

Study on optimal conditions and adsorption kinetics of copper from water by collodion membrane cross-linked poly- γ -glutamic acid

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(Received 27 October 2012 • accepted 6 April 2013)

Abstract—Poly- γ -glutamic acid (γ -PGA) is a novel polyamino acid formed through microorganism fermentation and biosynthesis. In the present test, membrane (PGA-C) formation by γ -PGA and collodion was performed by using 0.1% glutaraldehyde as a cross-linking agent. A study was conducted on the PGA-C adsorption of Cu^{2+} , specifically the related adsorption equilibrium and kinetics, desorption and regeneration. The results show that with an initial solution pH=5.5 and at 318 K, the static adsorption isotherm behavior of PGA-C is in compliance with the Langmuir model and is beneficial to the adsorption of the metal. Meanwhile, with the reaction lasting for 30 min, adsorption equilibrium was reached with a maximum adsorption capacity up to 7.431 mg/g. The entire reaction process follows the pseudo-second-order kinetics. By using PGA-C, good regeneration results were obtained after adsorption-generation-adsorption cycling with an HCl solution (0.1 mol/L) as regeneration liquid.

Key words: γ -PGA, Cu^{2+} , Collodion, Adsorption Kinetics, Optimal Conditions

INTRODUCTION

Owing to the increasing presence of heavy metal pollutants in many environmental media and their difficult removal, people have become more and more concerned about the hazard they pose to human health [1-3]. The sodium sulfide precipitation process is most commonly used in the treatment of copper-containing wastewater from the metal surface treatment, smelting and processing industries. However, this process is not ideal for eliminating large amounts of alkali metals. Furthermore, the process uses S^{2-} [4,5], thus creating a secondary pollution. γ -PGA (short for Poly- γ -glutamic acid) is a novel polyamino acid prepared by the biosynthesis of *Bacillus* strains. It has excellent degradability in nature and thus is non-toxic to humans and environment [6,7]. With free carboxyl groups on its side chains and an ultra-high molecular weight, γ -PGA can be used for adsorbing heavy metals in industrial and agricultural wastewater but not independently because of its water solubility. However, owing to its good membrane-forming properties, application of γ -PGA to the above treatment is made possible by forming a membrane with collodion using a cross-linking agent (Collodion is also called gun cotton and consists of nitrocellulose, alcohol and ether. In the liquid state, it is a transparent gel.).

In the present study, a membrane referred to as PGA-C was prepared by using collodion and γ -PGA, the latter being produced from high-yield *Bacillus cereus* obtained through self-screening; the optimal conditions for PGA-C synthesis were discussed and an evaluation of the adsorption kinetics of PGA-C to copper ions' was conducted. By using an HCL solution as a regenerating liquid, a process of adsorption-regeneration-adsorption cycling was performed

to maintain a maximum adsorption capacity of PGA-C to Cu^{2+} . The study provides a theoretical basis for recycling metal ions in wastewater treatment and environmental protection.

MATERIALS AND METHODS

1. Materials

γ -PGA (molecular weight: 500-600 kDa), collodion, cross-linking agents (glutaraldehyde, triton X-100 and Polyvinylpyrrolidone K-30, both at a concentration of 0.1%), copper nitrate and triketohydrindene hydrate (analytical pure) were used in this study. All the used reagents were purchased from Wenzhou Medicine Company, China. The analytical instruments used for the study are BioMate 5 ultraviolet-visible spectrophotometer (made by Thermo, US) and PEAA800 atomic absorption spectrophotometer (made by PerkinElmer, US).

2. Methods

2-1. Preparation of Collodion Membrane

A small amount of collodion was poured into a culture dish and then dried naturally, forming a membrane that was peeled from the dish for later use.

