

폴리아스파르트아미드/알지네이트 하이브리드 젤의 중금속이온 흡착물성

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Metal-ion Adsorption by Hybrid Gel based on Polyaspartamide and Alginate

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초록: 폴리(2-히드록시에틸 아스파르트아미드)(PHEA)와 알지네이트(Alg) 유도체로부터 클릭반응에 의한 가교젤을 제조하고, 이 하이드로젤을 수용액상의 중금속이온 제거를 위한 흡착제로 사용하였다. PHEA/Alg 하이브리드젤은 중금속이온 Cu(II)와 Ni(II)에 대해 각각 75 mg/g과 60 mg/g의 높은 흡착능을 보였다. 하이드로젤은 이온함유 수용액에서 약 60~80 g/g의 수팽윤비를 나타내었다. 흡착 거동에 미치는 접촉시간, pH, 온도, 및 농도의 영향을 조사하였다. SEM과 FTIR을 통해 젤의 다공성 모폴로지 및 금속이온과 고분자 구조간의 상호작용을 고찰하였으며, 또한 농도에 따른 흡착량 데이터로부터 흡착등온선(isotherm)을 이론식에 적용하여 분석하였다. 그 결과로 Cu(II)와 Ni(II)의 흡착거동은 Freundlich보다는 Langmuir 모델에 잘 부합하였으며, 동력학적으로는 유사 2차 동역학적 모델(pseudo-second-order kinetic model)로 더 정확하게 묘사할 수 있음을 알았다.

Abstract: A hydrogel based on poly(2-hydroxyethyl aspartamide) (PHEA) and alginate (Alg) derivatives, prepared by the 'click' reaction, has been utilized as a sorbent for the removal of metal-ions from aqueous media. PHEA/Alg hybrid gel exhibited high adsorption capacity for Cu(II) and Ni(II) with 75 and 60 mg/g, respectively. The hybrid gel possessed swelling degrees in the range of 60~80 g/g in ion-containing (2 wt/v%) water. The effects of pH, initial metal-ion concentration, temperature, and contact time, on the adsorption were investigated. The gel morphology and interaction between polymer and metal-ion were characterized by using SEM and FTIR spectroscopy. The kinetics and adsorption isotherms were better fitted to Langmuir model than Freundlich model, and pseudo-second-order adsorption kinetics described well the adsorption process.

Keywords: hydrogel, metal-ion adsorbent, alginate, polyaspartamide, adsorption kinetics and isotherm.

Introduction

Heavy metal pollutions cause serious environmental issues due to their potential toxicity, even at low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms where they have a deleterious impact on human health and the natural ecosystem.¹⁻³ Heavy metals are discharged into the environment without treatment via mining activities, fossil fuels, battery manufacture, automobile emissions,⁴ agricultural chemicals, industrial water waste and natural trace elements. Heavy metal pollution has

become an urgent issue and there is increasing interest in eliminating or reducing the concentration of heavy metals in aquatic ecosystems. Various conventional techniques have been employed to treat effluent before it is discharged into the environment such as chemical precipitation, ion exchange, reverse osmosis, membrane separation, filtration, electrochemical treatment, and evaporative recovery.⁵⁻¹⁰ However, these methods are often costly and ineffective, especially at removing heavy metal ions at low concentrations.¹¹ The adsorption method has outstanding advantages such as flexibility and minimal chemical use compared to other physicochemical methods, and it is considered the most environment-friendly, effective, efficient and economic method of waste purification among physicochemical treatment processes.^{12,13}

In recent years, increasing demand has required new cheap

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and effective materials with high adsorption capacities that are also reusable. Several natural adsorbents such as bacteria,¹⁴ algae,¹⁵ Phoenix tree leaf powder,¹⁶ wheat shell,¹⁷ seed powder of *Strychnos potatorum*,¹⁸ and *Caesalpinia bonducella* seed powder can be used to remove heavy metal ions from waste water.¹⁹ Hydrogels with sponge-like structures can mimic these high adsorption properties. A number of simple and cost-effective hydrogels have recently been developed for use as adsorbents to remove heavy metals from contaminated water. In addition, unlike natural adsorbents, the properties of hydrogel can be controlled and modified for specific applications. Biosorbent hydrogels derived from chitosan,²⁰ cellulose,^{21,22} and starch²³ are abundant, biodegradable, and environment friendly. Alginate, which contains various active functional groups, such as carboxylic and hydroxyl, is considered the most promising candidate for heavy metal absorption applications.

