

Poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co-1-vinyl-2-pyrrolidone) Hydrogel and its use in the Removal of Cd(II), Pb(II) and Cu(II)

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Poly(2-acrylamido-2-methyl-1-propanesulfonic acid-co-1-vinyl-2-pyrrolidone), P(AMPS-co-VP), hydrogel was prepared by free radical cross-linking polymerization method. Prepared hydrogel was used in the competitive removal of Cd(II), Pb(II) and Cu(II) ions from aqueous solution. The characterization of P(AMPS-co-VP) before and after sorption was carried out by the Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy. Atomic absorption spectrometer was used to found the concentration of metal ions in the aqueous solution. The selectivity of P(AMPS-co-VP) was as follows: Cd(II)>Pb(II)>Cu(II). Kinetic study showed that competitive removal of heavy metal ions on poly(AMPS-co-VP) was in accordance with a pseudo-second-order model.

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1. Introduction

Heavy metals like Cu(II), Ni(II), and Cd(II) lead to many environmental problems and these toxic metals affect the human health seriously at even their low concentrations [1, 2]. The removal of heavy metals has become a major problem since they do not have a biodegradable property naturally in the environment [1]. Hydrogels, hydrophilic, cross-linked and three-dimensional networks, have an excellent water absorbing capacity without being soluble [3–5]. These smart materials are widely used in the removal of heavy metal ions because of the presence of the functional groups (i.e. $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{CONH}_2$) [4]. Polymers containing electron donor atoms like N, S, O, and P can be named as polychelators and these atoms are used to form coordinate bonds with the heavy metals [6, 7].

In this study, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and 1-vinyl-2-pyrrolidone (VP) were preferred to prepare hydrogels. AMPS is one of the important monomer with respect to its hydrolytically stable nature and strong acid functionality [7]. (VP) is a biocompatible monomer with high polymer surface activity [8]. Competitive removal of Cd(II), Pb(II), and Cu(II) was investigated at room temperature using P(AMPS-co-VP) and the kinetic mechanism for the sorption of these ions on P(AMPS-co-VP) was determined. Detailed characterization study both before and after sorption was performed by the Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) techniques.

2. Materials and methods

2.1. Materials

AMPS and VP were of Merck Schuchardt OHG (Germany) product. *N,N'*-methylenebisacrylamide (NMBA) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were also provided by Merck Schuchardt OHG (Germany). Ammonium peroxydisulfate (APS) (Merck KGaA Darmstadt (Germany)) was used as the free radical initiator. Copper(II) acetate monohydrate, lead(II) acetate trihydrate and cadmium(II) acetate dihydrate were provided by Merck KGaA (Germany). Deionized water was used in the preparation of hydrogel and heavy metal ion solution.

2.2. Preparation of hydrogel

P(AMPS-co-VP) hydrogel was prepared by free-radical cross-linking polymerization in deionized water at 60 °C for 24 h. While APS was the initiator, NMBA and TEMED were used as cross-linking agent and accelerator, respectively. In the feed, the initial monomer concentration was kept constant at 1 mol/l and the molar ratio of AMPS to VP was 80/20. APS and NMBA were used as 1 and 5 mol.% of the total monomer concentration, respectively, and the weight ratio of APS/TEMED was 1:1. Nitrogen gas bubbling (15 min) was applied to the solution containing cross-linker before the polymerization. P(AMPS-co-VP) in a cylindrical form was obtained in glass tubes (the inner diameter of 1.3 cm and length of 15 cm). The gel was sliced into small cylindrical parts, and then was placed in deionized water by changing the water twice a day to remove the residual monomers and linear polymers. These gels were dried first in ambient temperature and then in vacuum oven at 40 °C. After grinding process, they were used in the sorption of metal ions.

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In order to determine the equilibrium swelling value (ESV) of P(AMPS-co-VP), a certain amount of the dry sample was placed in deionized water (25 °C) up to swelling equilibrium. ESV of the polymers was found from the following equation:

$$ESV(g_{\text{water}}/g_{\text{polymer}}) = (W_s - W_d)/W_d. \quad (1)$$

W_s is the weight of the swollen hydrogel and W_d is the weight of the dry hydrogel.