2-2. Preparation of PGA-C

5 g of γ -PGA was dissolved in 100 mL of distilled water and a γ -PGA aqueous solution (0.05 g/mL) was obtained. 10 mL of resultant solution was placed in a cross-linking agent (10 mL, 0.1%) to form a mixture of γ -PGA and the cross-linking agent. Two optional methods for the preparation of PGA-C are as follows: (1) A specified volume of the resultant mixture is added into the collodion liquid and crosslinked for two hours, and the liquid is removed. The cross-linking agent on the liquid surface is washed with distilled water and dried at temperature of 298 K to be used as an adsorbent. (2) The collodion membrane is placed into the crosslinking for two hours.

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The cross-linking mixture is washed from the membrane with water, and the membrane is allowed to dry at normal temperature to form an adsorbent.

2-3. Selection of Temperature for PGA-C Cross-linking

The adsorbent for γ -PGA was prepared at various temperatures, including 278 K, 298 K, 318 K and 338 K, and the PGA-C cross-linking efficiency was tested.

2-4. Test of pH Value for Adsorption

Five beakers were prepared. A mass of 0.2 g of PGA-C and 20 mL of Cu^{2+} solution with an initial copper ion concentration of 100 $\mu\text{g/mL}$ was added into each of the beakers. Gradient pH values of 2, 3, 4, 5 and 6 were adopted for the test. In the presence of sodium hydroxide, a copper hydroxide precipitate was generated when the Cu^{2+} solution pH was >6 . The filled beakers were placed in a 318 K magnetic stirred water bath, and the solution in which was adsorbed for 30 min. and then filtered. The resultant filtrates were diluted by 100x. The Cu^{2+} concentration of the diluted solution was measured with an atomic absorption spectrometer, and the pH_{pzc} of the PGA-C was measured using Nomanbhay or other methods [8].

2-5. Equilibrium Test on PGA-C

A mass of 0.2 g PGA-C was added to the conical flasks containing 20 mL Cu^{2+} solution at various concentrations, including 25, 50, 75, 100, 150 and 200 $\mu\text{g/mL}$. The adsorption of the PGA-C was conducted in a 318 K magnetic stirring water bath for 30 min. Subsequently, the Cu^{2+} concentration of the resultant filtrates was measured by the same method as indicated in 2-4.

2-6. Adsorption Kinetics Test on PGA-C

A volume of 20 mL of Cu^{2+} solution at a concentration of 25, 50, 100, 200 or 300 $\mu\text{g/mL}$ was added into five groups (six bottles for each group) of flasks and then 0.2 g PGA-C was added into each bottle of flasks. All of the flasks containing the Cu^{2+} solution were placed in oscillators at a speed of 180 r/min and at 303 K, 318 K and 333 K. One bottle was taken from each group of the flasks after 2, 5, 10, 15, 20, 30 and 60 min., respectively. The solution in the bottle was filtered and the Cu^{2+} concentration in the filtrates measured.

2-7. Analysis and Regeneration of PGA-C

HCl solutions with varied concentrations of 0.05, 0.1, 0.5, 1 and 2 mol/L were prepared. An experiment was conducted in the following five steps. (1) The adsorption equilibrium relationship was established between 100 $\mu\text{g/mL}$ Cu^{2+} solution and PGA-C, and the Cu^{2+} concentration of the equilibrated solution was measured; (2) the PGA-C was removed from the flasks and the Cu^{2+} concentration in the residual solution was measured; (3) upon reaching adsorption equilibrium, the PGA-C was placed in a 20 mL hydrochloric acid solution of a specified concentration, and the solution was placed in an oscillator at 318 K and a speed of 180 r/min for 30 min. The solution was removed and the Cu^{2+} concentration in the solution was measured; (4) the desorbed PGA-C was removed, washed with deionized water and dried naturally for 2 h for future recycling; and (5) experiments to evaluate the regeneration efficiency involved conducting an adsorption equilibrium experiment in the equilibrated solution of PGA-C and Cu^{2+} .