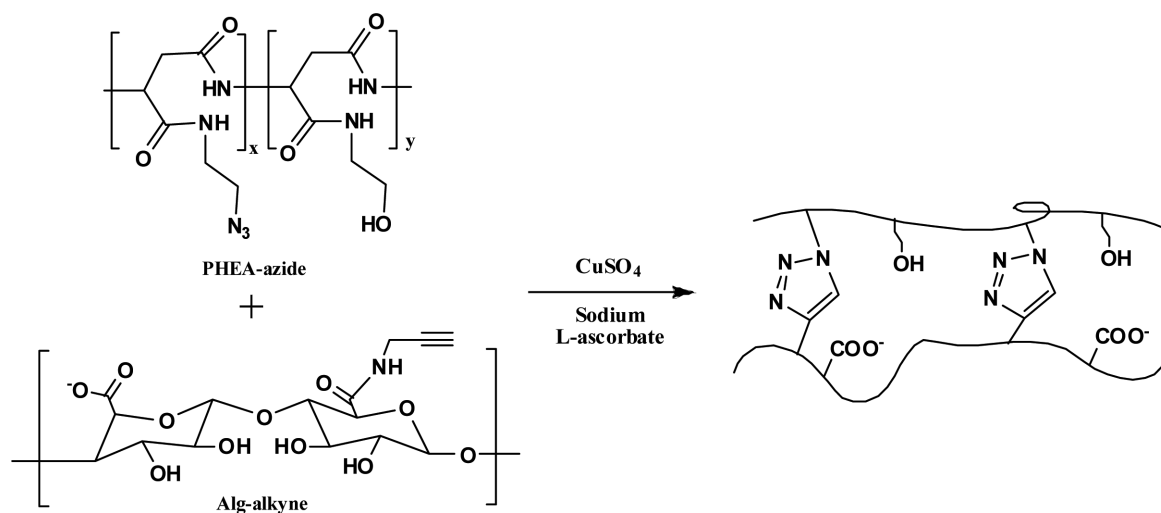
Poly(aspartic acid), PASP, is one of water-soluble biodegradable poly(amino acid)s, possessing carboxylic acid group in the side chain. It has been considered as an attractive alternative of conventional non-biodegradable polymers in various industrial and biomedical fields. Poly(2-hydroxyethyl aspartamide) (PHEA) is another important derivative polymer, which has been investigated as carriers for macromolecular prodrugs due to its unique properties such as biodegradability, water solubility, multipoint drug attachment, and biocompatibility.^{24,25} The attachments and chemical modifications of pendant groups, either through aminolysis reaction to PSI, the precursor polymer, or via a secondary reaction with the hydroxyl or carboxylic groups of PASP and PHEA, can provide

a variety of biodegradable functional polymers or the crosslinked gel with specific properties, as well as its macromolecular self-assembly structures.²⁶⁻³² These polymers have physicochemical characteristics suitable for the development of biomaterials in drug delivery systems in the forms of polymer prodrugs, hydrogels, or nanomaterials.³³⁻³⁸

A hybrid hydrogel based on polyaspartamide and alginate is interesting as a novel biodegradable and environment-friendly adsorbent material. Alginate (Alg) is one of naturally abundant and cheap polysaccharide. Polyaspartamides, on the other hand, can be easily synthesized and the introduction of various other functional groups onto the polymer is relatively facile to produce the derivative polymers for specific applications. The combination of natural alginate and synthetic polyaspartamide may provide hydrogel materials with not only good mechanical property but versatility of molecular design. In this study, we investigated the swelling and adsorption properties of the PHEA/Alg hybrid gel for heavy metal ions such as Cu(II) and Ni(II) in aqueous solution.

Experimental

Materials and Characterization. The PHEA-Alg hydrogel was prepared as described in our previous report (Scheme 1).³⁷ Copper(II) sulfate pentahydrate and nickel(II) sulfate hexahydrate were purchased from Deajung Chemicals & Metals Co., Ltd. (Shiheung, Korea), and Shinyo Pure Chemicals Co., Ltd. (CF, USA), respectively, to be used as heavy metal ion sources for the adsorption experiments. The other reagents were used directly without any purification.



Scheme 1. Preparation of PHEA-Alg 'click' hybrid gel.

Fourier transform infrared (FTIR) spectra were recorded using an FTIR spectrophotometer (Perkin-Elmer, SPECTRUM 2000). The morphology of the freeze-dried click gels was observed using field emission scanning electron microscopy (FE-SEM, JEOL 6320, Japan). The dried gels were quickly quenched and then cross-sectioned in liquid nitrogen. Porous gel samples were mounted onto a metal stub with double-sided carbon tape and coated with platinum for 30 s under vacuum (10^{-3} torr) using a plasma sputtering method (HC-21 ion sputter coater). The concentration of Cu(II) and Ni(II) were determined by a flame atomic absorption spectrometer (AAS; Buck Scientific 210VGP, USA).

Swelling Measurement. The swelling ratio (S_R) of the hydrogel was determined by the ratio between the weight of swollen gels (W_s) minus the weight of dry gels (W_d) and the weight of dry gels (W_d) according to the following equation:

$$S_R = \frac{W_s - W_d}{W_d} \quad (1)$$

Pre-weighed pieces of dry gel was immersed into an aqueous medium and allowed to swell. The swelled gel was sampled from the solution at regular intervals. The excess water was wiped off the surface of gel specimens with moistened filter paper and the weights of the gels were recorded.

