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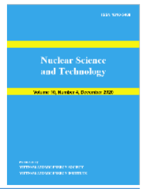

Preparation of hydrogel reinforced with bentonite by gamma irradiation for metal absorption

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Abstract: A natural-based sodium carboxymethyl cellulose (CMC) hydrogel reinforced with bentonite was prepared by using gamma irradiation technology. This is a novel hydrogel that uses natural polymer to absorb metal ions in wastewater. The influence of dose, concentration of CMC and bentonite on the sorption of hydrogels was investigated by atomic absorption spectrometry (AAS) method. According to the Langmuir isotherm model, the maximum adsorption capacities of CMC/bentonite hydrogel for Cu^{2+} and Pb^{2+} were 181.82 mg/g and 204.08 mg/g at room temperature, respectively. The pseudo-second-order model which describes the adsorption process of Cu^{2+} and Pb^{2+} was also studied.

Keywords: *carboxymethyl cellulose, bentonite, hydrogel, Cu^{2+} and Pb^{2+}.*

I. INTRODUCTION

Currently, the problem of removing metals from wastewater solutions is investigated in many researches [1-4]. One of the methods used for this purpose is using materials of natural or man-made polymers that have been treated like hydrogel materials.

Hydrogel are defined as hydrophilic polymers with three-dimensional structure, capable of swelling in water and will not dissolve in water. This ability of swelling makes hydrogel an ideal material used in drug transportation, tissue technology, agriculture,… [5]. In addition, hydrogels are also capable of responding to many physical stimuli such as temperature, pressure, and chemical stimulation. It was used for adsorption, enrichment, separation and recovery of metal ions, recovery of dyes and removal of harmful components in wastewater. Adsorption of heavy metals using hydrogel has been investigated in several studies. Ozay et al. used p(AMPS)t hydrogel networks to adsorb magnetic iron particles [6]; Wasikiewicz et al. investigated the adsorption efficiency of carboxymethyl chitin (CM-chitin) and carboxymethylchitosan (CM-chitosan) on scandium and gold [7]. The adsorption of lead by hydrolysis lignin-g-poly-(acrylic acid) hydrogel was studied by Sun et al. [8].

Carboxymethyl cellulose is a natural polymer with numerous carboxylic and hydroxyl groups which is suitable to prepare heavy metal adsorption materials. Bentonite is a natural clay mineral with a layer structure of

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2:1 consisting of 2 tetrahedra layers and an octahedral layer in the middle so it has a porous structure and has a large specific surface that can absorb large amounts of substances [9]. There are some studies using polymer/clay hydrogel such as chitosan-PVA/bentonite (10%) nanocomposites [10], CMC-g-poly(NIPAm-co-AA)/MMT [11] to adsorb metals in wastewater. However, by the authors understanding, until now, there is no research on preparation of CMC/bentonite hydrogel for adsorption purposes. The aim of this work is to prepare a new adsorption material which is simple and eco-friendly for removing heavy metals from wastewater. The efficiency of the CMC/bentonite hydrogel for the removal of Cu^{2+} and Pb^{2+} from aqueous solution was investigated.

II. CONTENT

A. Material and methods

1. Materials

Sodium Carboxymethyl cellulose (CMC) 1380, degree of substitution of 1.34 was purchased from Daicel Co., Ltd., Japan. Bentonite clay was provided by Hiep Phu JSC, Lam Dong, Viet Nam. $CuSO_4.5H_20$ and $Pb(NO_3)_2$ were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd., China.

Metal ion standard solutions were provided from Merck, Germany.

2. Sample preparation and irradiation

Solutions of 5% (w/w) of CMC and 0, 1, 3, 5% (w/w) of bentonite were prepared by dissolving 20 g CMC and 0, 0.2, 0.6, 1.0 (g) bentonite in distilled water and further stirred at room temperature for an hour for dispersion. The mixture was sealed in polyethylene bags for air-free irradiation. According to the ratios of CMC/bentonite, the prepared hydrogels were named as CMCB/0 (20:0, CMC:bentonite), CMCB/1 (20:1, CMC:bentonite),CMCB/3 (20:3, CMC:bentonite), CMCB/5 (20:5, CMC:bentonite), correspondingly.

Gamma irradiation was carried out by a ^{60}Co gamma source irradiation dose of 20 kGy at room temperature at the Radiation Technology Center, Dalat Nuclear Research Institute.

3. Absorption studies

The adsorption experiments were carried out using solutions of $CuSO_4$, $Pb(NO_3)_2$ with concentrations of metal ions from 50 ppm to 400 ppm. The dried hydrogel samples (0.2 g) were soaked in 100 ml of aqueous metal ions for 8 hours at room temperature.