2-8. Test on γ -PGA Cross-linking Amount

A specified amount of γ -PGA adsorbent prepared by using different methods was hydrolyzed using strong (concentrated) hydrochloric acid. The pH value of the resultant solution was adjusted to

7.0 with NaOH. Five milliliters of sample solution was poured into a test tube, and 1 mL each of triketohydrindene hydrate reagent and buffer solution was added to increase the solution to 7 mL. The filled tube was plugged and agitated. The tube was then placed in a 100 °C water bath and heated for 15 min. The solution, after being cooled, the absorbance at 520 nm was measured using an ultraviolet-visible spectrophotometer, in which the standard curve for glutamic acid was obtained with glutamic acid concentration (20-100 $\mu\text{g/mL}$) as a horizontal ordinate and the corresponding A_{520} value as a vertical ordinate. The regression equation from the ordinates is $y=13.11x-0.007$, $r^2=0.9713$.

2-9. Cu^{2+} Concentration Test

Cu^{2+} concentration was measured by atomic absorption spectrometry to determine the adsorption quantity of PGA-C to Cu^{2+} , in which the standard curve of Cu^{2+} was obtained with Cu^{2+} concentration ($\mu\text{g/mL}$) as a horizontal ordinate and the corresponding light absorbency value as vertical ordinate. The regression equation obtained from the standard curve is $y=0.0373x-0.0009$, $r^2=0.9998$.

3. Data Analysis

Upon adsorption equilibrium, the adsorption quantity (q_e) of PGA-C to Cu^{2+} was calculated with formula (1), where the Cu^{2+} adsorption quantity (q_t) of PGA-C after a period of time, t (min) was calculated by using formula (2). All treatments were repeated three times with the average values taken as measured results. With the aid of the software SAS, the nonlinear regression analytical method was adopted to fit the data from the experiment to calculate each parameter of the mathematical model, the r^2 value and predicted values. The χ^2 value was calculated by using formula (3) [9,10]. The smaller the χ^2 value is, the better the model fits the experimental results. The formula for calculation of the metal ion adsorption quantity [11,12]:

$$q_e = (C_o - C_e)V/m \quad (1)$$

$$q_t = (C_o - C_t)V/m \quad (2)$$

$$\chi^2 = \sum [(q_{exp} - q_{cal})^2 / q_{cal}] \quad (3)$$

where q_e and q_t are the values for the equilibrium adsorption and the quantity of adsorption (mg/g) after a period of time (t), respectively; C refers to concentrations (mg/mL) of metal ions in the solution before adsorption; C_o and C_e are the concentrations (mg/mL) of metal ions at equilibrium in the solution and concentrations after a period of time (t), respectively; V represents the absorbate volume (mL) in the solution; m refers to the dry weight (g) of the adsorbent; q_{exp} and q_{cal} represent the experimental values of quantity of Cu^{2+} adsorbed by the PGA-C and the predicted value (mg/g) of adsorbed quantity calculated by the means of the model, respectively [13,14].

RESULTS AND DISCUSSION

1. Effect of γ -PGA Adsorption Preparation, Methods and Different Cross-linking Agents on Cross-linking Efficiency

Table 1 shows the cross-linking efficiency of the γ -PGA adsorbents prepared by using different methods and various cross-linking agents. In the Group P_0 , no γ -PGA was added; in Group P_1 , γ -PGA was added during the membrane formation; in Group P_2 , γ -PGA was added after the formation. As collodion itself has a certain amount

Table 1. Crosslinking efficiency γ -PGA sorbent produced in different ways

Crosslinking agent	Glutaraldehyde			Triton X-100			Polyvinylpyrrolidone K-30		
	P ₀	P ₁	P ₂	P ₀	P ₁	P ₂	P ₀	P ₁	P ₂
Absorbance	0.178	0.237	0.217	0.214	0.271	0.231	0.105	0.163	0.123
Glutamate concentration ($\mu\text{g/ml}$)	14.23	18.77	17.23	17.00	21.39	18.31	8.615	13.08	10.00
γ -PGA sorbent ($\mu\text{g/g}$)	-	1866	1233	-	1803	573.6	-	1834	569.2

Table 2. Crosslinking efficiency γ -PGA sorbent produced at different temperature