2.3. Characterization techniques

FTIR analysis (Bruker Vertex 70 FT-IR Spectrometer) was performed to observe the changes in the structure of P(AMPS-co-VP) after the metal sorption. Thermal characterization of P(AMPS-co-VP) both before and after the metal sorption was performed by Shimadzu, DTG 60 instrument. Thermogravimetric analysis of samples was performed under nitrogen atmosphere (flow rate: 20 ml/min) by heating from 25 to 800 °C at a rate of 20 °C/min. The SEM images of the P(AMPS-co-VP) and its metal sorbed counterpart were obtained using a JSM 5600, JEOL instrument.

2.4. The removal of Cd(II), Pb(II) and Cu(II) and kinetics

Batch sorption technique was used for the competitive removal of metal ions from aqueous solutions. The metal ion solution contains Cd(II), Pb(II), and Cu(II) ions together (the concentration of each metal is 200 mg/l). A predetermined amount of polymer was added to the metal ion solution (200 ml), and during the sorption experiments, the mixture was stirred at 25 °C with a 200 rpm rate. Atomic absorption spectrometer (AAS) (Varian Spectra AA 220-FS) was used to determine the concentration of metal ions. The following equations were used to calculate the experimental metal ion sorption capacities of the polymers [9–11]:

$$q_e = (C_0 - C_e) \frac{V}{m}, \quad (2)$$

$$q_t = (C_0 - C_t) \frac{V}{m}. \quad (3)$$

Here, q_e , q_t , C_0 , C_t , C_e , V and m show the amount of metal ion sorbed at equilibrium [mg/g], the amount of metal ion sorbed at time t [mg/g], the initial metal ion concentration [mg/L], the concentration of metal solution at any time [mg/L], concentration of metal ion in solution at equilibrium [mg/L], the volume of metal ion in solution [L] and the amount of the polymer [g], respectively.

The change in pH of the metal ion solution with time was measured by a pH-meter (Orion 720A+, Thermo Electron Corporation, USA).

The sorption kinetics of Cd(II), Pb(II), and Cu(II) on poly(AMPS-co-VP) was investigated. The Lagergren pseudo first-order and pseudo-second-order models were applied to determine the sorption mechanism [9, 11–15].

Pseudo-first-order model

$$\ln(q_e - q_t) = \ln q_e - k_1 t. \quad (4)$$

Pseudo-second-order model

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t. \quad (5)$$

Here, q_e [mg/g] and q_t [mg/g] are the sorption capacity at equilibrium and at time t [min], respectively. The kinetic rate constants for the pseudo-first-order and the pseudo-second-order models are k_1 [1/min] and k_2 [g/(mg min)], respectively.

The initial sorption rate constant, h [mg/(g min)], was found using k_2 and q_e [9, 13, 14]:

$$h = k_2 q_e^2. \quad (6)$$

3. Results and discussion

3.1. FTIR analysis of the gels

FTIR technique was used for the structural characterization of polymers and the spectra have been given in Fig. 1. The band between 3000 and 3600 cm^{-1} is due to the stretching of N–H and O–H [7, 9]. In the spectrum of P(AMPS-co-VP), stretching vibration of C=O (amide I band) results from the amide group is seen at 1643 cm^{-1} [4, 7, 9]. Both the intensity and band position of amide I band decrease in the spectrum of metal sorbed gel. The bands seen at 1540 cm^{-1} are attributed to the amide II band [4, 9]. The intensity of amide II band increased after sorption because of the coordination of metal ions [7]. The shifting of this band is also evident because of the sorption of metal ions. The stretching of C–N bond is seen at 1456 cm^{-1} [4, 7]. The band at 1036 cm^{-1} in the spectrum of P(AMPS-co-VP) is assigned to the symmetric stretching of S=O group [4, 7, 9] and it shifts to the lower wave number (1027 cm^{-1}) in the spectrum of metal sorbed gel.