After the adsorption, the remaining solutions were filtered out and diluted to proportions as shown in Table I. The dilution factor depends on the measuring limit of the instrument. The metal ions concentration in solution was measured by atomic absorption spectrometer model AA-6800, Shimazu, Japan.

Table I. Concentration and the dilution of metal ions solution

Concentration (ppm)	50	100	200	300	400
Dilution factor (times)	10	25	50	100	100

The efficiency of hydrogel was calculated according to Eq. (1) [12]:

$$\text{Removal (\%)} = \frac{C_0 - C_i}{C_0} \times 100\% \quad (1)$$

Whereas, Co and Ci are the concentrations of metal ions in mg/L before and after the adsorption, respectively.

The value for q_e (mg/g) is the maximum adsorption capacity at equilibrium was calculated as [12]:

$$q_e = \frac{(C_0 - C_i) \times V}{m} \quad (2)$$

Where V is the solution volume (L) and m is the mass of the hydrogel (g).

B. Result and discussion

1. Effect of clay content on metal ions sorption

As seen in Fig. 1, the sorption of Cu^{2+} and Pb^{2+} ions onto CMC/bentonite hydrogel increased by the increasing of bentonite concentration in hydrogel. The sorption efficiency reaches to the maximum value at 3% of bentonite in the hydrogel, 81.26% and 68.24% for Cu^{2+} and Pb^{2+}, respectively. It can be explained that when the concentration of bentonite increases from 1% to 3%, the absorption increases with the increasing of gel faction. However, when the concentration of bentonite is more than 3%, the adsorption efficiency of metal ions decreases. This is because bentonite act as a multifunctional crosslinker in which the more of its content in hydrogel, the tighter the carbon network between CMC and bentonite [13]. When the bentonite concentration reached 5%, the bonding network becomes too tight which prevents the penetration of metal ions. The metal ions in solutions can not bind to hydrogel as well as in CMCB/3 sample. As a result, the hydrogel based on CMC/Bentonite with the ratio of 20% CMC and 3% bentonite (CMCB/3) was selected for further heavy metal ions adsorption investigation.

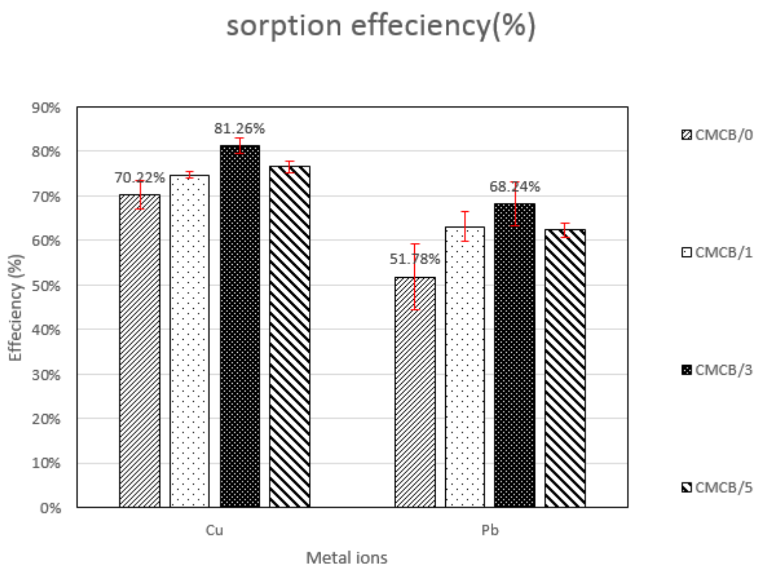

Fig. 1. Sorption efficiency of Cu^{2+} and Pb^{2+} on four hydrogels CMCB/0, CMCB/1, CMCB/3, CMCB/5

2. Effect of contact time

The effect of adsorption time on metal ions adsorption has also been investigated. The effect of contact time on the adsorption of Cu^{2+} and Pb^{2+} ions is shown in Fig. 2. The metal ions uptake is found to be rapid for the first 240 min. When adsorption begins, all active adsorbent sites on the adsorbent surface are available to interact with metal ions. When the adsorption time increases, the adsorption rate decreases when the active sites are exhausted and it finally reaches a state of dynamic equilibrium. Therefore, the optimal vibration time was determined to be about 240 min for Cu^{2+}, 360 min for Pb^{2+} (Fig. 2).