Temperature	278 K		298 K		318 K		338 K	
	P ₀	P ₁	P ₀	P ₁	P ₀	P ₁	P ₀	P ₁
Absorbance	0.125	0.144	0.145	0.189	0.137	0.246	0.179	0.240
Glutamate concentration ($\mu\text{g/ml}$)	10.15	11.62	11.69	15.08	11.08	19.46	14.31	19.00
γ -PGA sorbent ($\mu\text{g/g}$)	-	352.5	-	816.4	-	2022	-	1132

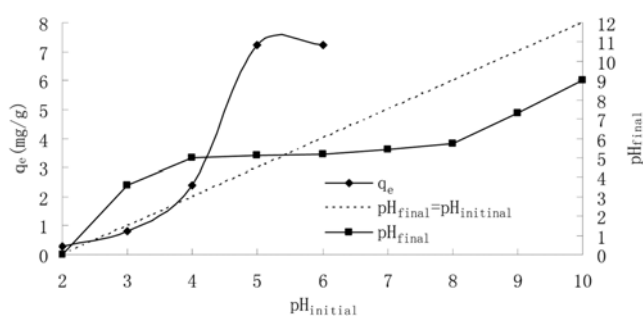
of glutamic acid, the quantity of γ -PGA that cross-linked in the above each adsorbent group is a D-value between the γ -PGA quantity from Groups P₁ or P₂ and that from P₀. As shown in Table 1, among the γ -PGA adsorbents prepared at the same temperature, with the same γ -PGA solubility and using the identical cross-linking agent, an adsorbent prepared with γ -PGA added to the membrane was cross-linked with the largest amount of glutamic acid, while at the same temperature, with the same γ -PGA solubility and using the identical preparation method, the adsorbent prepared by using 0.1% glutaraldehyde as an agent contained the largest amount (1866 $\mu\text{g/g}$) of γ -PGA. As the γ -PGA amount in the membrane increases, the hydroxy and carboxyl that can form complexation with heavy metal ions was raised, resulting in a rise of the adsorbent rate. The test shows the higher γ -PGA concentration the adsorbent has, the higher the adsorption rate. Therefore, in the subsequent experiments, the γ -PGA adsorbent prepared by using 0.1% glutaraldehyde was selected as a cross-linking agent and γ -PGA was added during the formation of collodion-contained membrane [15].

2. Selection of Cross-linking Temperatures

The cross-linking efficiencies of the γ -PGA adsorbent at various cross-linking temperatures are shown in Table 2. P₀ is a control group containing no γ -PGA and P₁ is the sample group, but γ -PGA was added at a corresponding temperature. At a crosslinking temperature of 318 K, γ -PGA has the largest quantities of crosslinking with collodion. The cross-linking quantity γ -PGA had an upward tendency with a rise in cross-linking temperature, which peaked at 318 K and declined at >318 K. Cross-linking that was performed with an agent between the hydroxy in collodion cellulose and the amino and carboxyl γ -PGA molecules has specific relationship with temperature, resulting in inadequate bonding or broken bonds at an excessively low or high temperature. The three substances themselves have a strong hydrogen-bonding function. Therefore, 318 K was chosen as the temperature for cross-linking in the present test.

3. Effect of Solution pH

The effect of pH on the adsorption of Cu^{2+} by PGA-C is shown in Fig. 1. With the adsorbate solution at a pH of 2-4, the adsorption quantity of Cu^{2+} by PGA-C increases rapidly with the increment of the pH values. At pH 5-6, the absorption reaches a maximum. The form in which Cu exists and its effectiveness in water is affected by pH values as indicated here: at pH<4, the primary form is Cu^{2+} ;