Synthesis of PHEA/Alginate Hybrid Gel. The PHEA-Alg hydrogel were prepared by click reaction between polyaspartamide derivatives modified with azide groups and alginate functionalized with alkyne groups. CuSO_4 and sodium L-ascorbate were used as the catalyst system in the hydrogel forming (Scheme 1). All the preparation processes and the characterization of the hydrogel were performed according to our previous work.^{39,40} Briefly, an equal weight of PHEA-azide and Alg-alkyne was reacted in aqueous solution using click catalyst system. The substitution degree of each complementary click functional group on both polymers was in the range of approximately 20 mol%. The gel yield was high with over 95%.

Batch Metal-ion Adsorption and Desorption Study. Batch adsorption studies of Cu(II) and Ni(II) ions using copper sulfate pentahydrate and nickel sulfate hexahydrate were carried out by using equilibrium experiments. Twenty milligrams of the gels were added into a 70 mL vial containing 50 mL of the metal ion, Cu(II) or Ni(II), solution (0.4 mg gel/1 mL deionized water). During the adsorbing process, the hydrogels changed color from light yellow into light blue in copper solution and to light green in nickel solution. After 3 h, (enough

time to reach an equilibrium value) the adsorption of gels was calculated from the concentration difference between the initial and final Cu(II), Ni(II) solution, which was prepared by diluting 1 mL initial and final Cu(II), Ni(II) solution in 99 mL deionized water. Measurements were conducted using an AAS. The volume of deionized water was measured precisely with a 25 mL burette. The pH of the solution was controlled with HCl (0.1 and 0.01 N) and NaOH (0.05 N) solutions. The adsorption capacity was calculated based on the difference of initial and equilibrium metal concentration in aqueous solution, the volume of aqueous solution (50 mL) and the weight of the adsorbent (20 mg) according to the equation below:

$$q(\text{mg/g}) = (C_{\text{in}} - C_{\text{eq}}) \frac{V}{m} \quad (2)$$

Where C_{in} is the initial metal concentration (ppm), C_{eq} is the equilibrium metal concentration (ppm), V is the volume of the metal solution (mL) and m is the weight of gel adsorbent.

Desorption studies are conducted to evaluate the feasibility of regeneration of the adsorbent. Batch desorption experiments were carried out by placing 20 mg of Cu(II)- or Ni(II)-adsorbed hydrogels in 50 mL of HCl at 0.1 N at room temperature for 6 h. The filtrate was diluted in deionized water and the percent recovery was estimated by AAS measurement.

Results and Discussion

Swelling Properties of Hydrogel in Different Metal-ion Containing Solutions. The preparation of PHEA/Alg hybrid gel, its structure and the basic swelling behavior including pH-sensitive swelling were described in our previous work.³⁹ The swelling behavior of the hydrogel in different metal ion-containing media suggested the fundamental adsorption capability of the material. Various metal ions with the same and different ionic numbers were used to investigate the swelling property of the gel. Figure 1 shows that the swelling ratios of the hydrogel in Cu(II), Ni(II), and Ca(II) solutions was strongly decreased from that in distilled water. This will be partly due to metal ion binding with carboxylate groups on the hydrogel structure through polar ionic interaction, causing the gel matrix to shrink and decrease the free carboxylate groups within the structure. Additionally, the effect of different ionic number of metals on the swelling was also examined. The degree of swelling was measured in three different ionic solutions with different valency, i.e. Na(I), Ca(II), and Fe(III). The swelling decreased in the order of Na(I) ($S_R \sim 123$) > Ca(II)

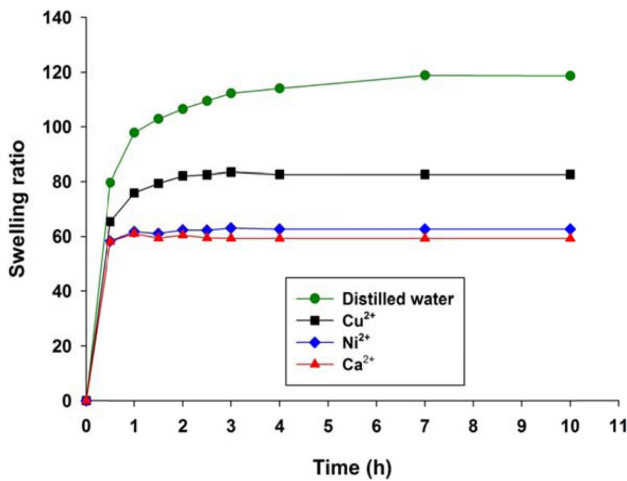
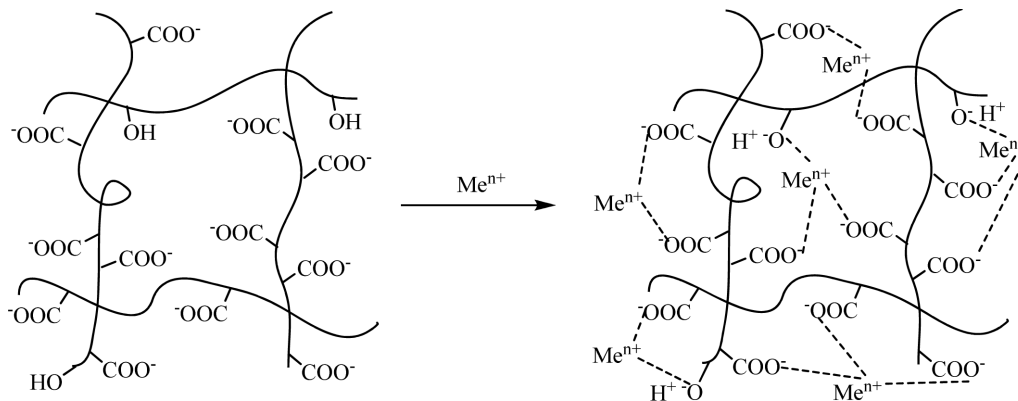


