Heavy Metals Removal from Solution by Polyaniline/Palygorskite Composite

Yong Kong,[1] Jingxuan Wei,[1] Zhiliang Wang,[2] Tao Sun,[1] Chao Yao,[1] Zhidong Chen[1]

[1]*Faculty of Chemistry and Chemical Engineering, Changzhou University, Changzhou 213164, China*
[2]*Jiangsu Provincial Academy of Environmental Science, Nanjing 210036, China*

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ABSTRACT: Batch adsorption experiments were carried out to remove heavy metal ions such as Cu (II), Ni (II), Cd (II), and Cr (VI) from single-metal solutions using a polyaniline/palygorskite (PP) composite. Different parameters affecting the adsorption capacity such as contact time and pH of the solution have been investigated. The structural characteristics of the PP composite were studied in this work. Atomic absorption spectroscopy was used for the measurement of heavy metal contents, and the adsorption capacity (q_e) calculated were 114 mg Cu (II) g^{-1}, 84 mg Ni (II) g^{-1}, 56 mg Cd (II) g^{-1}, and 198 mg Cr (VI) g^{-1} under optimal conditions. The removal of the metal ions from solutions was assigned to chelation, ionic exchange, and electrostatic attraction. Data from this study proved that the novel organic/inorganic composite presents great potential in the recovery and elimination of noble or heavy metal ions from industrial wastewater. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2054–2059, 2011

Key words: palygorskite; polyaniline; composite; adsorption; heavy metal ions

INTRODUCTION

Removal of heavy metal ions such as Cu (II), Ni (II), Cd (II), Cr (VI), and Pb (II) from aqueous solutions is necessary because of the frequent appearance of these metal ions in wastewater from many industries, such as metal plating, tannery, mining, and chemical manufacturing.[1] The conventional methods for heavy metal ions removal from wastewater include chemical precipitation, ionic exchange, filtration, etc. In the last few years, adsorption has been shown to be an alternative method for removing dissolved metal ions from wastewater[2] and the use of various adsorbents such as coal,[3] natural zeolites,[4] peat,[5] mica,[6] and kaolin[7] has been intensively reported.

Palygorskite is a crystalline hydrated magnesium silicate with fibrous morphology, large specific surface area, and moderate cationic exchange capacity. It is a 2 : 1 mineral with one octahedral layer and two silica-oxygen layers, and layers are held together by van der Waals forces. Palygorskite has been used for adsorption of organic substances[8] and heavy metal ions[9–11] from solutions.

Recently, the application of conducting polymers has been proposed for environmental remediation.[12–14] In particular, polyaniline (PANI) is being considered for the removal of heavy metal ions because it possesses chelating properties attributed to the electron donating groups (amine and secondary amino groups) on the polymer chains. Thus, PANI exhibits a potential application as an adsorbent for the removal of heavy metal ions from aqueous solutions.

Obviously, palygorskite and PANI can be combined together and one can take the advantage of the reactive functionalities of the PANI/palygorskite (PP) composite for the removal of hazardous heavy metal ions from wastewater without having to use an external energy source. So, in this study, the PP composite was synthesized and used to remove heavy metal ions from single-metal solutions. The adsorption conditions of Cu (II), Ni (II), Cd (II), and Cr (VI) have been investigated and the structural characteristics of the composite were evaluated in this article.

Correspondence to: Z. D. Chen (czd_chen@yahoo.com.cn).

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EXPERIMENTAL

Materials and reagents

Palygorskite was obtained from Jiangsu NDZ Technology Company (Changzhou, China) and washed with distilled water to remove impurity and dried at room temperature. Aniline (>99.5%) was purchased from Fluka Company and distilled under reduced pressure before use. The stock solutions (500 mg L^{-1}) of Cu (II), Ni (II), Cd (II), and Cr (VI), prepared by dissolving $CuSO_4$, $NiSO_4$, $CdCl_2$, and K_2CrO_4 in distilled water respectively, were taken as the adsorptive solutions. Other agents used, such as NaOH, HCl, $(NH_4)_2S_2O_8$, were all of analytical grade.