**Fig. 1. Point of zero charge of adsorbent and effect of solution pH on Cu^{2+} adsorption by to PGA-C.**

at pH=4-5, Cu^{2+} and CuOH^+ ; at pH=5-6, CuOH^+ and Cu(OH)_2 ; at pH>6, Cu(OH)_2 [16], which is precipitated and not favorable for adsorption [17]. In addition, the adsorbent surface property is affected by pH [18-20]. When the pH is at the point of zero charge (pH_{pzc}), the adsorbent surface is not altered, but when the pH value is less than the pH_{pzc} , the adsorbent is positively charged, which is not favorable for adsorption of positively charged Cu^{2+} and CuOH^+ , thus contributing to electrostatic repulsion. When the pH exceeds pH_{pzc} , the adsorbent is negatively charged, which enhances adsorption of Cu^{2+} and CuOH^+ . At a low pH, H^+ and Cu^{2+} compete with CuOH^+ for binding sites on the adsorbent, which is not favorable for the adsorption of Cu^{2+} . Furthermore, this study revealed that based on the zeta potential measured on the Cu^{2+} -adsorbed PGA-C surface by an electrophoresis test, the measured pH_{pzc} (i.e., zero) of the PGA-C was at 5.3; that the increase of Cu^{2+} concentration would result in increased positive charges and a higher pH_{pzc} , while the decrease of the concentration would have opposite effects on positive charges and pH_{pzc} , which indicates varied Cu^{2+} concentrations do have an effect on pH_{pzc} . The present test was conducted with an initial Cu^{2+} concentration at 100 $\mu\text{g/mL}$, at which the highest adsorption rate was obtained. In the adsorbate solution with a pH at 6, there is more Cu(OH)_2 generated. Therefore, the optimal pH value for PGA-C to adsorb copper ions is 5.5, at which Cu^{2+} ions exist in the form of Cu^{2+} and CuOH^+ , and PGA-C is negatively charged, which is conducive to adsorbing Cu^{2+} and CuOH^+ [21,22]. Hydroxy and carboxyl in the chemical composition of PGA-C, as active groups for

biological adsorbents to adsorb heavy metals [23], can combine with Cu^{2+} in the form of the solution bonds or ion exchanges [17]. With $\text{pH} < 5.3$, the solution carries a large number of positive charges with PGA-C positively charged and carboxyl in the form of $-\text{COOH}$ combining mainly with Cu^{2+} ; with $\text{pH} > 5.3$, the solution carries more negative charges with PGA-C negatively charged and carboxyl in the form of $-\text{COO}^-$ combining with more Cu^{2+} . Therefore, the adsorption rate is higher with $\text{pH} = 5.5$.

4. Adsorption Isotherms

The theoretical saturation adsorption quantity of heavy metal ions onto PGA-C to is a significant index for measuring PGA-C's adsorbing and purifying capacity. Under isothermal conditions, to accurately characterize the adsorption phenomenon occurring on a solid surface in a solution, the relations between the adsorption quantity on a solid surface and the solution concentration at equilibrium used for fitting models are the Langmuir and Freundlich isotherms, which are defined by formulas (4) and (5) respectively:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_m indicates the maximum adsorption quantity (mg/g) of PGA-C to Cu^{2+} upon saturation, K_L and K_F (L/mg) are adsorption isotherm constants from the Langmuir and Freundlich equations, respectively, and n is a constant related to temperature. From the data obtained from three different isotherm equilibrium tests at varied temperatures, shown in Table 3, the Langmuir model has a better fitting at 318 K ($r^2 = 0.9977$ and $\chi^2 = 0.0321$) [24]. As shown in Fig. 2, the predicted values obtained from the Freundlich model at a high equilibrium concentration deviate significantly from the experimental values with poor fit results compared to the Langmuir model [25]. Therefore, the static adsorption behavior of PGA-C conforms to the Langmuir model, representing chemical adsorption characteristics (i.e., the fact that adsorption sites with the same affinity are

