Study on adsorption of Pb(II) and Cr(VI) by MMT/St-g-P(DMC-AA)

Caining Zhang, Xuman Wang*

School of Materials Science and Engineering, Xi’an Polytechnic University, Xi’an, People’s Republic of China

*Corresponding author’s e-mail: wangxuman@163.com

Abstract. By applying methacryloyloxyethyl trimethyl ammonium chloride (DMC) and acrylic acid (AA) as the monomers, starch (St) as the main chain polymer, the composite MMT/St-g-P(DMC-AA) was prepared. Applied the composite as the adsorbent, Pb(NO₃)₂ (Pb(II)) and K₂CrO₇ (Cr(VI)) as the adsorbates, the effects of adsorption time and the initial heavy metal ions concentrations on the adsorption capacities were studied. The adsorption data were evaluated by adsorption kinetics models. The experimental results showed that the adsorption capacities for heavy metal ions increased with the increasing of adsorption time, and then saturated after 60 min. And adsorption capacities for Pb(II) and Cr(VI) were 140.79 mg/g and 32.25 mg/g, respectively. The adsorption capacities also increased with the increase of initial concentrations. The adsorption data of Pb(II) and Cr(VI) by MMT/St-g-P(DMC-AA) were well described by the pseudo-second-order kinetic model.

1. Introduction

Industrial wastewater is the main water pollution source, and a major environmental concern. Especially the heavy metals such as Cr, Pb, Cd and Hg in wastewater have caused serious harm to human health and the environment because of their toxicity and accumulation in living body[1]. Among many wastewater treatment methods, adsorption is the more effective method, due to its low-cost and high removal efficiency. Montmorillonite (MMT) and its modified products were widely applied as adsorbents to deal with heavy metals wastewater[2]. In order to be easily separated from water, MMT must be embedded into polymer network. Some polymers, such as polyacrylamide and poly(vinyl alcohol) were used. However, these polymers would decrease the adsorptive capacity of MMT. Due to their low degradability, polymers would lead to secondary pollution. As a natural source polymer, St has attracted considerable scientific attention owning to its advantages of low cost, nontoxicity and biodegradability[3]. Accordingly, St derivatives used as adsorbents to remove heavy metals have been attracting increasing research interest in recent years[4]. In this study, MMT/St-g-P(DMC-AA) composite was fabricated. The effects of the initial concentrations of heavy metal ions and adsorption time on the adsorption capacities of MMT/St-g-P(DMC-AA) were studied. The adsorption data were evaluated by adsorption kinetics models. Meanwhile, the adsorption mechanism was preliminarily studied.
2. Materials and methods

2.1 Materials and reagents
Chemicals were generally reagent grade and purchased from Xi'an Reagent Company. Water was deionized, doubly distilled.

2.2 Preparation of MMT/St-g-P(DMC-AA)
2 g St was dispersed in 100 mL MMT water dispersion which contained 2 g MMT, and then gelatinized for 1 h at 90 °C. After the resulting mixture was cooled to 60 °C, 2 g DMC, 2 g AA, 70 mg ammonium persulfate and 70 mg N,N'-methylene-bis-acrylamide were added and reacted for 24 h at 60 °C. The product was washed 6 times with water and air dried for 16 h at 55 °C.

2.3 Batch Adsorption Studies
Batch experiments were performed to investigate the adsorption behaviors of Pb(II) and Cr(VI) from aqueous solution using MMT/St-g-P(DMC-AA). Those samples shook at 298 K after mixed thoroughly, and then were centrifuged at 5000 rpm for 10 min. The adsorbate concentrations in the aqueous phase were analyzed by atomic absorption spectrophotometry (Sollar M6, Thermo, US). The adsorption capacity of heavy metal ions by MMT/St-g-P(DMC-AA) at equilibrium, \( q_e \) (mg/g) was calculated by using the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \( C_0 \) is the initial concentration (mg/L), \( C_e \) is the equilibrium concentration (mg/L), \( m \) is the mass (g) of adsorbent used and \( V \) is the volume of metal ions solution used (L).

