Efficient Removal of Cr(VI) from Aqueous Solution Using Polypyrrole/Rectorite Composites

Yaolei Xu, Jinyi Chen*, Xiaofeng Wang and Peiling Yu
School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430000, China
*Corresponding author

***Abstract*—Cr(VI) is considered to be a toxic contaminant in water sources because of its risk to human health. In this study, Polypyrrole/rectorite (PPy/REC) clay composites were prepared via in situ polymerization. SEM, FTIR and XRD analysis provided information of the morphology and structure of the PPy/REC composites. Ca-REC was selected as the template in terms of its low cost. The equilibrium data were fitted well by the Langmuir isotherm model with the maximum adsorption capacity of 689.7-854.7 mg/g at 25-45 ℃.**

Keywords—heavy metal; wastewater treatment; clay-based materials; Cr(VI) removal mechanism; adsorption isotherm

I. INTRODUCTION

Chromium (Cr) is a transition metal that can form various compounds, some of which cause serious environmental pollution risks from various industries [1]. In aqueous solution, the toxicity of Cr(VI) is 500 times than that of Cr(III). Therefore, it is necessary to control the concentration of Cr(VI) to an acceptable level before it is discharged into the environment.

Polypyrrole (PPy) is composed of pyrrole N structures and shows good adsorption capacity for negative Cr(VI). Due to the ion exchange characteristics and inherent ability of PPy [2-3], PPy has been widely used as an adsorbent for Cr(VI) removal. However, due to the particle agglomeration, the Cr(VI) removal by PPy from wastewater was limited [4-5]. Rectorite (REC) is a kind of interlayer silicate mineral, which consisting of a regular stacking of mica-like layer and montmorillonitelike layer [6]. There are broad application prospects for developing REC-based composite materials and the REC can also solve the problem of agglomeration and dispersion of PPy in aqueous solution.

In this study, PPy/REC as adsorbents for Cr(VI) removal were discussed. scanning electron microscopy (SEM), fourier transform infrared spectra (FTIR) and X-ray diffraction (XRD) analyses provided information to determine the morphology and structure of the PPy/REC composites. The effects of the REC species, initial concentration and temperature were investigated in batch mode.

II. MATERIALS AND METHODS

A. Materials

Calcium Rectorite (Ca-REC) and Na-rectorite (Na-REC) was obtained from Zibo Kangnengda Rare Earth Materials Co., Ltd. Organic modified REC (CTAB-REC) was prepared by a method that has been published [7]. Pyrrole monomer (Py) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ammonium persulfate (APS), hexadecyl trimethyl ammonium bromide (CTAB), sodium hydroxide, diphenylcarbazide, anhydrous ethanol, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

B. Synthesis of the PPy/REC Composites

PPy/REC composites were prepared by chemical oxidation method. Firstly, an amount of 2 g of Ca-REC was dispersed in 100 mL of deionized water. Then, 3 mL of pyrrole monomer was added into the aqueous solution and stirred for 30 min. Next, a certain amount of APS solution (3.4 g of APS in 16.67 mL of 5 M HCl) was injected into the intermixture using a syringe, stirred for 12 h to ensure adequate polymerization. Finally, the product was dried at 60 ℃ in an oven. The PPy/Na-REC composites, PPy/CTAB-REC composites and PPy homopolymer were prepared according to the above-mentioned method.

C. Characterization Methods

The obtained composites were characterized by SEM (JEOL JSM-5510LV). The surface properties of rectorite were characterized by ATR-FTIR (Perkin Elmer) and XRD (Bruker AXS D8 Advance).

D. Adsorption Experiments

20 mg PPy/REC composites were added into 20 mL aquatic solution containing 250 mg/L Cr(VI). After vibrating for 8 h, the solution was filtered to analyze the content of Cr(VI).

Isotherm experiments at three different temperatures (25 ℃, 35℃, and 45 ℃) were carried out by changing the initial concentration of Cr(VI) from 200 to 1500 mg/L. The process was like the procedure above except for vibrating for 14 h.

III. Results and Discussion

A. *Characterization of the PPy/REC Composites*

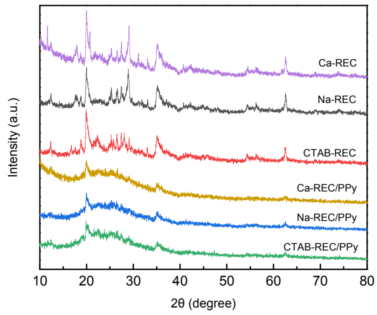

FIGURE I. XRD PATTERNS OF REC AND PPY/REC COMPOSITES

Wide-angle X-ray diffraction plots of samples are depicted in Fig. 1. The diffraction peaks at 19.97°, 29.09°, 35.15° and 62.61° were attributed to REC [6]. The wide peak at 25° in PPy/REC composites is the characteristic peak of amorphous PPy [8]. The decrease of peak intensity in PPy/REC composites might be due to the coating of the polymer matrix on REC.

