Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 89 (2016) 299 – 306
Energy Procedia

Towards novel adsorbents: the ratio of PVA/chitosan blended hydrogels on the copper (II) ion adsorption

Tongsai Jamnongkan* and Kritiya Singcharoen

Department of Basic Science and Physical Education, Faculty of Science at Siracha, Kasetsart University, Chonburi 20230, Thailand.

Abstract

Recently, the one of most environments problems is a heavy metal contamination in water therefore it is very important to remove these metal before discharging to environment. In this work, the efficacy of Cu (II) adsorption on the polymer hydrogel blends of poly(vinyl alcohol) and chitosan (PVA/CS), at various polymer compositions, from the aqueous solution was investigated. The Fourier transform infrared spectroscopy was used for verify the chemical structure of polymer hydrogels. Water absorbency of the polymer hydrogel films was investigated by water swelling ratio measurement. We found that the PVA/CS were crosslinked by using glutaraldehyde, and the PVA/CS hydrogel at the ratio of 100/0 highly showed the water swelling ratio due to the PVA has highly hydrophilicity property. In addition, the adsorption capacity of the Cu (II) ion on the PVA/CS hydrogel adsorbents were investigated. All of samples showed good adsorption capacity, the efficacy of adsorption depend on the composition of polymer hydrogel. Increasing adsorption capacity with increasing the CS content within the network. Finally, the kinetic of adsorption also was studied. It was found that the pseudo-second-order kinetic, having up to 1.00 of a correlation coefficient, is best described the adsorption process of this adsorbent.

Peer-review under responsibility of the organizing committee of the 12th EMSES 2015

Keywords: Biopolymer; Heavy metal removal; Polymer hydrogel; Wastewater

1. Introduction

In this present, the most of the researchers over cross the world paid attractive attention the water resources problem particularly the heavy metal contamination problems, due to its directly affected to the toxic on human, animals and plants [1]. It is well know that the heavy metals are easily dissolved in the water. Therefore, the toxicity heavy metals, i.e., copper, lead, cadmium, and chromium [2, 3], must be removing from the wastewater before

* Corresponding author. Tel.: +66-38-354-587
E-mail address: sfscitsj@src.ku.ac.th

1876-6102
Peer-review under responsibility of the organizing committee of the 12th EMSES 2015
doi:10.1016/j.egypro.2016.05.038

discharging to environments. In particularly, copper (Cu) is a higher level it is toxic to humans even though it has contaminated in wastewater.

Recently, we found that the several techniques have been applied for the remove the heavy metal ions in wastewater, i.e., chemical precipitation, photocatalytic degradation, membrane filtration, electro-chemical technologies, and reverse osmosis method [4]. Among these techniques, it is well know that the adsorption is one of methods for remove the heavy metals from aqueous waste solution.

Nowadays, a lot of materials made as absorbents for waste water treatments. Considering to environmental concerns, the biopolymer have received attention to made as absorbent. Chitosan (CS), being its biocompatible, biodegradable and nontoxic, is one of these materials has been used as materials for making as absorbents. However, it is well know that the CS has a lower mechanical properties such as a flexibility and swelling ratio. In particular, the CS was formed the hydrogel structure. To overcome this disadvantage, we blended chitosan with other hydrophilic polymers for improving the flexibility and water absorbency of CS hydrogel. Poly (vinyl alcohol) (PVA) is one of materials for interesting blends with CS due to the PVA is a biocompatibility and has an excellent hydrophilicity properties. Also, PVA can be dissolved in water with characteristics non-toxicity, and biodegradability [5]. Recently, we found that the PVA has manufactured into a variety of adsorbent types, i.e., ion-exchange film [6] and hydrogel [7]. The mechanical strength and chemical stability of the polymer chains was increased by the chemical reaction within the network. Most of method for enhancing these properties was through crosslinking by chemical reaction, which the polymeric structure become as three-dimensional network. Recently, Wang et al., [8] reported that the PVA hydrogel can remove the heavy meter in water, and its shows fast adsorption kinetic rate.

In this work, we investigate the efficacy of Cu (II) adsorption on PVA/CS blended hydrogel at ratio of 100/0, 75/25, 50/50, 25/75, and 0/100. This number denoted to the percentage of weight polymer solutions. Here, the glutaraldehyde was used as crosslinker for crosslinking the PVA/CS blends. The Fourier transform infrared spectroscopy was used for investigating the chemical reaction of PVA/CS hydrogels. The efficacy of hydrogel water absorbency has been carried out by the swelling ability. Finally, the influences of experiments parameter, i.e., contact time and composition ratio of hydrogels, were studied on the efficacy of Cu (II) adsorption.