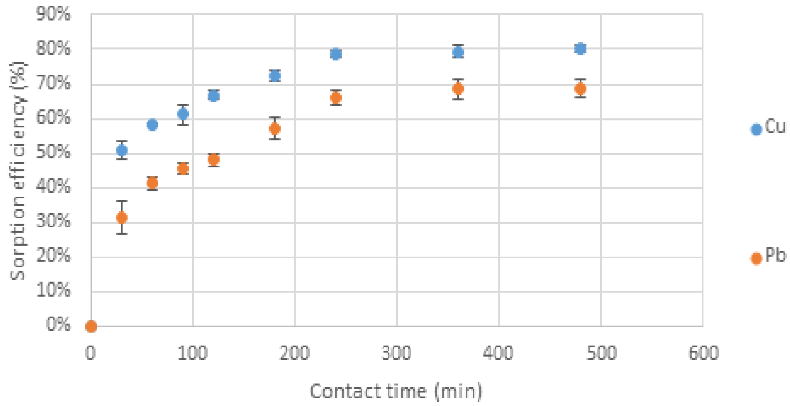

Fig. 2. The sorption of Cu^{2+} and Pb^{2+} onto hydrogel at various adsorption time

3. Adsorption kinetics

The time adsorption of metal ions to CMC/bentonite hydrogel was investigated with initial concentration of 100 mg/L for each metal solution. Common mathematical models used to describe adsorption kinetics included Lagergren's pseudo-first-order kinetic equation, pseudo-second-order kinetic equation. The pseudo-first-order kinetics is described by [14]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

The pseudo-second-order kinetic model is given by Eq 4:

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

Where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), respectively. The fitting parameters k_1 and k_2 in Eq. (3) and (4) represent the pseudo-first-order (1/min) and the pseudo-second-order rate coefficients (g $mg^{-1}min^{-1}$), respectively.

The fitting of pseudo-first-order and pseudo-second-order kinetic models to experimental data is displayed in Fig. 3 and 4 and the fitting parameters (k and q_e) of both models are shown in Table II.

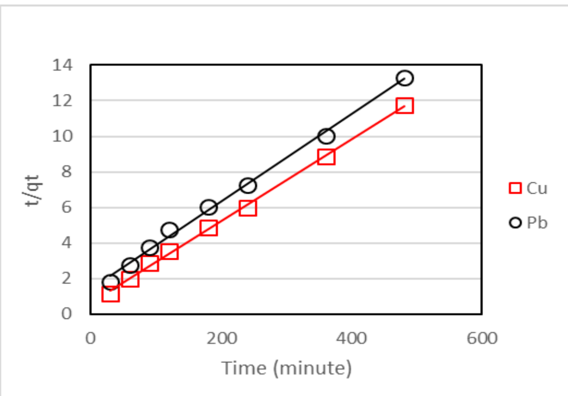

Fig. 3. Pseudo-first-order kinetic models

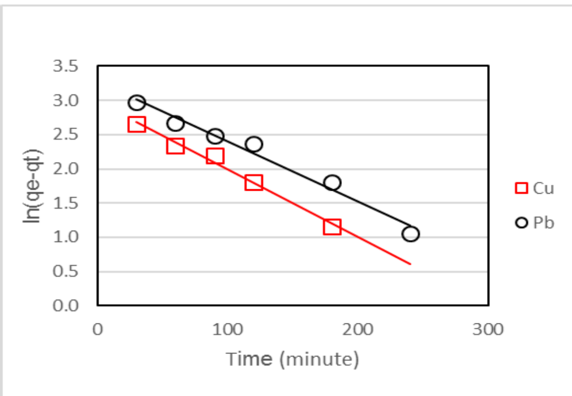

Fig. 4. Pseudo-second-order kinetic model

It can be seen that the coefficients (R^2) of the pseudo-second order kinetic model are more suitable than the pseudo-first-order kinetic model. When comparing experimental ($Q_{e,exp}$) and theoretical values ($Q_{e,cal}$) as shown in Table I, the pseudo-second order kinetic model is also more appropriate. The pseudo-second order kinetic model suggests that the adsorption mechanism governs the adsorption process, and the adsorption rate of metal ions onto the gel can be controlled by chemical process through sharing or electron exchange between the adsorbent and metal ions in solution. The pseudo-second order kinetic model demonstrates that the combination of bentonite particles gives a structure and a higher number of available adsorption positions on the surface of the hydrogel for metal ions.

Table II. Kinetic parameters of metal sorption onto CMC/bentonite hydrogel

Metal ions	$Q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		R^2	$Q_{e,cal}$ (mg/g)	k_1 (min $^{-1}$)	R^2	$Q_{e,cal}$ (mg/g)	k_2 (mg/g min $^{-1}$)
Cu^{2+}	40.16	0.9885	18.94	0.0099	0.9987	43.48	0.0008
Pb^{2+}	35.95	0.977	24.94	0.0087	0.9962	40.65	0.0004

4. Sorption isotherm

We used Langmuir isotherm models to analyze the sorption data. Langmuir isotherm is usually used to describe monolayer adsorption where all reactive sites on the sorbent's surface are energetically homogenous where there is no lateral interaction and steric hindrance between the adsorbed molecules. The linearized form of this model represented by Equation 5:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}} c_e \qquad (5)$$

Where:

+ K_L is Langmuir equilibrium constant (l/mg).