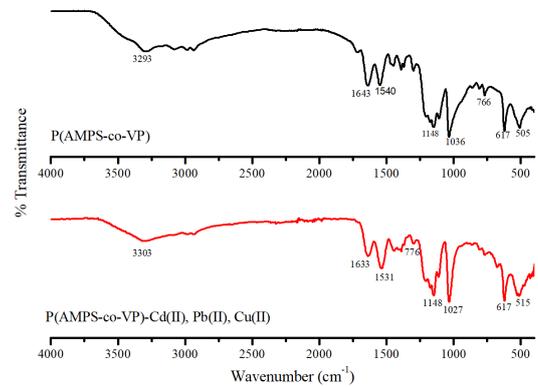


Fig. 1. FTIR spectra of P(AMPS-co-VP) before and after removal experiments.

The changes in the wave numbers and intensities of the bands after the sorption process are attributed to metal sorption through ion exchange between the metal ions and $-\text{SO}_3\text{H}$ groups.

3.2. Thermal characterization

The thermal properties of P(AMPS-co-VP) both before and after sorption were studied by TGA, and corresponding thermograms are shown in Fig. 2. Sorption process strongly affected the thermal stability and degradation steps of polymers. Metal sorbed form of polymer displayed higher thermal stability than pristine P(AMPS-co-VP).

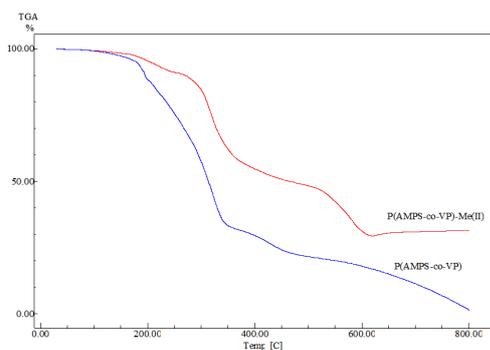


Fig. 2. Thermograms of P(AMPS-co-VP) before and after removal experiments.

While the degradation between 250 and 300 °C is due to the $-\text{SO}_3\text{H}$ groups decomposition [9, 16], the main chain degradation and following cross-linking bridges can be seen at 300–500 °C [9, 16]. 44 and 15.8% mass loss was observed starting from 25 to 300 °C for P(AMPS-co-VP) and its metal sorbed counterpart, respectively. At 500 °C their mass losses became 81.2 and 52.8%.

3.3. Morphology

The morphologic character of P(AMPS-co-VP) differ from the P(AMPS-co-VP)-Me(II) (Fig. 3). P(AMPS-co-VP) has irregular, rough and cracked structure before sorption but less rough nature was seen after sorption.

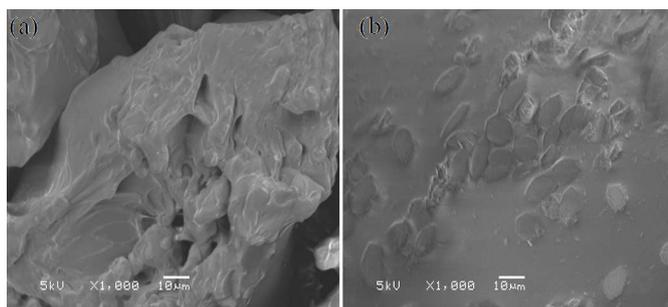


Fig. 3. SEM images of P(AMPS-co-VP): (a) before and (b) after removal experiments.

3.4. Sorption study and kinetics

P(AMPS-co-VP) gel was used to investigate its efficiency on the competitive removal of Cu(II), Pb(II), and Cd(II) ions from aqueous solution at room temperature. During the removal of metal ions, the pH of solution was also measured. Kinetics of sorption of Pb(II), Cu(II), and Cd(II) ions on P(AMPS-co-VP) was investigated for pseudo-first and second-order kinetics. In addition, ESV of the hydrogel was determined and it was found to be $236 \text{ gH}_2\text{O}/\text{g}_{\text{polymer}}$. The pH of solution strongly affects the sorption process especially in terms of the complexation mechanism. In this case, the optimum pH for the removal of metal ions should be considered. The pH-dependent selectivity of the polymers was reported previously [1, 7, 17].