2. Experimental

2.1 Materials

High molecular weight CS and PVA, M_w = 140,000 g/mol with 87-89% hydrolyzed, were purchased from Sigma–Aldrich, Germany. Glutaraldehyde was purchased from Wako Chemical Industries, Japan and copper (II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) was from Merck, Germany. All other chemicals were used as received without any further purification. The deionized-water was used throughout these experiments.

2.2 PVA/CS blended hydrogel preparation

The PVA/chitosan hydrogels were prepared by mixing 10 %w/v PVA solution with 1 %w/v CS solution, which its dissolved in 2 %w/v of acetic acid, and then constantly stirring the mixture until homogeneous solution. Then, the crosslinking agents was added the solution under constant stirring. After homogeneous mixing, pour the mixture into Petri-disc and the mixture formed hydrogel within 30 minutes at room temperature. Then, the obtained PVA/CS hydrogel dried and kept at 40 ^{o}C in a vacuum oven for 24 h. The amount of PVA, CS, glutaraldehyde, and crosslink solution used for preparing the PVA/CS hydrogel at various compositions, are shown in Table 1.

Table 1 Composition of the PVA/CS hydrogel used in this study

(PVA/CS) hydrogels	CS (mL)	PVA (mL)	crosslink* (mL)	1.25% GA (mL)
100/0	-	10.00	5.71	-
75/25	2.50	7.50	4.28	0.02

50/50	5.00	5.00	2.86	0.04
25/75	7.50	2.50	1.43	0.06
0/100	10.00	-	-	0.08

*Crosslinking solution is making up at the ratio 3:2:1:1 of the solution of 50% methanol, 10% acetic acid, 1.25% glutaraldehyde (GA) and 10% sulfuric acid, respectively.

2.3 PVA/CS blended hydrogel characterization

We begin investigate the chemical structure of the PVA/CS hydrogels by using a FTIR spectrophotometer. The IR spectra of the investigated film was performed in the wavenumber range of 4000-400 cm^{-1} at the ambient condition. Then, we investigate the swelling ability of the PVA/CS hydrogel which is one of important properties for use as an adsorbent. Therefore, the PVA/CS hydrogel was determined the water uptake capacity (%WC) as its will be calculate as following the equation (1):

$$\%WC = \frac{W_t - W_i}{W_i} \times 100 \quad (1)$$

where, W_t and W_i refer to the weights of wet PVA/CS hydrogel at time t and initial time, respectively. The hydrogel films of preweight, defined as W_i, was immersed into the deionized water at room temperature for different intervals time durations (every 10 min). The samples were taken out from water and the filter paper was used for removing the excess water on the surface of adsorbents, and subsequently weighed to define as Wt. The percentage of water remaining (%WR) was calculated as follows (2):

$$\%WR = \frac{W_t - W_i}{W_t} \times 100 \quad (2)$$

2.4 Adsorption capacity study

The efficacy of the adsorption onto the PVA/CS hydrogels investigate with Cu (II) ion at ambient condition. The experiments was done as follows: A 30 mL of 50 mg/L of copper (II) ion solution were incubated with the dry PVA/CS hydrogel, approximately 1 g, and the solutions were agitated at the fixed speed (150 rpm) with thermostatic stirrer. Samples were separated from the aqueous phase for investigate the Cu (II) concentration. The remained concentration of Cu (II) ion in solution was determined by Perkin Elmer model AAnalyst 200 atomic absorption spectrophotometer [9]. The samples solution were determined in triplicate for each condition. The amount of Cu (II) ion adsorbed per weight of adsorbents were calculated as following equation (3):

$$\text{Adsorption} = \left(\frac{C_0 - C_t}{m}\right) \times V \quad (3)$$

where, C_0 and C_t refer to the concentration of initial and the time t of Cu (II) ion (mg/L), respectively. The volume of the samples solution (mL) denoted as V, and m is the weight of the dry adsorbents (g). In addition, we continue investigate the percentage of Cu (II) ion adsorption was calculated as follows:

$$\%\text{Adsorption} = \frac{C_0 - C_t}{C_0} \times 100$$

The initial and the time at t concentrations of Cu (II) ion (mg/L) adsorption were denoted as C_o and C_t, respectively.

3. Results and Discussion

3.1 PVA/CS blended hydrogel characterization

The chemical reaction of PVA/CS hydrogels was revealed by the result of FTIR spectroscopy. We found that the glutaraldehyde can be crosslinked the polymer chain within the network, as reported in the previous study [10].