3. Results and discussion

3.1 The effect of adsorption time on the adsorption capacities
The effect of adsorption time on the adsorption capacities was studied, and the result was demonstrated in figure 1. With the increasing of adsorption time, the adsorption capacities for both metal ions first rapidly increased, and then gradually increased until equilibrium was reached. The adsorption time required of Pb(II) and Cr(VI) to reach equilibrium was 60 min. Furthermore, the equilibrium adsorption capacities for Pb(II) and Cr(VI) were 140.79 mg/g and 32.25 mg/g, respectively. These results indicated that the prepared MMT/St-g-P(DMC-AA) was an excellent adsorbent for the removal of heavy metals from water.

![Figure 1. The effect of adsorption time on the adsorption capacities.](image-url)
3.2 The effect of the initial heavy metal ions concentrations on the adsorption capacities

The effect of the initial heavy metal ions concentrations on the adsorption capacities was investigated. As shown in figure 2, adsorption capacities for Pb(II) and Cr(VI) increased with initial concentrations. This meant that the adsorption process of Pb(II) and Cr(VI) was concentration dependent. Due to the higher initial concentrations of heavy metal ions, more greater driving force was providing to overcome the resistance of mass transfer between the liquid and solid phases.

![Figure 2. The effect of the initial heavy metal ions concentrations on the adsorption capacity.](image)

3.3 Adsorption kinetics and mechanism

Lagergren’s pseudo-first-order model and pseudo-second-order model (equation 2 and 3) \(^{[5]}\) were used to fit the kinetic sorption experiments.

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  \hspace{1cm} (2)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm} (3)

where \(q_t\) is the amount (mg/g) of Pb(II) or Cr(VI) adsorbed on the MMT/St-g-P(DMC-AA) at time \(t\) (min), respectively. \(k_1\) and \(k_2\) are the rate constants of the pseudo-first-order kinetic model (min\(^{-1}\)) and the pseudo-second-order kinetic model [g/(mg min)], respectively.

The experimental data in figure 1 were processed and fitted with the kinetics models. The kinetics models plots for adsorption of Pb(II) and Cr(VI) on the adsorbent were shown in figure 3. And all the values of parameters and correlation coefficients (R\(^2\)) of each model obtained were tabulated in table 1. Based on the R\(^2\) values, it was found that the pseudo-second-order model obeyed better than the pseudo-first-order model for both Pb(II) and Cr(VI). And the calculated \(q_e\) (\(q_{e,cal}\)) values fitted well with the experimental \(q_e\) (\(q_{e,exp}\)) values. These results indicated that adsorption of Pb(II) and Cr(VI) on MMT/St-g-P(DMC-AA) was chemical adsorption process.
Figure 3. Linear fitting of kinetic sorption experiments data using of the pseudo-first-order model (a) and pseudo-second-order model (b) for adsorption of Pb(II) and Cr(VI) on the adsorbent.

Table 1. Pseudo-first-order model and pseudo-second-order model parameters for the adsorption of Pb(II) and Cr(VI) on the adsorbent.

|          | Pseudo-first-order model | Pseudo-second-order model |
|----------|--------------------------|---------------------------|
|          | $k_1$ (min$^{-1}$)       | $q_{e,cal}$ (mg/g) | $R^2$ | $k_2$ [g (mg/min)] | $q_{e,cal}$ (mg/g) | $R^2$ |
| Pb(II)   | 0.047                    | 38.97                    | 0.96  | 140.79            | 0.0031              | 142.85 | 0.98  |
| Cr(VI)   | 0.049                    | 44.42                    | 0.79  | 32.25             | 0.0013              | 36.54  | 0.97  |

Generally, the adsorption mechanism of metal ions on adsorbents includes electrostatic attraction, ion exchange, coordination bonding, etc[6]. In water solution, Pb(II) and Cr(VI) usually exist in positive ion and negative ion forms, respectively. According to the composition of MMT/St-g-P(DMC-AA), there are hydroxyl, carboxyl, carbonyl groups, and quaternary ammonium salt cations on the surface of MMT/St-g-P(DMC-AA).