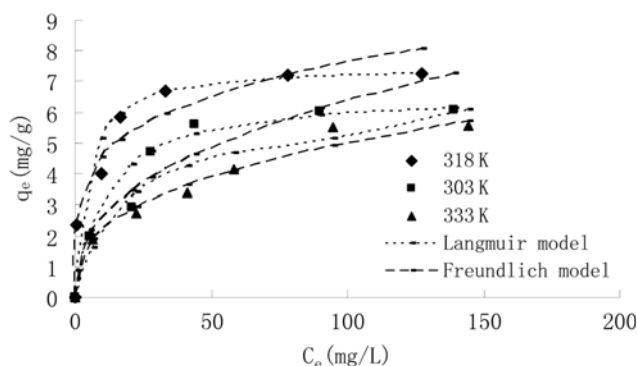


Fig. 2. Adsorption isotherms and their modelling at different temperatures.

uniformly distributed onto an adsorption surface and a monomolecular layer adsorption is formed between adsorbents and adsorbates) [26].

As the rate curve shows, the PGA-C adsorption of Cu^{2+} is divided into two stages. At the first stage, adsorption is conducted at a rapid rate because a large number of active sites exist on the PGA-C surface and the initial Cu^{2+} concentration is high, resulting in a difference in concentration, which produces a high mass transfer force and rapid adsorption. The adsorption quantity increases linearly. At the second stage, the adsorption occurs gradually, and the adsorption rate declines until it reaches equilibrium. This kinetics is attributed to the fact that a significant amount of Cu^{2+} is adsorbed on the PGA-C surface and therefore the active sites ($-\text{COO}^-$) provided on the periphery decrease rapidly. Therefore, in order to be exchanged and adsorbed, free Cu^{2+} ions in the solution need to enter the inside, namely, active adsorption sites where adsorption is not saturated. In doing so, the Cu^{2+} ions have to travel around the peripheral γ -PGA where adsorption has been saturated. The rate of Cu^{2+} adsorption is thus delayed, resulting in non-linear adsorption, which complies with the Langmuir model.

The separating factor R_L value (6) can be used to determine whether adsorption equilibrium is favorable. $R_L > 1$ indicates unfavorable adsorption, $R_L = 1$ for linear adsorption and $R_L = 0$ for irreversible adsorption.

$$R_L = 1 / (1 + K_L C_0) \quad (6)$$

As shown in Fig. 3, R_L value at 318 K is lower than the value at both 303 K and 333 K and decreases with the increase of initial Cu^{2+} concentration. These results indicate that increasing the initial concentration is favorable for adsorption, and $0 < R_L < 1$ further proves that the adsorption is favorable. The saturation adsorption capacity of PGA-C to Cu^{2+} has a tendency to gradually become constant [27].

5. Adsorption Kinetics

Kinetic models are usually used for the study of rate alteration in the adsorption process to determine the steps for limiting adsorption rates. In the present study, a pseudo-first-order kinetic model

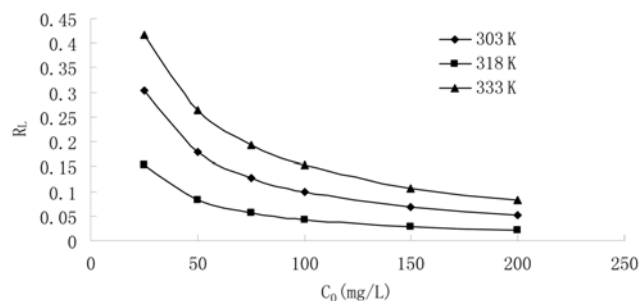


Fig. 3. Plot of separation factor versus initial Cu^{2+} concentration.

Table 3. Modelled isotherm parameters for Cu^{2+} adsorption on PGA-C at different temperatures

Temperature (K)	Langmuir				Freundlich			
	q_m (mg/g)	K_L (L/mg)	r^2	χ^2	K_F ($\text{L}^n \text{mg}^{1-n}/\text{g}$)	n	r^2	χ^2
303	6.588	0.092	0.977	0.113	1.040	2.539	0.951	0.001
318	7.530	0.221	0.998	0.032	2.709	4.439	0.941	0.0003
333	6.086	0.056	0.952	0.145	0.968	2.811	0.988	0.032