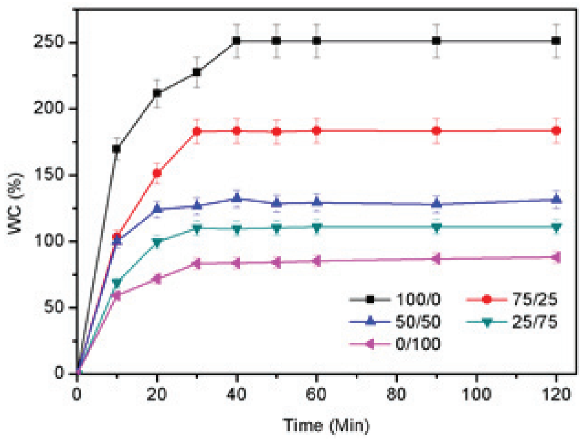

Fig. 1 Water uptake capacity of PVA/CS hydrogels for different contact time.

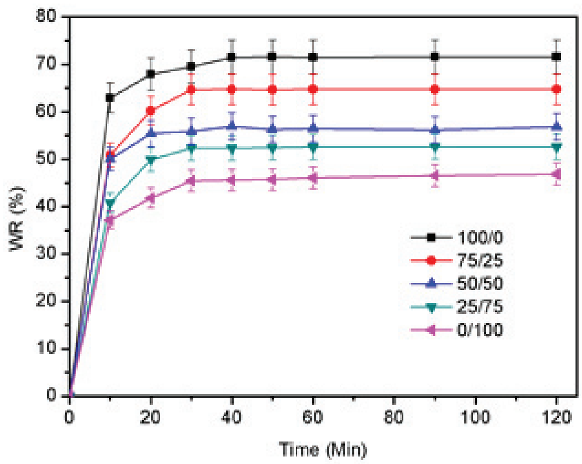

Fig. 2 Percentage of water remaining of PVA/CS hydrogels for different contact time.

3.2 Water absorbency of PVA/CS hydrogel

Figure 1 and Figure 2 showed the effect of the composition of the adsorbents on percentage of swelling ratio (%WC) and water remaining (%WR), respectively. We found that the, during the period of 40 min, all of the composition of the PVA/CS hydrogel adsorbents highly exhibited initial water adsorption rate and then completely reached to equilibrium state. We also found that the water uptake capacity and water remaining increased with increases in the PVA content within the network. This is probably due to the hydrophilicity properties within the PVA/CS structure. It is well know that the water absorbency ability was proportionally with the amount of hydrophilic groups in the network. Therefore, the higher the PVA content within the adsorbent structure would be increased the water absorbency.