+ q_{max} (mg/g) is maximum sorption capacity.

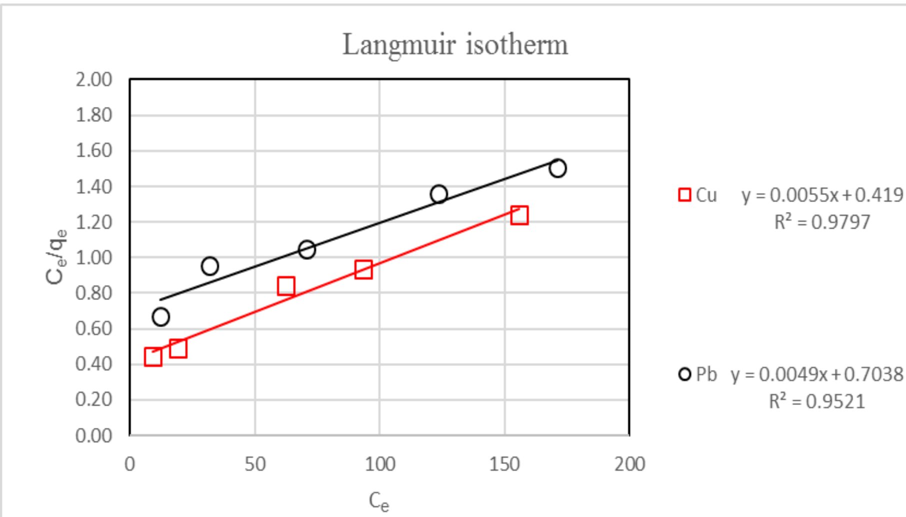

Fig. 5. Adsorption isotherm of metal ions by CMC/bentonite hydrogel

Table III. Isotherm parameters of metal sorption onto CMC/bentonite hydrogel

metals	Langmuir		
	R^2	K_L	Q_{max}
Cu	0.9797	0.013	181.82
Pb	0.9521	0.007	204.08

Fig. 5 shows the Langmuir isotherm obtained by plotting C_e and C_e/q_e, and the values of KL, Q_{max}, and R^2 are listed in Table 3. Based on these coefficients obtained, it can be concluded that the Langmuir equation ($R^2 > 0.90$) gives a good fit to the experimental data of lead and copper ions. From the slope and intercept of Langmuir isotherm, the values of q_{max} were calculated to be 181.82mg/g for Cu^{2+} and 204.08 mg/g for lead adsorption. Some carboxymethylated CMC-based adsorbents are found to be from 70 to 170 mg/g for Cu [11, 15] or 76.70 - 84.9 for lead [11, 16]. Compared to their data, it can be seen that crosslinked CMC/bentonite hydrogel can be efficiently used as adsorbent for the removal of Pb^{2+} and Cu^{2+} ions.

Table IV lists the q_{max} values of some materials for removal Pb^{2+} and Cu^{2+}. The q_{max} value of the CMC/bentonite hydrogel was higher than that of most absorbents.

Table IV. Comparison of maximum adsorption capacity of some materials

Materials	Cu^{2+}	Pb^{2+}	Reference	Kind of materials
CTS-PVA/BT (10%) Nanocomposites	24.97	18.00	[10]	Polymer/clay
CMC-g-poly (NIPAm-co-AA)/MMT	70.5	84.9	[11]	Polymer/clay
CMC/Chitosan hydrogel	169.5	---	[15]	Polymer/polymer
Graphene oxide/carboxymethyl monoliths	82.93	76.70	[16]	Polymer/graphite
Chitosan/cellulose	26.50	26.31	[17]	Polymer/cellulose
Chitosan/PVC	87.9	---	[18]	Polymer/polymer
Thiosemicarbazide modified green CMC	144.92	---	[19]	Modify Polymer
CMC/bentonite hydrogel	181.82	204.08	This work	Polymer/clay

III. CONCLUSIONS

A natural-based sodium carboxymethyl cellulose (CMC) hydrogel reinforced with bentonite was successfully prepared by irradiation of a mixture of CMC and bentonite clay. The prepared hydrogel showed a good adsorption ability for heavy metal ions. The obtained result showed that CMC/bentonite hydrogel with the ratio of 20:3 (CMCB/3) is the most suitable for the Pb^{2+} and Cu^{2+} adsorption, which are 181.82 and 204.08 mg/g for Cu^{2+} and Pb^{2+} at room temperature, respectively. The prepared CMC/bentonite hydrogel can be efficiently used as an adsorbent for the removal of Pb^{2+} and Cu^{2+} ions and has a potential application for removal of heavy metal ions from wastewater.

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