Scanning electron microscope (SEM) observation of the PP and PANI was carried out with a JSM-6360LA SEM instrument. Fourier transform infrared (FTIR) spectra measurements were done on a Nicolet 460 spectrophotometer using KBr pellets. A model ASAP2010C surface area and porosimetry system was used to determine the specific surface area, the total pore volume, and average pore size of the PP composite and PANI.

Preparation of the polyaniline/palygorskite (PP) composite

The chemical method using the reaction between aniline and $(NH_4)_2S_2O_8$ for the synthesis of PANI powder are widely known.[15–16] In this work, palygorskite was applied as the substrate for *in situ* polymerization of aniline and thus PANI obtained was used as the coating polymer of palygorskite. The synthesis procedures were as follows: 3.4 mL freshly distilled aniline was injected in a 100 mL aqueous solution containing HCl (1.0 mol L^{-1}) and $(NH_4)_2S_2O_8$ (0.45 mol L^{-1}) and 0.7 g palygorskite was placed in the solution beforehand. The mixture was continuously stirred at room temperature for 24 h. The resulting product was filtered, washed with 0.1 mol L^{-1} HCl and distilled water, respectively, and then dried at 60°C for 48 h, producing a dark green product. For comparative purpose, PANI was synthesized according to the same procedures without adding palygorskite.

It could be concluded that PANI acted as a binding agent of the palygorskite particles during the preparation process. Hence the preparation of the PP composite was achieved by the means of an *in situ* polymerization of aniline onto the surface of the palygorskite particles. Finally, the prepared composite was stocked in a desiccator ready for adsorption test.

Adsorption studies

Adsorption experiments were performed in batch equilibrium mode. All experiments were carried out by placing 0.05 g PP composite into 50 mL single-metal solutions. The mixtures were agitated at 200 rpm at room temperature for different contact time. Then the PP composite and the liquid were separated by filtration and a sample of the filtrate was analyzed by a model SP-3520 atomic absorption spectrometer (AAS) (China). The pH values of the initial solutions were adjusted with dilute NaOH or HCl by using a model pHs-2C pH meter. The adsorption capacity of the PP composite for heavy metal ions was calculated according to the following equation:

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

where q_e is the adsorption capacity for metal ions on the composite (mg g^{-1}), V is the volume of the single-metal solution, C_0 is the initial concentration of the metal ions (mg L^{-1}), C_e is the equilibrium concentration of the metal ions (mg L^{-1}), and m is the mass of the composite used (g). All assays were carried out in triplicate and only mean values were presented.

RESULTS AND DISCUSSION

Morphology of the PP composite

For comparison, SEM images of the PP composite and PANI are presented in Figure 1. PANI, prepared without adding palygorskite, possesses a loose, porous, and coral-like microstructure [Fig. 1(a)]. However, a microstructure consisting of fibers and particles appeared on the SEM image of the PP composite [Fig. 1(b)]. The appearance of microfibers was attributed to the palygorskite existing in the composite, because our previous research had pointed out that the palygorskite particles consisted of many gracile and compact fiber-like crystal bundles.[17] It was obvious that PANI was introduced into the PP composite as the shell surfaces of palygorskite, and the resulting composite had combined the advantages of PANI and palygorskite.

Analysis of the PP composite by FTIR

Curve a of Figure 2 is the FTIR spectrum of the PP composite. A strong peak at 3446 cm^{-1} which also appeared in the FTIR spectrum of PANI was attributed to the *N*-H stretching vibrations in aniline, since the stretching vibrations of the *N*-H bond in aromatic amines are in the range of 3400–3000 cm^{-1}.[18] The peaks at 1563 cm^{-1} and 1482 cm^{-1} were assigned to the C=C stretching vibrations of the quinone ring and benzene ring, respectively. The peak at 1237 cm^{-1} was attributed to the C—N stretching