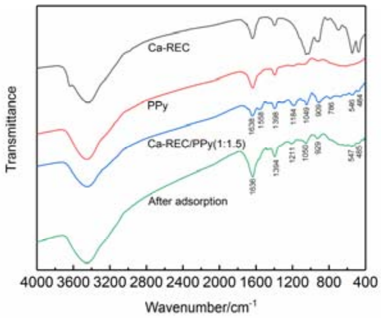

FIGURE II. FT-IR OF CA-REC, PPY, PPY/CA-REC COMPOSITES

The FTIR results of the PPy/Ca-REC composites were shown in Fig. 2. At 1630–1640 cm^{-1}, there are the bands of flexing vibrations of free water in clay margin and clay pore. The strong band at 1184 cm^{-1} is attributed to the stretching vibrations of Si-O. Si-O-Al flexing vibration band occurs at about 474 cm^{-1}. The frequency band at about 3440 cm^{-1} is attributed to the bending vibration of adsorbed water [9]. The spectra of the characteristic absorption bands of PPy at 1558, 1398, 1184, 1083 and 909 cm^{-1} were attributed to C=C stretching of pyrrole rings, C-N stretching of pyrrole rings, in-plane deformation of C-N rings, in-plane vibration of C-H rings and outer-bending vibrations of C-H, respectively [5]. These characteristic bands also existed in PPy/Ca-REC composites, thus confirming the presence of both the Ca-REC and PPy in the composites.

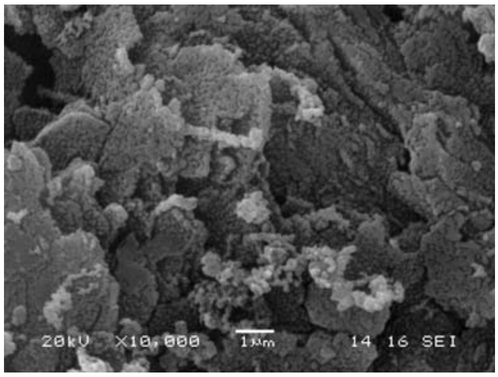

FIGURE III. SEM OF PPY/CA-REC COMPOSITES

The morphology of PPy/Ca-REC composites was shown in Fig. 3. The lamellar structure of the Ca-REC clay was covered by polypyrrole after PPy modification, and the surface of the Ca-REC became highly rough as PPy uniformly covered the surface of Ca-REC.

B. *Effect of the REC Species*

Different composites were prepared by varying the REC species. As shown in Fig. 4, for REC, With the increase of d-spacing, the adsorption surface increases, and CTAB-REC with the largest d-spacing has the largest adsorption surface. But it is interesting that different rectorites show good removal effect after coating PPy. On the one hand, PPy has excellent adsorption/reduction properties for Cr(VI). On the other hand, PPy mainly covers the surface of REC uniformly, and the distance between layers of composite materials has little effect on Cr(VI) removal. Therefore, Ca-REC was selected as the template of synthesis from the point of view of low cost and simple preparation method.

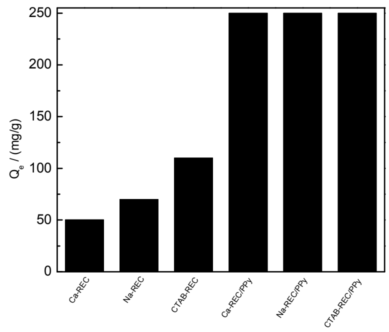

FIGURE IV. EFFECT OF THE RECTORITE SPECIES ON CR(VI) REMOVAL

C. *Adsorption Isotherm*

In order to describe the interaction between adsorbates and to successfully design and operate the adsorption system, equilibrium adsorption isotherm data are very important. The date obtained for Cr(VI) adsorption by PPy/Ca-REC composites at three different temperatures are presented in Fig. 5. Table 1 shows the Freundlich and Langmuir isotherms parameters for the fittings. The R^2 (0.9955-0.9980) values obtained for the Langmuir model were higher than the Freundlich model (0.8442-0.9637), which indicated that the former fits the data better. When the temperature increased from 25 ℃ to 45 ℃, the maximum adsorption capacity increased from 689.7 mg/g to 854.7 mg/g, which implied the endothermic nature of the adsorption process. These results also show that the adsorption of Cr(VI) occurred by forming a single layer at a limited number of the identical adsorption sites on a homogeneous surface.

The adsorption capacity of the PPy/Ca-REC composites (689.7 mg/g) was higher than the adsorption capacity of the clay-based materials, such as exfoliated PPy-organically modified montmorillonite (119.30 mg/g) [10], polypyrrole-sepiolite nanofibers (302.00 mg/g) [11], polypyrrole-coated halloysite nanotube (149.25 mg/g) [12]. These results indicate that the PPy/Ca-REC composites can be considered as a promising adsorbent for the Cr(VI) removal from industrial wastewater.