Figure 1. Swelling ratio of PHEA-Alg gels in different divalent metal-ion-containing solution (ion concentration: 2 wt/v%).

($S_R \sim 60$), $> Fe(III)$ ($S_R \sim 40$) as are expected. Again, this result can be ascribed to the effect of ionic interaction between carboxylate group and metal ion, i.e. metals with higher ionic numbers allow multiple interactions to result in the shrinkage of networks more. In other words, the degree of additional ionic crosslinking increases with the ionic number of metal, so the swelling ratio decrease.

Heavy Metal-ion Adsorption from Aqueous Solution.

The click hybrid gels based on poly(2-hydroxyethyl aspartamide) (PHEA) and alginate (Alg) derivatives can exhibit prominent characteristics of removal of metal-ions from aqueous media (Scheme 2). Under analysis of atomic adsorption spectroscopy, the hybrid gels showed effective adsorption behavior on toxic heavy metal-ions such as Cu(II) and Ni(II). The adsorption characteristics were elucidated by FTIR analysis, the effect of solution pH, sorption rate, temperature, and



Scheme 2. Structure of metal-ion binding within the crosslinked hybrid gel.

initial ion concentrations.

Effect of pH. Solution pH is one of the factors affecting surface charge and degree of ionization, which strongly influence the adsorption of heavy metal ions from an aqueous solution. Figure 2 shows the influence of pH on the adsorption of Cu(II) and Ni(II) from aqueous solution using PHEA/Alg hybrid gel as the adsorbent. The effect of solution pH on the Cu(II) ion and Ni(II) ion removal was investigated within the pH range of 2~5 at 200 ppm metal ion. Precipitation of the initial solution was observed at higher pH above pH 6. It was evident in Figure 2 that the adsorption capacity increased with pH increases from pH 2 to 5. This result is due to the fact that the carboxylate groups, the ionized form of carboxylic acid, in the hydrogel structure will interact more strongly with metal ions via ionic bonding each other. In other words, at low pH, more H^+ might compete with metal ions in the adsorption sites, resulting in a decrease in divalent metal ion binding. Therefore, at low pH the carboxyl groups existed in the form of $-COOH$

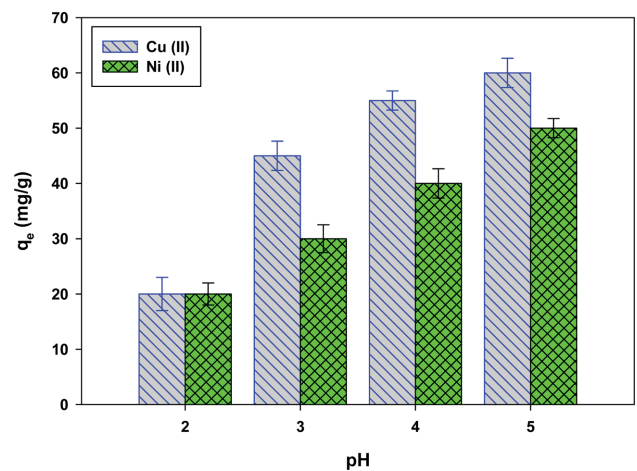


Figure 2. Effect of pH on adsorption of Cu(II) and Ni(II).

rather than $-\text{COO}^-$, which could reduce the interaction between metal ions and the hydrogel.⁴¹ The higher adsorption took place at pH 5.