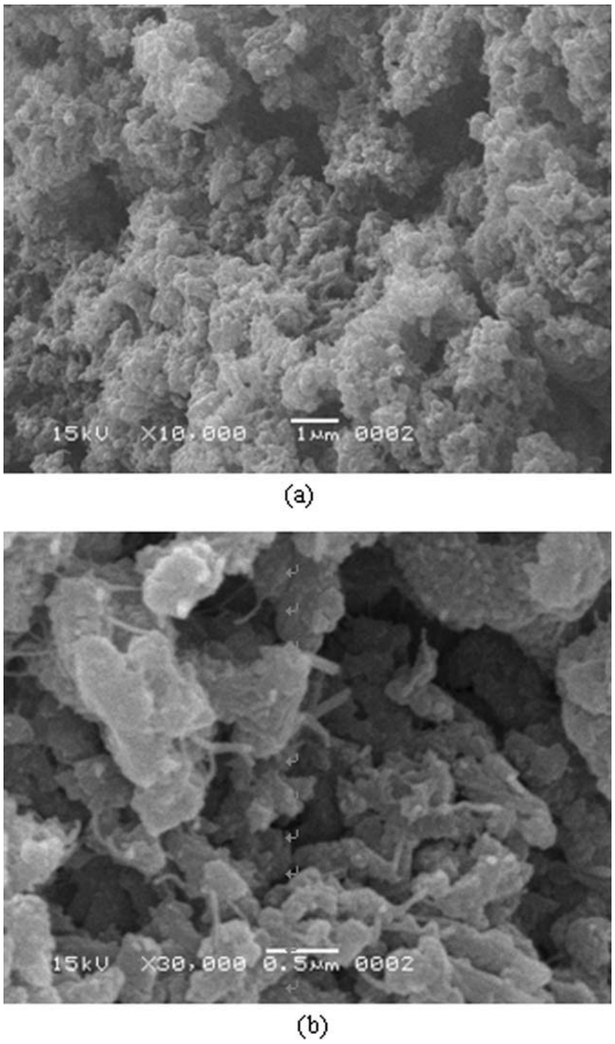


Figure 1 SEM micrographs of PANI (a) and the PP composite (b).

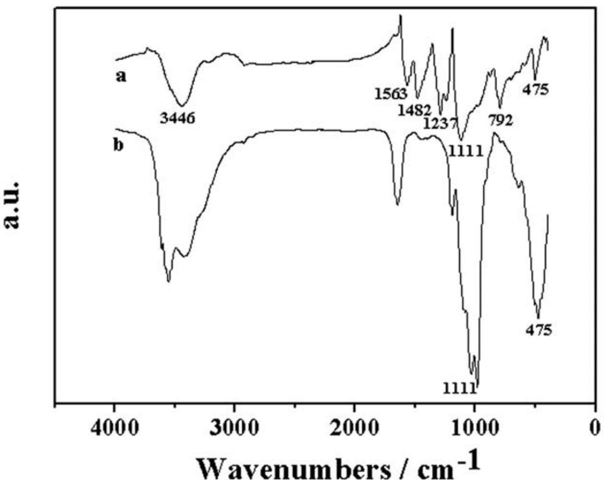


Figure 2 FTIR spectra of the PP composite (a) and palygorskite (b).

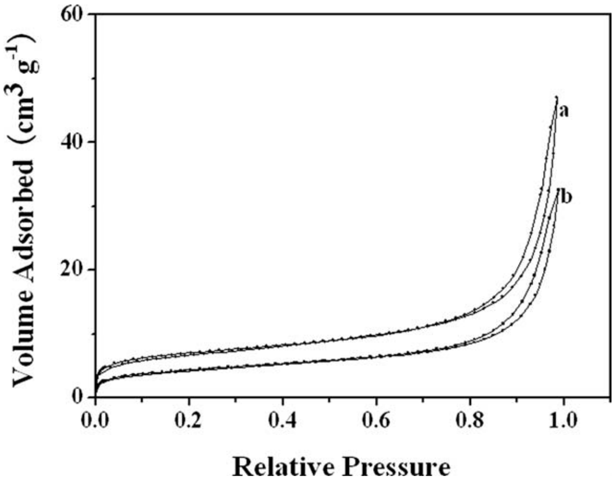


Figure 3 N_2 adsorption-desorption isotherms of the PP composite (a) and PANI (b) at 77 K.

