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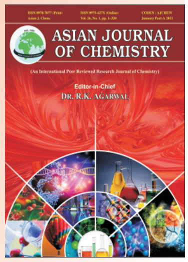

Adsorption of Heavy Metal Ions from Aqueous Solution by Tannin Based Hydrogel

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Hydrogel based on tannin prepared by the cross-linking reaction of tannin and the copolymer of allyl glycidyl ether with acrylamide was used as sorbent for Pb(II). The data of the adsorption demonstrated fast adsorption property of hydrogel for Pb(II). The ratio of metal ions adsorbed to initial metal ions was over 99 % when the concentration of Pb(II) ion was lower than 0.5 mmol/L. The adsorption isotherms of hydrogel for Pb(II) can be well fitted by the Langmuir equation, the maximum adsorption amount of hydrogels for Pb(II) from Langmuir model were 49.3 mg/g.

Keywords: Hydrogel, Tannin, Adsorption.

INTRODUCTION

Heavy-metal pollution occurs in many industrial wastewater produced by a variety of industries such as metal plating facilities, mining operations, battery manufacturing process, the production of paints and pigments and the glass production industry. Heavy metals constitute a serious threat to the environmental and public health even at very low concentrations because these substances are not biodegradable and are highly toxic to living organisms. It is very significant to remove heavy metal ions from wastewater. Many technologies that have been employed to remove heavy-metal from aqueous environments include chemical precipitation[1], ion exchange[2], adsorption[3] and reverse osmosis, *etc*.[4]. Among these technologies, adsorption using sorbent is one of the most popular and effective processes for the removal of heavy metals from wastewater. Recently, adsorption materials based on natural polymers, *e.g.*, cellulose[5], starch[6] and chitosan[7] are currently of great interest because of their unique advantages: abundance of raw material, distinctive properties, safety and biodegradability.

Tannin is an abundant natural biomass that contains multiple adjacent phenolic hydroxyls and has the properties of specific affinity to metal ions[8]. However, tannin is water-soluble compound, which restricts its practical application as an adsorbent. Therefore, great efforts have been made to overcome this disadvantage, mainly by immobilizing tannins onto various water-insoluble matrices such as activated carbon[9], agarose[10] and cellulose[11]. Hydrogel is a network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure[12], which have been widely used in food packaging[13], bioengineering[14], environmental protection[15] and other fields. It is suggested that the combine of tannin and hydrogel would be contributed to the contact of immobilized tannin with metal ions in solution due to the excellent hydrophilic properties of the hydrogel, which would help to improve the adsorption properties of the hydrogel.

In this study, hydrogels were prepared from tannin by the cross-linking reaction of the copolymer of allyl glycidyl ether (AGE) and acrylamide (AM), the adsorption properties of the hydrogels for Pb(II) were evaluated.

EXPERIMENTAL

Preparation of hydrogels: 2 g of allyl glycidyl ether and 4 g of acryl amide were dissolved in deionized water with potassium persulfate as initiator and deoxygenated with dry nitrogen for about 10 min. The reaction flask sealed and the reaction conducted with stirring at 60 °C for 2 h. After that, 1,4-dioxane was added into the reactor to precipitate the products,the copolymers of allyl glycidyl ether and acryl amide were obtained. Then, the copolymers and 4 g of tannin were dissolved in deionized water and pH was adjusted to 9. The mixture was allowed to stand for 4 h after stirring at 25 °C for 0.5 h. The samples were taken out and cut into small pieces after the gelation was finished, then immersed into deionized water to remove any unreacted components and residual alkali.

Swelling properties of hydrogels: Pre-weighed dried samples were immersed in solution with varied pH for 24 h. The swollen samples were weighed after free water was wiped with a filter paper. The swelling ratio (SR) was used to evaluate the swelling performance of the hydrogels in different media. Swelling ratio was calculated according to the following eqn. 1.

$$SR = (W_t - W_d)/ W_d \quad (1)$$

where W_t and W_d represent the weight of swollen sample at different times and the weight of the dried sample, respectively.

Adsorption properties of hydrogels for Pb(II): Dried hydrogels were placed in a buffer solution of pH 7 at 25 ºC for 24 h to complete the swelling. Then the hydrogels were transferred into 25 mL of a known concentration of Pb(II) ion solution for pre-determined time at 25 ºC. After that, the hydrogels were taken out and the concentration of Pb(II) ions in the remaining solution was measured by atomic absorption spectrophotometry with a Hitachi Z-5000 apparatus (Japan).