Effect of Initial Metal-ion Concentration. The adsorption capacity of the hydrogel for heavy metals was studied at different initial metal ion concentrations in the range of 50 to 500 ppm. As shown in Figure 3(a) and 3(b), it was found that on increasing the initial metal ion concentration in solution, the adsorption capacity increased and leveled off at higher concentration. The amount of metal ions adsorbed increased from 16 to 75 mg/g for Cu(II) and from 15 to 60 mg/g for Ni(II), respectively. The maximum adsorption was observed to be higher in Cu(II) compared to Ni(II), suggesting Cu(II) exhibit stronger affinity for gel adsorbent. At higher concentration of solution, it reach a plateau because the adsorption approach saturation.^{42,43}

Effect of Contact Time and Temperature. The effect of contact time on the absorption of Cu(II) and Ni(II) ions was

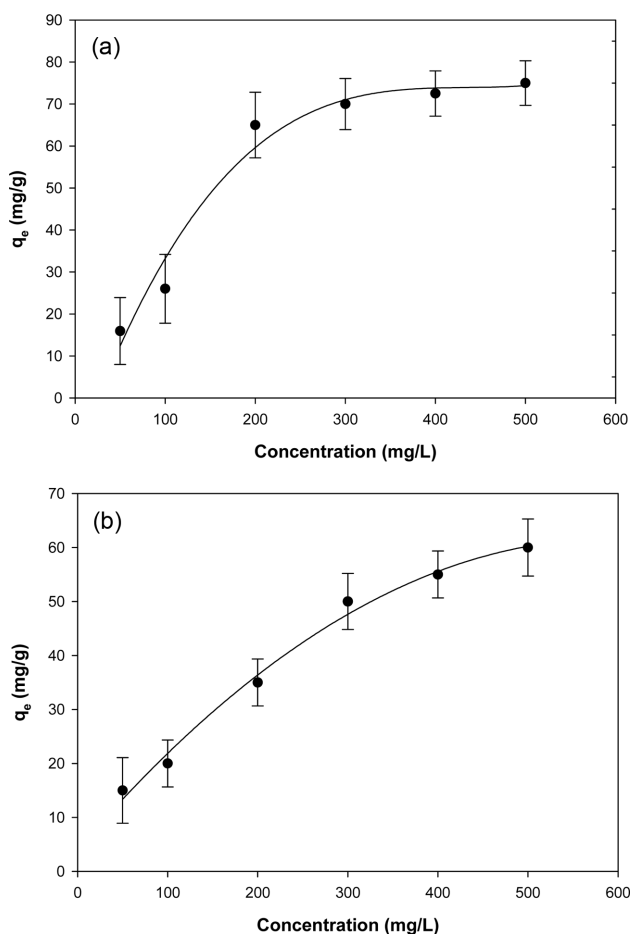


Figure 3. Effect of initial metal ion concentration on adsorption of Cu(II) (a); Ni(II) (b).

represented in Figure 4. The results showed that the adsorptions of Cu(II) and Ni(II) ion increased rapidly with increasing time initially and reached the equilibrium value after 150 min for Cu(II) and 120 min for Ni(II), respectively. This is likely due to a larger surface site being available initially for the adsorption of copper and nickel ions⁴⁴ but further increase in contact time did not offer any improvement due to rapid exhaustion of the adsorption sites after a certain contact period.^{11,45}

The effect of temperature on the adsorption capacity of Cu(II) and Ni(II) ions was investigated at different temperatures in the range of 25 to 60 °C at the metal ion concentration of 200 ppm. The results in Figure 5 revealed that adsorption increased gradually with increasing temperature. For Cu(II), the adsorption capacity increased from 56 mg/g at 25 °C to

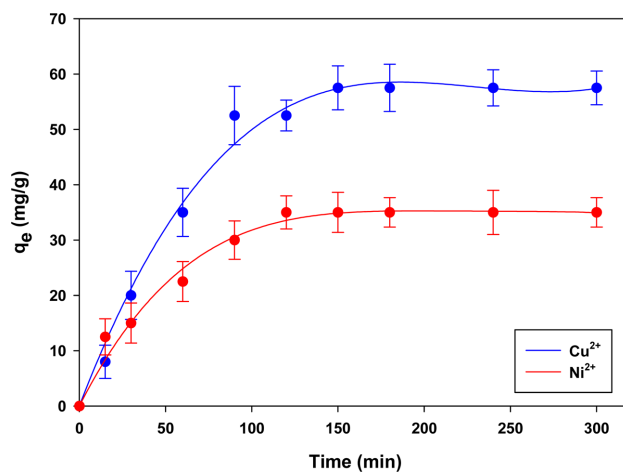


Figure 4. Effect of contact time on adsorption of Cu(II) and Ni(II) ions.

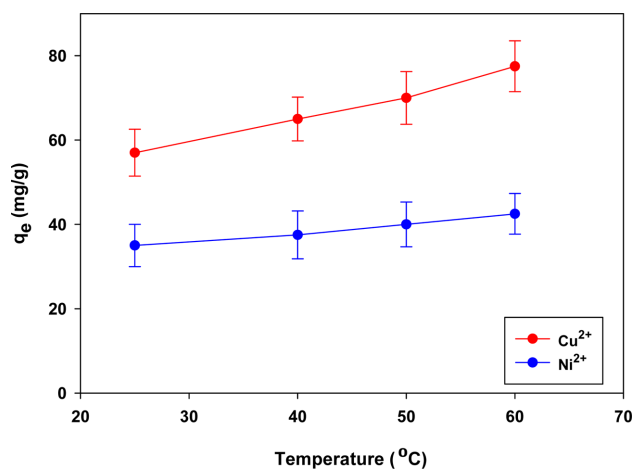


Figure 5. Influence of temperature on adsorption capacity (at concentration of 200 ppm).