3.3 Adsorption capacity study

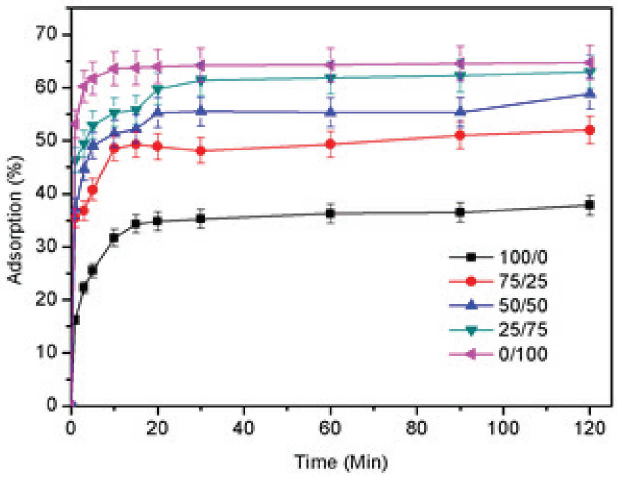

Fig. 3 The efficacy of Cu (II) ion adsorption onto the adsorbents

Figure 3 showed the result of the efficacy of Cu (II) ion adsorption with the function of time. We found that the all adsorbents exhibit highly increased the adsorption rates within 20 min, and then roughly changed increases, as shown in Fig. 3. From these behavior, all PVA/CS hydrogels, it is possibility the adsorption rates of hydrogel approached to the equilibrium state. At this state, it is well know that the adsorption behavior is become to the equilibrium state between desorption and adsorption of Cu (II) ion in aqueous solution. Looking at the Fig. 3, it was observed that the adsorption process classified into three stages. At first step, the Cu (II) ion adsorption was rapidly and it became slower at near of the equilibrium region. This behavior probably due to the fact that during the initial stage, the Cu (II) ion approached to the boundary layer of hydrogels. Secondary step, the Cu (II) slowly diffused from the boundary layer film to the adsorbent surface. Finally, the Cu (II) ion will be diffused into the porous structure of hydrogels [11]. Additionally, we found that the, both at initial and equilibrium states, PVA/CS hydrogel at the ratio of 0/100 showed the highest adsorption capacity of Cu (II) ion among the five hydrogels. We believe the composition of the polymer hydrogel have affects to the Cu (II) ion adsorption capacity. To confirm this hypothesis, we plot the variation in the adsorption capacity with the chitosan content within the polymer hydrogels, as you can see in Fig. 4. Obviously, the increase in the chitosan content upon increasing the Cu (II) ion adsorption capacity. This behavior is probably due to the CS molecules have lone pair electrons of the amine ($-NH_2$) groups and the hydroxyl (–OH) groups which it can be bonding with the metal ions. Therefore, the blending hydrogels with CS it will be increases the number of hydroxyl and amine groups on the network within hydrogels. As these results, the efficacy of Cu (II) ion adsorption on CS hydrogels (0/100) is superior the other compositions due to this composition higher content of hydroxyl and amine groups as compared to the other composition of PVA/CS hydrogel absorbents. However, this phenomenon is quite interesting, further investigations into this possibility are currently underway. We intend to address this phenomenon in more detail in a future publication.

The adsorption kinetic rates of PVA/CS hydrogels were checked by pseudo-first-order and pseudo-second-order models in order to understand the adsorption kinetic of Cu (II) ion process. The PVA/CS hydrogels at the ratio of 100/0, 50/50, and 0/100 were chosen for this study. The pseudo-first-order kinetic model is given as [12]:

$$\log(q_e - q) = \log q_e - (k_1/2.303)t$$

where, q_e and q are the amounts of Cu (II) ion adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}). The k_1 can be calculated from the slop of the straight-line plots of the $\log(q_e$-q) against contact time. The correlation coefficient (R^2) values of the Cu (II) ion under different concentration range were also calculated from these relationships. The results of the pseudo-first-order kinetic parameters for Cu (II) ion adsorption are given in Table 2. We found that the composition ratio has affecting to the value of rate constant. The k_1 exhibited different values, which depended on the composition of the adsorbents. In addition, we also found that the R^2 in this model showed quite low values, as depicted in Table 2. Therefore, we can mentioned that the Cu (II) ion adsorption is not fitted of cannot predict by the pseudo-first-order kinetic model. Therefore, we continue examined the pseudo-second-order kinetic model, and the equation can be expressed as follows [13]:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$$

where, the pseudo-second-order rate constant ($g.mg^{-1}min^{-1}$) is represented as k_2. The k_2 can be calculated by plotting t/q against contact time. Additionally, the R^2 was also can be found from this plotted. These parameter would be suggests the appropriate the adsorption kinetic rate model.

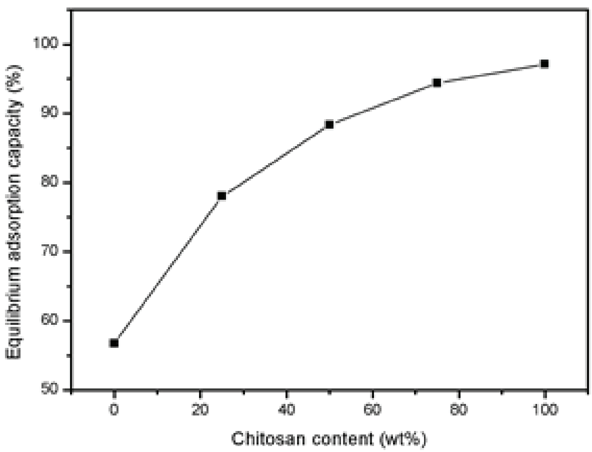

Fig. 4 Relationship of the equilibrium adsorption capacity of Cu(II) ion and chitosan contents

With regarding to the correlation coefficients, as we shown in Table 2. We found that the R^2 of pseudo-second-order kinetic model are quite high. Therefore, the kinetic rate of Cu (II) adsorption is fitted and its best described by the pseudo-second-order kinetic model. Typically, the pseudo-second-order kinetic model assumes that the rate-limiting step might be chemical adsorption [14]. Hence, we suggest that the adsorption behavior of PVA/CS might be the intermolecular forces through the interaction of electrons between Cu (II) ion and adsorbents.