vibrations, because the C—N stretching vibrations in aromatic amines are in the range of 1280–1180 cm^{-1}.[19] The peak at 792 cm^{-1} was assigned to the C—H out-of-plane bending vibrations. However, the peaks at 475 and 1111 cm^{-1} were not the characteristic peaks of PANI and they must be caused by the palygorskite in the composite, which was proved by the FTIR spectrum of palygorskite (Curve b). The peak at 1111 cm^{-1} was attributed to the stretching vibrations of Si—O—Si bonds which exist in palygorskite and the peak at 475 cm^{-1} was assigned to the bending vibrations of Si—O—Si bonds.[20] The PP composite possessed functional groups of PANI and palygorskite, and therefore its adsorption capacity was considered to be better than that of PANI or palygorskite.

Adsorption isotherms

The equilibrium adsorption isotherm is an important parameter to understand the mechanism of adsorption systems. Hence, N_2 adsorption–desorption isotherms of the PP composite and PANI at 77 K were measured to study the adsorption effects of the composite (Fig. 3). The shapes of the two isotherms were similar, which were of the typeII by IUPAC classification.[21,22] The typeII isotherm is characteristic for both macroporous and nonporous adsorbents. At relative pressure higher than 0.8, a broad hysteresis loop was observed for both the composite and PANI, which was ascribed to the development of mesoporosity. The volume of N_2 adsorbed by the PP composite was much larger than that by PANI at the same relative pressure, which suggested that the PP composite had larger adsorption capacity than PANI. Other parameters for the isotherms were shown in Table I.

TABLE I
The Parameters for the Isotherms of N_2 Adsorbed on the PP Composite and PANI at 77K

Isotherms parameters	PP	PANI
Specific surface area ($m^2\ g^{-1}$)	22.8	14.6
Total pore volume ($cm^3\ g^{-1}$)	0.03	0.01
Average pore size (Å)	127.7	137.7

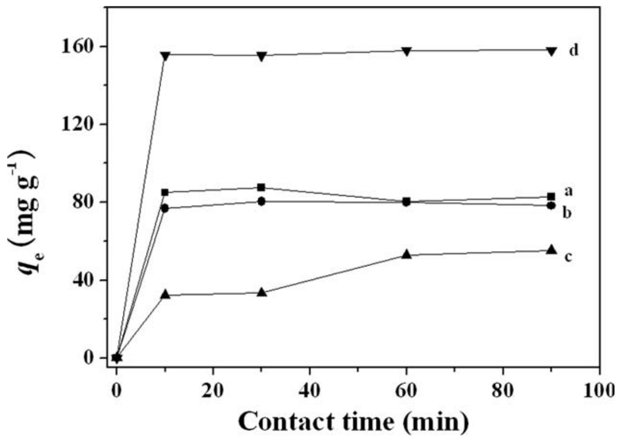


Figure 4 Effect of contact time on the adsorption of Cu (II) (a), Ni (II) (b), Cd (II) (c), and Cr (VI) (d) onto the composite.