The capacity of adsorbed Pb(II) ions, Q_e (mg/g), was calculated according to the following eqn. 2 and the ratio of metal ions adsorbed from the solution to initial metal ions in the solution, R, was calculated according to the following eqn. 3.

$$Q_e = [(C_0 - C_e) \times V]/m \quad (2)$$

$$R = [(C_0 - C_e)/C_0] \times 100 \% \quad (3)$$

where C_0 and C_e are the initial and remaining concentrations of the Pb(II) ion in the solution, respectively, V is the volume of the Pb(II) ion solution and m is the mass of dried hydrogel.

FTIR characterization of hydrogel: The spectra of tannin and the hydrogel were recorded in KBr pellets using a Nicolet Is10 Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

Characterization of hydrogels: The infrared spectra of tannin and hydrogel are shown in Fig. 1. The bands at 1450, 1500 and 1600 cm^{-1} in the spectrum of tannin can be assigned to the skeletal vibration of benzene ring from tannin. The band at 3715 cm^{-1} in the spectrum of hydrogel can be assigned to the absorption of $-NH_2$ in polyacrylamide. The band at 2900 cm^{-1} in the spectrum of hydrogel can be assigned to the stretching vibration of $-CH_3$ in the copolymer of allylglycidyl ether and acrylamide, the bands at at 1450, 1500 and 1600 cm^{-1} representing the skeletal vibration of benzene ring in tannin are retained and the band at 1700 cm^{-1} representing absorption peak of carbonyl is significantly enhanced. The results indicate that the cross-linking reaction has occurred between tannin and the copolymer of allylglycidyl ether and acrylamide.

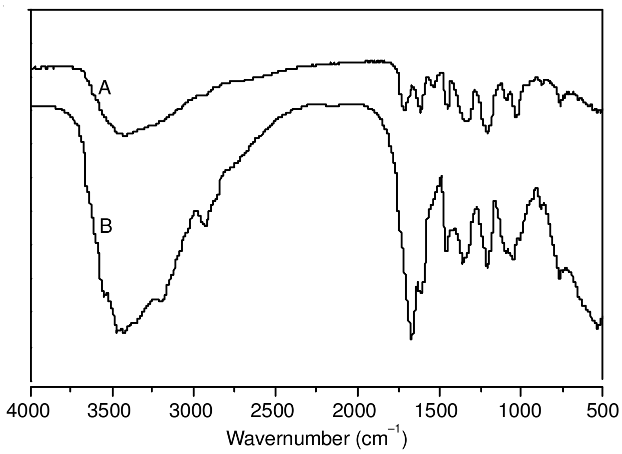

Fig. 1. Infrared spectra of tannin (A) and hydrogel (B)

Swelling properties of hydrogels: Fig. 2 shows the swelling ratio of the hydrogel in solution with varied pH. The swelling ratio of the hydrogel in alkaline solution is greater than that in acid solution. Generally, the pH-sensitive swelling behavior of anionic hydrogels results from the ionization or deionization of functional groups in response to the change of pH[16]. There are many phenolic hydroxyl groups from tannin in the hydrogel network. Most of the phenolic hydroxyl groups are ionized and the repulsive interaction between these groups causes the hydrogel to swell at pH 9, which resulted in the greater swelling ratio of the hydrogel in alkaline solution.