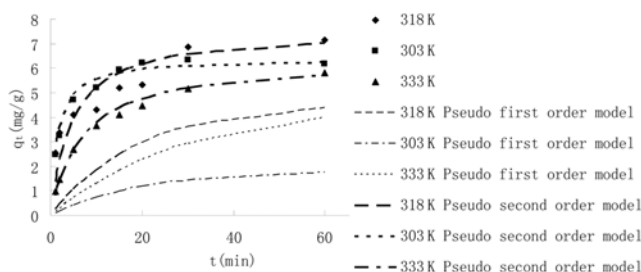


Fig. 4. Adsorption kinetics and their modelling at different temperatures.

expressed by Eq. (7) and a pseudo-second-order kinetic model expressed by Eq. (9) were employed to fit the process of the PGA-C adsorption of Cu^{2+} (Fig. 4). In addition, the integral formula (8) was adopted for Eq. (7) to plot $\ln(q_e - q_t)$ and t . Eq. (9) was transformed into Eq. (10) [28], which was used to plot t/q_t and t . By performing regression analysis on all of the data, k_1 , k_2 and q_e indicating the PGA-C adsorption of Cu^{2+} , as well as the related coefficients r^2 and χ^2 were obtained from the slope rates and intercepts (Table 4).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (8)$$

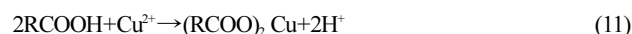
$$q_t = k_2 q_e^2 t / (1 + k_2 q_e t) \quad (9)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (10)$$

where t is the adsorption time (min); q_t and q_e indicate the quantity (mg/g) of PGA-C adsorption of Cu^{2+} with an adsorption time, t , and upon adsorption equilibrium, respectively, k_1 is a first order adsorption rate constant (1/min) and k_2 is a second order adsorption rate constant (g/(mg·min)).

As shown in Fig. 4 and Table 4, the reaction, driven by the van der Waals force, was performed rapidly in the first 15 min, when the adsorption was mainly physical with an adsorption amount up to about 85-95%. With the reaction lasting for 30 min, adsorption equilibrium was reached with a maximal adsorption capacity of 7.431 mg/g. At different concentrations and temperatures, r^2 values from the pseudo-second-order kinetic model are all higher than 0.98 and χ^2 values are less than 0.0071, with the actual values similar to the theoretical ones calculated by the model. These results indicate that the pseudo-second-order kinetic model has a good fit, while r^2 values from the pseudo-first-order kinetic model are lower than 0.98 and χ^2 values are relatively higher, with a large difference between the theoretical values calculated by the model and the actual values. These results indicate that this model fits the results poorly and does not perform as well as the pseudo-second-order model. As the maximal adsorption capacity is obtained ($q_e = 7.431$) at 318 K and good

adsorption is achieved at a static adsorption temperature of 318 K, it is recommended to select 318 K as the temperature for the experiments. At the later stage of PGA-C adsorption of Cu^{2+} , the adsorption was carried out at a lower rate by chemical bonds and therefore is chemical. In addition, the calculation of enthalpy and entropy for the adsorption gave negative values, which indicates the PGA-C adsorption is exothermic and thus has a high adsorption capacity. Ion exchanges existed between carboxyl ($-\text{COOH}$) and Cu^{2+} (as shown in the formula 11), which proves that the adsorption rate is jointly controlled by both the complexation of $-\text{COO}^-$ and $-\text{OH}^-$ in PGA-C with Cu^{2+} and the diffusion of Cu^{2+} and CuOH^+ inside the adsorbent. As the pseudo-second-order kinetic model is established on the basis of consumed chemical adsorption [29], the rate-limiting procedures for the PGA-C adsorption of Cu^{2+} are a chemical adsorption process. Therefore, [30]



where R indicates the construction in the molecular structure of PGA-C except carboxyl.