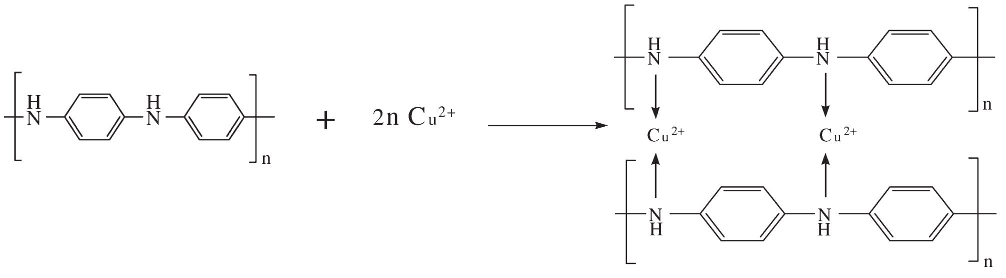
Effect of contact time

The time-dependent adsorption behavior of Cu (II), Ni (II), Cd (II), and Cr (VI) were measured for given initial concentrations of the solutions (500 mg L^{-1}; Fig. 4). The pHs were kept at 5.0 for Cu (II) and Ni (II) single-metal solutions, while for Cd (II) and Cr (VI) solutions, the pHs were kept at 3.0. The equilibrium was reached quickly for Cu (II), Ni (II), and Cr (VI) (only 10 min), indicating that the active sites of the composite were well exposed. However, the equilibrium needed for Cd (II) was much longer (60 min).

Potgieter et al.[1] reported that the adsorption capacity were 30.7 mg Cu (II) g^{-1}, 33.4 mg Ni (II) g^{-1} and 58.5 mg Cr (VI) g^{-1}, when only palygorskite was used as the adsorbent. However, in this work, the adsorption capacity for the metal ions from single-metal solutions were improved a lot with the PP composite as the adsorbent, which were 114 mg Cu (II) g^{-1}, 84 mg Ni (II) g^{-1}, and 198 mg Cr (VI) g^{-1}, respectively. The difference in the adsorption capacity was attributed to the existence of PANI in the composite. When only palygorskite was used, the removal of the metal ions was caused by ionic exchange and electrostatic attraction (physical adsorption) between the metal ions and palygorskite. On the one hand, palygorskite carries a net negative charge due to the broken bonds around the edges of the Si-Al units that would give rise to unsaturated charges, which would be balanced by the adsorbed metal ions. The strong electrostatic attraction between the positive adsorbate species and the palygorskite particles would lead to adsorption of metal ions.[23] On the other hand, ionic exchange between heavy metal ions and the cations within palygorskite could be represented by Eq. (1), taking Cu (II) as an example:

$$\begin{aligned}\text{Palygorskite}(M^{n+}) + Cu^{2+} &\leftrightarrow \text{Palygorskite}(Cu^{2+})\\ &+ M^{n+}(M\\ &= \text{Mg, K, Ca, Na, etc.})\end{aligned} \tag{1}$$

When the PP composite was used as the adsorbent, the third removal mechanism of chelation existed simultaneously. The PANI chains contained amine and secondary amino groups which acted as linkages between the benzene rings and the metal ions, as shown in Eq. (2). Hence, the adsorption capacity for heavy metal ions could be improved a lot when the PP composite was used as the adsorbent. The improvement of adsorption behavior of the PP composite in comparison with other adsorbents were shown in Table II. As can be seen, the adsorption capacity of the PP composite was superior to that of other adsrbents.



(2)

TABLE II
Comparison of Different Adsorbents for Removal of Metal Ions

	Adsorption capacity (mg g^{-1})				
Adsorbent	Cu (II)	Ni (II)	Cd (II)	Cr (VI)	References
Palygorskite		33.4	58.5	30.7	1
Crosslink cationic starch				97.08	24
Acid activated palygorskite	32.24				25
Expanded perlite	8.62				26
Activated carbon	24.21	27.21	33.57	34.70	27
PANI	92	64	19	101	This article
PP	114	84	56	198	This article

In addition, by comparing the adsorption capacity for Cu (II), Ni (II), Cd (II), and Cr (VI) displayed in Figure 4(a–d), the adsorption of metal ions from the single-metal solutions was in the order: Cr > Cu ≈ Ni > Cd, and the adsorption capacity for Cr (VI) was much larger than other metal ions. The differences of adsorption capacity between Cr (VI) and other metal ions could be attributed to the fact that Cr (VI) is not a hexavalent chromium cation but occurs as chromate/dichromate anion interacting with the adsorbent, which is quite different from other metal cations.