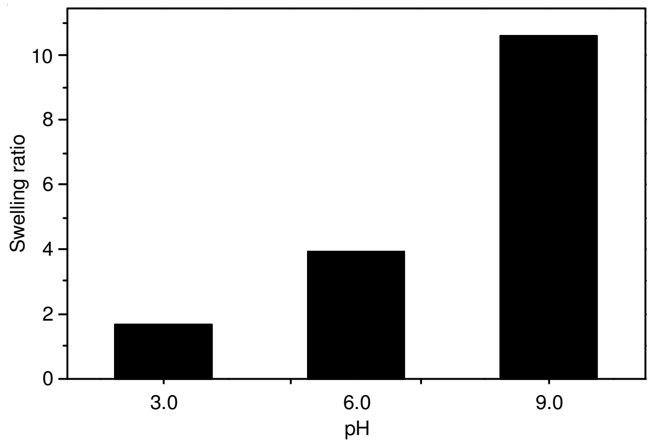

Fig. 2. Swelling ratio of the hydrogel in solution with varied pH

Adsorption properties of hydrogels for heavy metal ions

Effect of pH on adsorption: The effects of the solution's pH on adsorption are shown in Fig. 3. The adsorption amount of Pb(II) increased with the increasing pH and then decreased when pH is over 4.5. The removal of metal ions from aqueous solutions by adsorption depends on the solution's pH and the pH affects both the degree of ionization of the species and the surface characteristics of the adsorbent due to its capacity to adsorb protons[17]. There were many residual phenolic hydroxyl groups from TA in the hydrogel network and the adsorption of hydrogels for Pb(II) were carried out by the chelation of the phenolic hydroxyl in network of hydrogel. The chelating interaction of hydrogel with Pb(II) is shown in Fig. 4. The

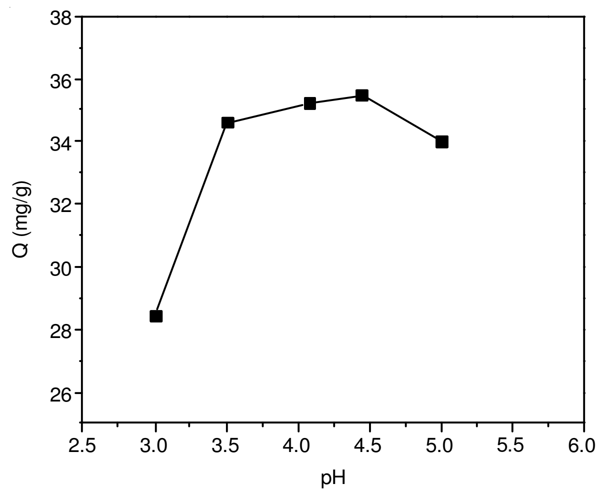

Fig. 3. Adsorption amount of hydrogel for Pb(II) at varied pH

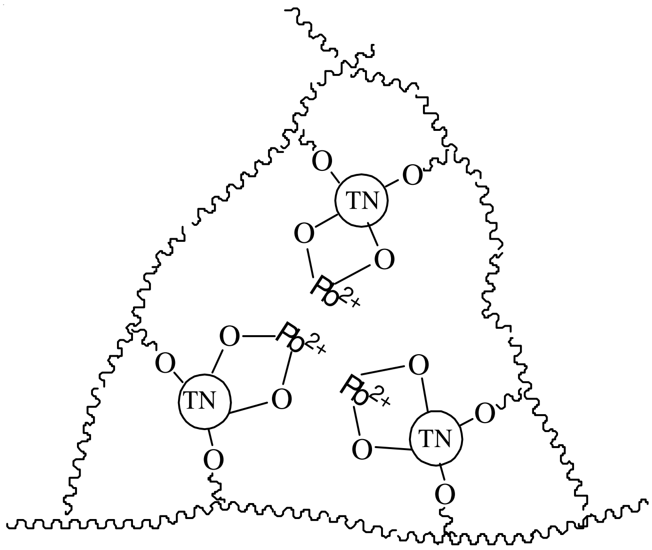

Fig. 4. Chelating interaction of hydrogel with Pb(II)

adsorption of hydrogels for Pb(II) diminished at lower pH due to the competition for adsorption sites between the metal ions and H^+ ions; most of the phenolic hydroxyl groups were ionized at higher pH and the chelation reaction of the phenolic hydroxyl with Pb(II) was enhanced, which resulted in the increasing adsorption. However, the precipitation of Pb(II) hydroxide occurs simultaneously with the sorption of Pb(II) ions when pH is above 4.5, which resulted in the reducing adsorption.

Effect of contact time on adsorption: The effect of contact time was evaluated for the removal of Pb(II) by hydrogel and the result is shown in Fig. 5. The data of the adsorption demonstrated fast adsorption property of hydrogel for Pb(II) and adsorption equilibrium time was attained in 40 min. Possible reason is that the interfacial energy between hydrogel and water decreased due to the hydrophilic properties of the hydrogel, which contributed to the contact of hydrogel and Pb(II) ion in solution.