TABLE I. LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR CR(VI) ADSORPTION BY PPY/CA-REC COMPOSITES

Temperature (℃)	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	B (L/mg)	R^2	K_F (mg/g)	1/n	R^2
25	689.7	0.0465	0.9980	277.9	0.1384	0.9637
35	740.7	0.0857	0.9964	353.2	0.1179	0.8442
45	854.7	0.0732	0.9955	351.8	0.1412	0.9222

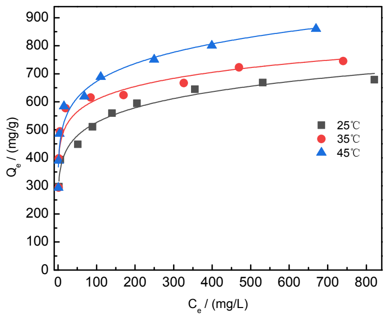

FIGURE V. EQUILIBRIUM ISOTHERMS OF CR(VI) ADSORPTION ONTO THE PPY/CA-REC COMPOSITES

IV. CONCLUSION

The Cr(VI) removal was studied through batch adsorption using PPy/REC composites as a promising adsorbent. This adsorbent was synthesized through in situ polymerization of pyrrole monomer in the presence of Ca-REC which can effectively remove Cr (VI) from aqueous solution. The characterization results showed that the composites were successfully synthesized. Ca-REC was selected as the template in terms of low cost and simple preparation method. The adsorption isotherm can be well described by Langmuir adsorption isotherm model, the maximum adsorption capacity of PPy/REC composites was 689.7-854.7 mg/g at 25-45 ℃, suggesting that the adsorption process might be chemical adsorption and might occur on the surface of PPy/Ca-REC composites by a monolayer adsorption. These results indicated that PPy/Ca-REC composites could be a promising adsorbent for removing Cr(VI).

ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (No.51374157).

REFERENCES

[1] Yao. C, Xu. Y, Kong. Y, Liu. W, Wang. W, Wang. Z, Wang. Y, and Ji. J, “Polypyrrole/palygorskite nanocomposite: A new chromate collector,” Appl. Clay. Sci. Amsterdam, vol. 67-68, pp. 32-35, July 2012.

[2] Bhaumik. M, Agarwal. S, Gupta. V.K, and Maity. A, “Enhanced removal of Cr(VI) from aqueous solutions using polypyrrole wrapped oxidized MWCNTs nanocomposites adsorbent,” J. Colloid Interface Sci. San Diego, vol. 470, pp. 257-267, February 2016.

[3] Karthik. R, and Meenakshi. S, “Removal of hexavalent chromium ions from aqueous solution using chitosan/polypyrrole composite,” Desalin. Water Treat. Hopkinton, vol. 56, pp. 1-14, November 2014.

[4] Gupta. V. K, Rastogi. A, and Nayak. A, “Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material,” J. Colloid Interface Sci. San Diego, vol. 342, pp. 135-141, September 2009.

[5] Li. S, Lu. X, Li. X, Xue. Y, Zhang. C, Lei. J, and Wang. C, “Preparation of bamboo-like PPy nanotubes and their application for removal of Cr(VI) ions in aqueous solution,” J. Colloid Interface Sci. San Diego, vol. 378, pp. 30-35, June 2018.

[6] Hong. H, Jiang. W. T, Zhang. X, Tie. L, and Li. Z, “Adsorption of Cr(VI) on STAC-modified rectorite, Appl. Clay. Sci. Amsterdam, vol. 42, pp. 292-299, January 2008.

[7] Huang. Y, Ma. X, Liang. G, Yan. Y, and Wang. S, “Adsorption behavior of Cr(VI) on organic-modified rectorite,” Chem. Eng. J. Switzerland, vol. 138, pp. 187-193, June 2007.

[8] Ballav. N, Maity. A, and Mishra. S. B, “High efficient removal of chromium(VI) using glycine doped polypyrrole adsorbent from aqueous solution,” Chem. Eng. J. Switzerland, vol. 198-199, pp. 536-546, May 2012.

[9] Zhao. D, Yang. S, Chen. S, Guo. Z, and Yang. X, “Effect of pH, ionic strength and humic substances on the adsorption of Uranium (VI) onto Na-rectorite,” J. Radioanal. Nucl. Ch. Hungary, vol. 287, pp. 557-565, October 2010.

[10] Setshedi. K. Z, Bhaumik. M, Songwane. S, Onyango. M. S, and Maity. A, “Exfoliated polypyrrole-organically modified montmorillonite clay nanocomposite as a potential adsorbent for Cr(VI) removal,” Chem. Eng. J. Switzerland, vol. 222, pp. 186-197, February 2013.

[11] Chen. J, Hong. X, Xie. Q, Li. D, and Zhang. Q, “Sepiolite Fiber Oriented-Polypyrrole Nanofibers for Efficient Chromium(VI) Removal from Aqueous Solution,” J. Chem. Eng. Data. United States, vol. 59, pp. 2275-2282, May 2014.

[12] Ballav. N, Choi. H. J, Mishra. S. B, and Maity. A, “Polypyrrole-coated halloysite nanotube clay nanocomposite: Synthesis, characterization and Cr(VI) adsorption behaviour,” Appl. Clay. Sci. Amsterdam, vol. 102, pp. 60-70, October 2014.