%, and 75% of *NaOH* and the intramolecular properties. The thermal stability of hydrogels using *TGA* showed the maximum degradation temperature of 368°*C* of *AMPS* hydrogel (*NaOH* 65%), in which 55% of the material is destroyed. The adsorption of Cu^{2+} and Pb^{2+} ions was performed by *AAS* on *AMPS* hydrogels prepared by polymerization. AMPS hydrogel kinetic adsorption of Cu^{2+} and Pb^{2+} was investigated and the second-order reaction was established for both adsorptions. Preparing the other copolymers of AMPS to study the adsorption capacity of heavy and toxic metals in the wastewater is among the list of our future investigations.

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