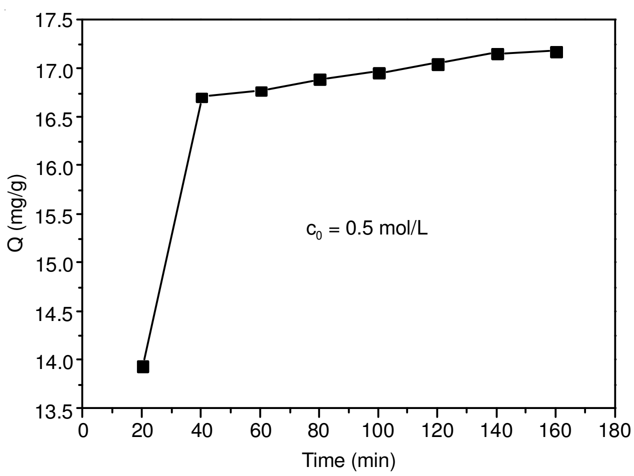

Fig. 5. Effect of contact time on adsorption at pH 4.5

Effect of lead Ion concentration on adsorption: Fig. 6 demonstrates the adsorption capacity of the tannin based hydrogel in Pb(II) ion solution with different Pb(II) concentrations. The adsorption capacity of the hydrogel for Pb(II) increased with the increasing concentration of Pb(II) and the ratio of metal ions adsorbed to initial metal ions was over 99 % when the concentration of Pb(II) in solution was lower than 0.5 mmol/L. The result shows that the hydrogel based on tannin had a high, efficient adsorption performance for Pb(II) ion from dilute aqueous solutions.

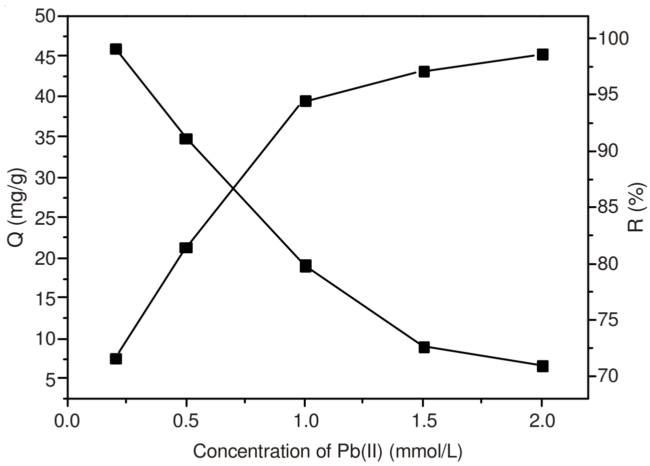

Fig. 6. Adsorption capacity of the hydrogel in different concentrations of Pb(II)

Langmuir isotherms and Freundlich isotherms were used to evaluate the adsorption experiments as a function of the initial metal ion concentrations in aqueous solutions[18,19]. The adsorption studies were conducted at pH 4.5 and the contact time used was 20 min, a linearized form of Langmuir equation and Freundlich equation is demonstrated by Eqn. (4) and by Eqn. (5), respectively.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{4}$$

where Q_{max} and b are the Langmuir constants related to maximum monolayer adsorption capacity and adsorption energy, respectively.

$$\log Q_e = \log K_F + (1/n)\log C_e \tag{5}$$

where K_f and n are the Freundlich constants related to adsorption capacity and intensity, respectively, C_e is the equilibrium concentration of metal ion in the solution.

The constant parameters and correlation coefficients were computed by the Langmuir and Freundlich isotherm and the resulted is shown in Table-I. The values of correlation coefficients (R > 0.99) from Langmuir isotherm model were higher than the values (R > 0.94) from Freundlich isotherm model. The adsorption isotherms of hydrogel for Pb(II) can be well fitted by the Langmuir equation. It is suggested that this sorption process takes place at the functional groups/binding sites on the surface of the hydrogels. The maximum adsorption amount of hydrogels for Pb(II) from Langmuir model was 49.3 mg/g.

Conclusion

Hydrogel based on tannin is prepared by the cross-linking reaction of tannin and the copolymer of allyl glycidyl ether and acrylamide. The hydrogel present strong adsorption capacity for Pb(II) and the adsorption behavior was very good correlation coefficients of linearized equations for Langmuir

TABLE-1
LANGMUIR AND FREUNDLICH MODEL PARAMETERS OF THE ADSORPTION OF HYDROGEL FOR Pb(II)

Temperature (K)	Langmuir			Freundlich		
	Q_m(mg/g)	k_b	R^2	k	1/n	R^2
289	49.30	0.0910	0.9934	51.3677	0.4832	0.9494

model. The hydrogels can be used as adsorbent for removal of heavy metal ions from dilute aqueous solutions.

ACKNOWLEDGEMENTS

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