75 mg/g at 60 °C. For Ni(II), only slight increase was observed, i.e. from 35 mg/g at 25 °C to 40 mg/g at 60 °C. The enhancement in the adsorption capacity at the elevated temperature may be explained by either the increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions or the increased activity of binding sites.⁴⁶

FTIR Analysis. FTIR spectra of the unloaded hydrogel and Cu(II) or Ni(II)-loaded hydrogel are shown in Figure 6. A characteristic strong and broad peak at 3400 cm⁻¹ corresponded to O-H stretching vibration of hydroxyl groups in the hydrogel. The hydroxyl groups existing on the sorbent were effective binding sites for metal ions, forming stable complexes by coordination. Two stretching bands at 1658 and 1543 cm⁻¹ were assigned to the -C=O and -NH- of polymer backbone, respectively. The band observed at 1039 cm⁻¹ was assigned to C-O stretching of alcohols and carboxylic acids. The stretching vibration at 3400 cm⁻¹ was shifted to 3437 and 3393 cm⁻¹ after Cu(II) and Ni(II) adsorption, respectively, indicating the effect of free hydroxyl groups in Cu(II) and Ni(II) adsorption. The

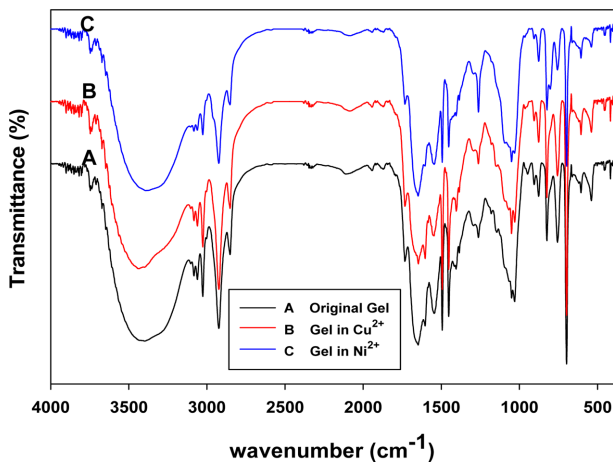


Figure 6. FTIR spectra of original gel (A); Cu(II)-adsorbed (B); Ni(II)-adsorbed (C) gels.

bands assigned to C-O at 1039 cm⁻¹ in the original gels were shifted to 1050 cm⁻¹ for both Cu(II) and Ni(II) adsorption, suggesting the participation of the C-O of carboxylic acid and alcohol groups. Based on these observations, the FTIR results suggested that the hydroxyl and carboxyl groups are involved in Cu(II) and Ni(II) adsorption onto the hybrid gels.

SEM of PHEA/Alg Hybrid Gel. Figure 7 shows SEM images of the cross-sectioned surface of dried gel before and after the metal ionic adsorption. The morphology in the as-prepared gel (Figure 7(a)) revealed the well-connected porous structure. Macro-pores with large surface area must be beneficial for water permeation and efficient diffusion of metal ions. On the other hand, those of Cu(II)- or Ni(II)-loaded gel possessed relatively small pores with more compact textures (Figure 7(b) and 7(c)). Electrostatic repulsion among the carboxylate groups in the pure gel structure led to expansion of the hydrogel network and an increase in the size of the pores. On the other hand, the adhesion and incorporation of cationic metal ions into the anionic surface of the hydrogel would reduce the electrostatic repulsion to result in a decreased pore sizes in the ion-loaded hydrogel.

Adsorption Kinetics. Sorption rate is an important factor determining the efficiency of the adsorption process.⁴² The Lagergren pseudo-first-order and the pseudo-second-order kinetic models are the two models most widely used to determine rate of absorption from experimental data, and are used in this study to analyze the adsorption kinetics for Cu(II) and Ni(II) ions. The linear form of the Lagergren pseudo-first-order rate equation⁴⁷ and the Morries-Weber pseudo-second-order rate equation,⁴⁸ respectively, are given as

$$\log(q_{e1} - q_t) = \log q_{e1} - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \quad (4)$$