Table 2 Kinetic parameters of Cu (II) ion on PVA/CS hydrogels at the ratio of 100/0, 50/50, and 0/100 at room temperature

PVA/CS hydrogel	First order		Second order	
	k_1 (x 10^{-2} min^{-1})	R^2	k_2 ($g.mg^{-1}min^{-1}$)	R^2
100/0	4.79	0.9116	0.48	0.9995
50/50	5.07	0.9383	0.75	0.9985
0/100	5.09	0.8899	3.86	1.0000

4. Conclusion

The biopolymer adsorbents were successfully prepared from PVA/CS blended hydrogel at various composition ratios. The PVA/CS blended hydrogels can be swollen in the aqueous medium. We found that the water absorbency decreased with increasing the amount of chitosan within the network of polymer hydrogel. All of PVA/CS hydrogel approached to equilibrium state within 40 min when the polymer hydrogel contact with aqueous media. The adsorption capacity of PVA/CS hydrogel was studied. From our results, the efficacy of Cu (II) ion adsorption dependence with the composition ratio of adsorbents. The composition of polymer hydrogel significantly affected on the Cu (II) ion adsorption onto PVA/CS hydrogel. The efficacy of Cu (II) ion adsorption increased with increases in the chitosan content within the polymer network. This is probably due to the higher amount of hydroxyl and amine groups within PVA/CS hydrogel networks. In addition, we also found that the rate of Cu (II) ion adsorption also depended on the contact time, and its will be approached to the equilibrium state within 20 min. Finally, in this study, the pseudo-second-order model was fitted and best described the kinetics rate of Cu (II) ion adsorption onto PVA/CS hydrogels.

Acknowledgements

This work was partially supported by the Faculty of Science at Siracha, Kasetsart University and Kasetsart University Research and Development Institute Grant No. 143.59. TJ also gratefully acknowledge to the Miss Ampawan Prasert and Miss Pusthira Kaewpijit, for contributing the experiments.

References

[1] Rai PK. Heavy metal pollution in aquatic ecosystems and its phytoremediation using wetland plants: an ecosustainable approach. *Int J Phytorem* 2008; 10: 133-160

[2] Fu F and Wang Q. Removal of heavy metal ions from wastewaters: A review. *J Environ Manage* 2011; 92: 407-418

[3] Demirbas A. Heavy metal adsorption onto agro-based waste materials: A review. *J Hazard Mater* 2008; 157: 220-229.

[4] Jamnongkan T, Wattanakornsiri A, Wachirawongsakorn P, Kaewpirom S. Effects of crosslinking degree of poly(vinyl alcohol) hydrogel in aqueous solution: kinetics and mechanism of copper(II) adsorption. *Polym Bull* 2014; 71: 1081-1100.

[5] Jamnongkan T, Sukumaran SK, Sugimoto M, Hara T, Takatsuka Y, Koyama K. Towards novel wound dressings: antibacterial properties of zinc oxide nanoparticles and electrospun fiber mats of zinc oxide nanoparticle/poly(vinyl alcohol) hybrids. *J Polym Eng* DOI: 10.1515/polyeng-2014-0319.

[6] Street KW, Hill CM, Philipp WH. Properties of a novel ion-exchange film. *Ind Eng Chem Res* 2004; 43: 7600-7607.

[7] Jamnongkan T, Kantarot K, Niemtang K, Pansila PP, Wattanakornsiri A. Kinetics and mechanism of adsorptive removal of copper from aqueous solution with poly(vinyl alcohol) hydrogel. *Trans Nonferrous Met Soc China* 2014; 24: 3386-3393

[8] Wang X, Zheng Y, Wang A. Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites. *J Hazard Mater 2009*; 168: 970-977.

[9] Association of Analytical Chemistry. Official methods of analysis,15th ed. Washington DC, USA, 1990.

[10] Jamnongkan T and Kaewpirom S. Potassium release kinetics and water retention of controlled-release fertilizers based on chitosan hydrogels. *J Polym Environ* 2010; 18: 413-421.

[11] Senthilkumaar S, Varadarajan PR, Porkodi K, Subbhuraam CV. Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. *J Colloid Interf Sci* 2005; 284: 78-82.

[12] Chiou MS and Li HY. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* 2003; 50: 1095-1105.

[13] Wu FC, Tseng RL, Juang RS. Comparative adsorption of metal and dye on flake and bead-types of chitosans prepared from fishery wastes. *J Hazard Mater* 2000; 73: 63-75.

[14] Wu FC, Tseng RL, Juang RS. Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. *J Hazard Mater* 2001; 81: 167-177