In order to further explore the adsorption mechanism, the zeta potentials of MMT/St-g-P(DMC-AA) were determined, and shown in figure 4. The pH value for zero charge of MMT/St-g-P(DMC-AA) was found to be 4.08. And the pH values of Pb(NO$_3$)$_2$ and K$_2$CrO$_7$ solutions were determined to be 5.81 and 5.32, respectively. Hence, the charge sign on the adsorbent surface was negative in the Pb(II) and Cr(VI) water solutions. As a result, the adsorbent possessed a better affinity towards Pb$^{2+}$ (Pb(II)) by the means of electrostatic attraction, while the affinity towards CrO$_7^{2-}$ (Cr(VI)) was worse. This was the reason why the adsorption capacity for Pb(II) was greater than that of Pb(II). However, Cr(VI) still showed considerable adsorption capacity, indicated the electrostatic attraction did not solely control the adsorption of the metal ions on MMT/St-g-P(DMC-AA).

As a heavy metal ion, Cr(VI) could adsorb on the MMT/St-g-P(DMC-AA) by the coordination bonding with oxygen-containing surface groups, such as carboxyl, hydroxyl and carbonyl groups[7]. And Pb(II) could also adsorb on the adsorbent by the coordination bonding with hydroxyl and carboxyl groups[8]. Moreover, MMT is a kind of layered silicate mineral carrying exchangeable cations, so Pb(II) could adsorb on the adsorbent by ion exchange[9].

Based on the above analysis, the possible adsorption mechanisms of Pb(II) and Cr(VI) on MMT/St-g-P(DMC-AA) included electrostatic interaction, coordination bonding, and ion exchange. In this study, MMT/St-g-P(DMC-AA) showed excellent adsorption capacity of 140.79 mg/g for Pb(II) and 32.25 mg/g for Cr(VI). This was caused by the multiple adsorption interaction mechanisms. It suggested that MMT/St-g-P(DMC-AA) could be used to remove cationic and anionic heavy metal ions from the wastewater.
4. Conclusions
The adsorption capacity of Pb(II) and Cr(VI) by MMT/St-g-P(DMC-AA) increased with the increasing of adsorption time, and then saturated after 60 min. And adsorption capacities for Pb(II) and Cr(VI) were 140.79 mg/g and 32.25 mg/g, respectively. The adsorption capacities of Pb(II) and Cr(VI) by MMT/St-g-P(DMC-AA) increased with the increasing of initial concentrations. The adsorption data of Pb(II) and Cr(VI) by MMT/St-g-P(DMC-AA) were well described by the pseudo-second-order kinetic model. The as-prepared MMT/St-g-P(DMC-AA) could be used as an effective adsorbent for the removal of heavy metals from the wastewater.

Acknowledgements
This work was supported by China National Textile and Apparel Council (grant number 2018039).

References
[1] Samiey B., Cheng C. H., Wu J. (2014) Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: a review. Materials, 7: 673-726.
[2] Bahadur Y. V., Ranu G., Sippy K. (2019) Clay based nanocomposites for removal of heavy metals from water: a review. J. Environ. Manage., 232: 803-817.
[3] Madhumitha G., Fowsiya J., Roopan S.M., Thakur V.K. (2018) Recent advances in starch-clay nanocomposites. Int. J. Polym. Anal. Charact., 23: 331-345.
[4] Xie Y., Zhang B., Li M., Chen H. (2019) Effects of cross-linking with sodium trimetaphosphate on structural and adsorptive properties of porous wheat starches. Food Chem., 289: 187-194.
[5] Qiu H., Pan L. L., Zhang Q. J., Zhang W., Zhang Q. (2009) Critical review in adsorption kinetic models. J. Zhejiang Univ. Sci., 10: 716-724.
[6] Srivastava S., Agrawal S. B., Mondal M. K. (2015) A review on progress of heavy metal removal using adsorbents of microbial and plant origin. Environ. Sci. Pollut. Res., 22:15386-15415.
[7] Zhang J., Chen S., Zhang H., Wang X. (2017) Removal behaviors and mechanisms of hexavalent chromium from aqueous solution by cephalosporin residue and derived chars. Bioresource Technol., 238: 484-491.
[8] Peng S., Liu Y., Xue Z., Yin W., Liang X., Li M., Chang J. (2017) Modified nanoporous magnetic cellulose-chitosan microspheres for efficient removal of Pb(II) and methylene blue from aqueous solution. Cellulose, 24: 4793-4806.
[9] Zhu S., Xia M., Chu Y., Khan M.A., Lei W., Wang F., Muhmood T., Wang A. (2019) Adsorption and desorption of Pb(II) on l-lysine modified montmorillonite and the simulation of interlayer structure. Appl. Clay Sci., 169: 40-47.