Effect of pH on metal ions removal

The pH of the solution was an important parameter which affected the adsorption of the metal ions at the composite–water interfaces and therefore the influence of pH on the adsorption of Cu (II), Ni (II), Cd (II), and Cr (VI) onto the PP composite was investigated in the pH range of 1–7. Because precipitation of metal hydroxides may occur when the pH rises above 7, the experiments on the effect of pH were only carried out in acidic and neutral single-metal solutions.

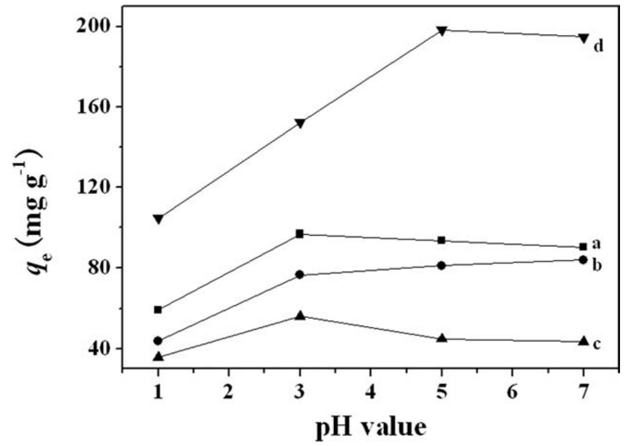


Figure 5 Effect of pH value on the adsorption of Cu (II) (a), Ni (II) (b), Cd (II) (c), and Cr (VI) (d) onto the composite.

For Cu (II), Ni (II), Cd (II), and Cr (VI), the effect of pH on the adsorption capacity followed a similar trend (Fig. 5). At low pH values, the PP composite exhibited a low adsorption capacity. This might be caused by two reasons. On the one hand, at low pH values where there was an excess of H$^+$ ions in solution, a competitive adsorption existed between the positively charged H$^+$ ions and the metal ions for the same active adsorptive sites, which would result in the suppression of the metal ions adsorption onto the composite. On the other hand, at low pH values, the functions of PANI in the composite were protonated, which would cause a cationic repulsion between the metal ions and the protonated PANI units in the composite. As the pH increased, the composite surface became less positive due to the decrease of proton competitive adsorption and the deprotonation of PANI and therefore ionic exchange and electrostatic attraction between the metal ions and the PP composite were likely to be increased. The adsorption capacity remained almost constant or decreased slightly as the pH became higher than 3 (for copper, nickel, and cadmium) or 5 (for chromium).

Again, it was found that the adsorption capacity for Cr (VI) is much larger than other metal ions at the same pH values.

Comparison of the adsorption capacity of the PP composite and PANI

The adsorption capacity of the PP composite and PANI for metal ions were also shown in Table II. As could be seen, when the PP composite was used as an adsorbent, the adsorption capacity for metal ions was much larger than that with PANI as an adsorbent. The differences in the adsorption capacity could be attributed to the different removal mechanism of metal ions. When PANI was used as an adsorbent, only chelation existed between metal ions and PANI. However, three removal mechanisms, chelation, ion exchange, and electrostatic attraction existed simultaneously when the PP composite was used as an adsorbent. As a result, the adsorption capacity of the PP composite was larger than that of PANI.

CONCLUSIONS

This study proved that toxic heavy metals could be efficiently removed from single-metal solutions by the PP composite. Both contact time and pH affected the adsorption capacity of the PP composite. The adsorption of metal ions was caused by chelation, ionic exchange, and electrostatic attraction, which existed simultaneously during the adsorption process. According to the calculated adsorption capacity for Cu (II), Ni (II), Cd (II), and Cr (VI), it was concluded that the PP composite could be used as an effective adsorbent for the removal of heavy metal ions from aqueous solutions. The novel organic/inorganic composite has great potential in the recovery and elimination of noble or heavy metal ions from industrial wastewater.

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