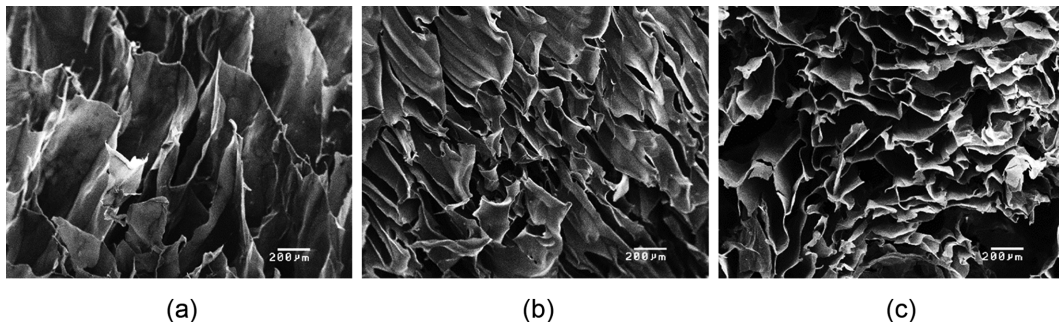


Figure 7. SEM micrographs of PHEA/Alg hydrogel: original (a); Cu(II)-adsorbed (b); Ni(II)-adsorbed (c).

where q_{e1} (mg/g), q_{e2} (mg/g) and q_t (mg/g) are the amounts of Cu(II) and Ni(II) ions adsorbed onto the hydrogel at equilibrium and at time t . k_1 (min^{-1}) and k_2 (g/mg/min) are the pseudo-first-order rate constant and the pseudo-second-order rate constant, respectively. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine k_1 and q_{e1} and in the same way q_{e2} and k_2 can be obtained from the plot of t/q_t against t .

Based on the time-dependent adsorption profile discussed above, the pseudo-first-order and pseudo-second-order kinetic models were fitted in Figure 8. The kinetic parameters evaluated from given equations together with correlation coefficients for Cu(II) and Ni(II) adsorption are listed in Table 1. The

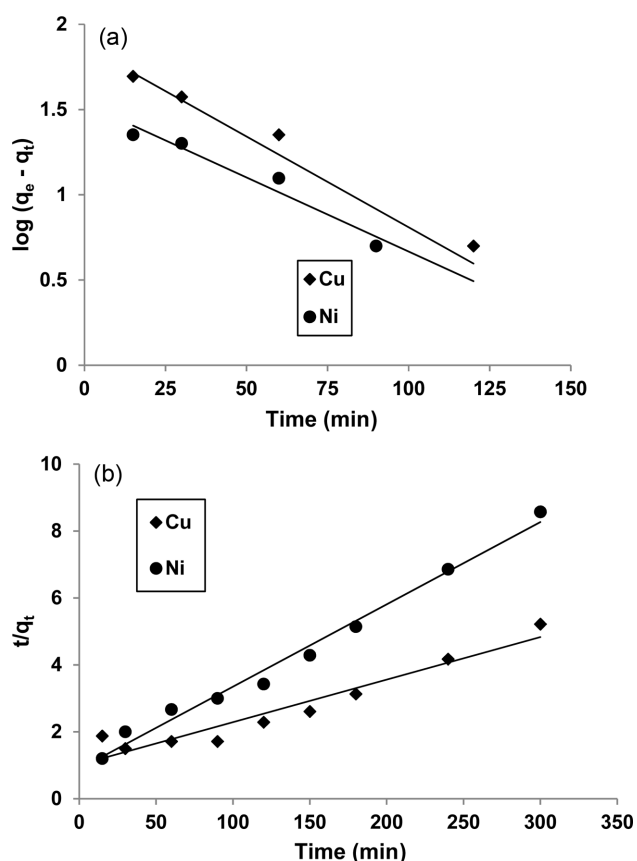


Figure 8. Pseudo-first-order (a); pseudo-second-order (b) kinetics plot for Cu(II) and Ni(II).

Table 1. Comparison of Pseudo-first-order and Pseudo-second-order Kinetics Parameters

| Metal ion | Pseudo-first-order kinetics | | Pseudo-second-order kinetics | |
|-----------|-----------------------------|-------|--|-------|
| | k_1 (min^{-1}) | R^2 | k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) | R^2 |
| Cu(II) | 0.023 | 0.920 | 0.0001 | 0.921 |
| Ni(II) | 0.018 | 0.949 | 0.0006 | 0.986 |

linear correlation coefficients (R^2) of the pseudo-second-order model were greater than those of the pseudo-first-order model and the theoretical equilibrium sorption capacity calculated from the pseudo-second-order equation was closer to the experimental sorption capacity determined from the contact time profile. The results suggest that the pseudo-second-order adsorption model describes well the adsorption process.