In the study of Valle et al. [7], the linear poly(*N*-vinylpyrrolidone-co-2-acrylamido-2-methylpropanesulfonate sodium), poly(VP-co-AMPS), was prepared and used for the removal of Cu(II), Cd(II), and Ni(II). The metal ion retention capacity of PAMPS did not change at pHs 3.2 and 5.7. There is no competition among the hydrogen ions and the metal ions due to pKa value (1.5) of sulfonic acid group [7]. They reported that linear poly(VP-co-AMPS) includes electrostatic and coordination interactions together for the metal ions due to AMPS and VP monomer units [7]. In our study, the initial pH value of the prepared metal ion solution was 6.21 and after 5 min it was measured as 5.03. At equilibrium, the measured pH value is 4.50 and the decrease in pH can be attributed to the exchange of metal ions with H^+ .

The sorption capacities of P(AMPS-co-VP) for Cd(II), Pb(II), and Cu(II) ions versus time are presented in Fig. 4. The lowest sorption capacity value was observed for Cu(II). The removal of metal ions (in equilibrium) occurs in the order of Cd(II) (70.26 mg/g) > Pb(II) (63.23 mg/g) > Cu(II) (56.15 mg/g). It can be concluded that the sorption capacity values of P(AMPS-co-VP) are satisfactory despite the high volume of the metal ion solution and high initial concentration of the metal ions.

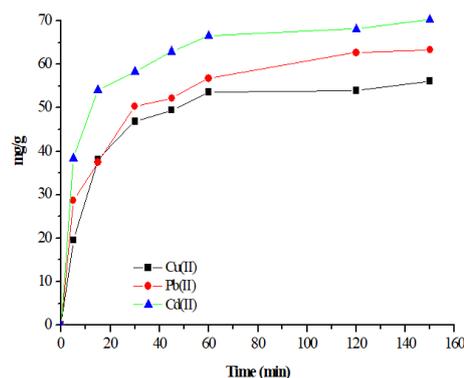


Fig. 4. The sorption capacity of P(AMPS-co-VP).

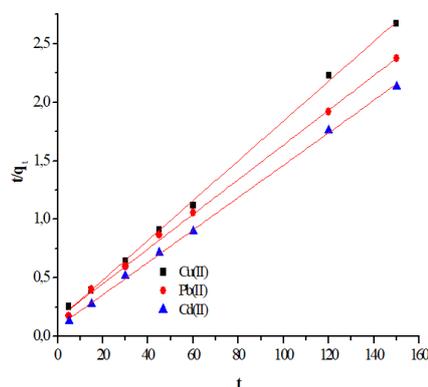


Fig. 5. Pseudo-second-order kinetic model plots.

The pseudo-second-order plot for the removal of Cd(II), Pb(II), and Cu(II) ions on P(AMPS-co-VP) was

depicted in Fig. 5 and the kinetic parameters are given in Table I. The correlation coefficients (R^2) are very high for the pseudo-second-order and q_{exp} and q_{theo} are very close. This shows that removal of Cd(II), Pb(II), and Cu(II) ions is explained well by a pseudo-second-order kinetic model. In the case of pseudo-second-order model, the rate-limiting step may occur by a chemical sorption [18]. The initial sorption rate (h) is calculated using the second order rate constant (k_2) and q_e . The order for k_2 and h were Cd(II)>Cu(II)>Pb(II). The initial sorption rates for the removal of Pb(II) and Cu(II) on the P(AMPS-co-VP) are very similar and they are considerably lower than that of Cd(II), which support the highest sorption capacity for the Cd(II).

TABLE I

The kinetic parameters.

Parameters	Cd(II)	Pb(II)	Cu(II)
q_{exp} [mg/g]	70.26	63.23	56.15
q_{theo} [mg/g]	72.46	67.57	58.80
$k_2 \times 10^3$ [g/(mg min)]	2.411	1.416	2.024
R^2 (pseudo-second-order)	0.9994	0.9985	0.9990
R^2 (pseudo-first-order)	0.8870	0.9985	0.7875
h [(mg)/(g min)]	12.66	6.46	7.00

4. Conclusion

The removal capacity of P(AMPS-co-VP) hydrogel for Cd(II) is higher than that of Pb(II) and Cu(II). The sorption of Pb(II), Cu(II), and Cd(II) ions on P(AMPS-co-VP) are well represented by the pseudo-second-order kinetic model. The change in the morphology and thermal stability of P(AMPS-co-VP) before and after sorption is evident.

Acknowledgments

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