6. Desorption and Regeneration

The PGA-C adsorbents that had reached adsorption equilibrium were desorbed and regenerated with HCl solutions at various concentrations. The experimental results show that the PGA-C desorbed using an HCl solution with an excessively high concentration (e.g., >0.5 mol/L) cannot be regenerated as its structure has been destroyed under highly acidic conditions. With an HCl solution at 0.05 mol/L, a portion of the Cu^{2+} adsorbed by the PGA-C could not be completely desorbed. With an HCl solution at 0.1 mol/L, Cu^{2+} could be completely desorbed from the PGA-C. The mass loss of the PGA-C itself was within an average of 8.75% after adsorption-generation-adsorption cycling, and the decrease in the maximal saturation capacity of the exchanges and adsorption of Cu^{2+} could be controlled within an average of 9.15%. After the desorption to the PGA-C by a HCl solution (0.1 mol/L) was repeated for 10 times, the porosity of the PGA-C was basically recovered to the normal level with only a very small part still occupied by Cu^{2+} . Therefore, it is estimated that the regeneration of PGA-C is possible in both lab conditions and mass water treatment.

CONCLUSION

For membrane (PGA-C for short) preparation using γ -PGA and collodion with a 0.1% glutaraldehyde solution as a cross-linking agent, better cross-linking results can be obtained at a temperature of 318 K. Heavy metal Cu^{2+} ions in water can be effectively removed with PGA-C and better adsorption results can be obtained with an initial solution of pH=5.5. The static adsorption isotherm behavior of PGA-C is consistent with the Langmuir model, and the model has

Table 4. Modelled kinetic parameters for Cu^{2+} adsorption on PGA-C at different temperatures

Temperature (K)	Experimental q_e (mg/g)	Pseudo first order model				Pseudo second order model			
		q_m (mg/g)	k_1 (L/min)	r^2	χ^2	q_m (mg/g)	k_1 (L/min)	r^2	χ^2
303	6.439	1.819	0.051	0.569	35.19	6.427	0.100	0.999	0.0001
318	7.431	4.625	0.051	0.933	5.108	7.564	0.029	0.986	0.007
333	6.532	4.589	0.034	0.940	2.467	6.419	0.022	0.998	0.006

a better fitting result at 318 K ($r^2=0.9977$, r^2 more close to 1 and $\chi^2=0.0321$). The low value of the separating factor R_L value also proves that the adsorption of Cu^{2+} can be facilitated at 318 K. The adsorption of Cu^{2+} by the PGA-C surface can be divided into two stages. At the early stage of the reaction, as there is a high concentration of Cu^{2+} in the sampled water and the PGA-C has abundant active functional groups (-COOH), the adsorption is conducted at a rapid rate, in the first 15 min. At the second stage, after the reaction has proceeded for 30 min, the adsorption equilibrium is achieved with the maximal adsorption capacity up to 7.431 mg/g. The entire reaction process complies with the pseudo-second-order kinetic model. Using a 0.05 mol/L HCl solution as a regeneration liquid, the mass loss of PGA-C itself was within an average of 8.75% after adsorption-generation-adsorption cycling, and the decrease in the maximal saturation capacity of the exchanges and adsorption of Cu^{2+} could be controlled within an average of 9.15%. Therefore, better regeneration results can be obtained.

Owing to the limited time and conditions, the present study leaves something to be desired. Further explorations in the following seem to be needed: First, for the application of the membrane (PGA-C) to the actual wastewater treatment as in reality, multiple kinds of heavy metal ions may exist in wastewater and they themselves can adsorb each other, which makes the membrane (PGA-C) adsorption difficult; secondly, a further study on porosity changes before and after the adsorption by means of an electromicroscope; thirdly, the mechanism of PGA-C adsorption of metal so as to pave the way for developing highly-efficient adsorbents; fourthly, heavy metal recycling by desorption with HCL after adsorption using the membrane (PGA-C).

ACKNOWLEDGEMENTS

We would like to acknowledge the Science Technology Department of Zhejiang Province (No. 2010C32005), the People's Republic of China for the financial funding, which allowed us to conduct the present study.

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