Adsorption Isotherms. The equilibrium isotherm is fundamental in describing the interactive adsorption behavior between solutes and adsorbent.⁴⁹ Two of the mostly commonly used isotherm theories were adopted in this study, namely Langmuir⁵⁰ and Freundlich⁵¹ isotherm theories. The Langmuir model assumes a totally homogeneous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogeneous sorption system. The two models are expressed by the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

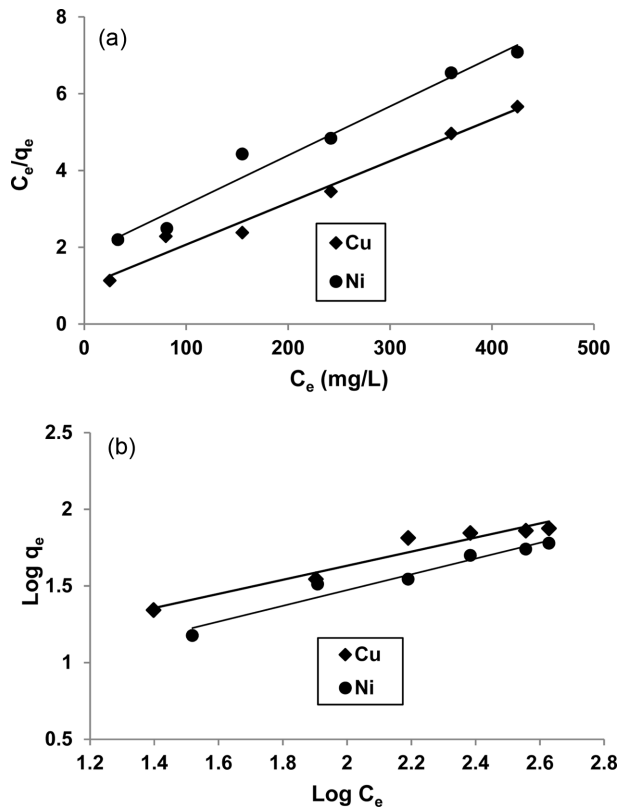
$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

Where, q_e (mg/g) is the equilibrium metal ion concentration on the sorbent, q_m (mg/g) represents the monolayer biosorption capacity of the sorbent, C_e (mg/L) is the equilibrium metal ion concentration in the solution, and b is the Langmuir adsorption constant related to the free energy of sorption. K_f and $1/n$ are the Freundlich adsorption constants indicating the adsorption capacity and adsorption intensity, respectively. The values of Langmuir constants b and q_m were obtained from the slopes and intercepts of plots of C_e/q_e versus C_e and Freundlich constant K_f and $1/n$ from plots of $\log q_e$ versus $\log C_e$ in the same way.

The Langmuir and Freundlich adsorption isotherm plots for the adsorption of Cu(II) and Ni(II) ions are shown in Figure 9. The constants and the correlation coefficients are listed in Table 2. Table 2 shows that the Langmuir model ($R^2 > 0.97$) gives a better fit for the experiment data than the Freundlich equation. This result implies that the binding sites are homogeneously distributed over the adsorbent surface, and the

Table 2. Comparison of Langmuir and Freundlich Isotherm Parameters

| Metal ion | Langmuir model | | | Freundlich model | | |
|-----------|----------------|--------------|-------|------------------|---------------|-------|
| | b (L/mg) | q_m (mg/g) | R^2 | K_f (mg/g) | $1/n$ (mg/mL) | R^2 |
| Cu(II) | 0.0065 | 100 | 0.971 | 5.164 | 0.459 | 0.938 |
| Ni(II) | 0.0102 | 83 | 0.978 | 2.786 | 0.513 | 0.951 |

**Figure 9.** Langmuir (a); Freundlich (b), isotherm plot for adsorption for Cu(II) and Ni(II) ions.

adsorption take place in a single monolayer on the surface of adsorbent.

Desorption Study. In practice, desorption and reusability are important factors for evaluating potential application of adsorbent material to meet economic and environmental requirements. Therefore, the regeneration ability of the metal ion-loaded hydrogel was examined. In desorption studies, the Cu(II), Ni(II) ion-loaded hydrogels in different concentrations of sorbate solution were taken out and immersed in vials containing 50 mL of 0.1 N HCl solution as a desorbing agent. The preliminary results indicate that the percent desorption of Cu(II) and Ni(II) ions out of hydrogel to be 79~86% and 86~95%, respectively, in the ion concentration ranges of 200~500 ppm. The desorption efficiency tended to increase

slightly with increasing initial metal ion concentrations. The desorption ratio of Ni(II) ion (>95%) was higher than that of Cu(II) ion (>86%) at the initial concentration of 500 ppm. The results suggest the potential usage of this hybrid gel as adsorbent for Cu(II) and Ni(II) removal.

Conclusions

The polyaspartamide and alginate-based hybrid gel was prepared and their adsorption behaviors for Cu(II) and Ni(II) ions were investigated. The effect of pH, contact time, temperature, and initial metal ion solution for adsorption were evaluated. The most efficient removal of heavy metal ions from aqueous solution occurred at pH 5. The hydrogel had a maximum sorption capacity of 75 mg/g for Cu(II) ions and 60 mg/g for Ni(II) ions. From the adsorption data depending on the time and initial ion concentration, the kinetic and adsorption isotherm were investigated. The results revealed a pseudo-second-order kinetic and Langmuir thermo model, respectively, being good to describe this adsorption process. This work reveals the polyaspartamide and alginate hybrid gels could be applied as an efficient adsorbent for heavy metal-ion present in aqueous solutions.

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