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Application of polyaniline and multiwalled carbon nanotube magnetic composites for removal of Pb(II)

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ABSTRACT

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Keywords: Sorption Pb(II) Plasma technique Polyaniline Carbon nanotubes Aniline molecules were polymerized and formed polyaniline (PANI) on multiwalled carbon nanotubes (MWCNTs) by using plasma induced polymerization technique. The PANI modified MWCNTs (PANI/MWCNTs) composites were characterized by using ultraviolet–visible spectrophotometry, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis–differential thermal analysis (TGA–DTA), field-emission scanning electron microscopy (FE-SEM), and vibrating sample magnetometer (VSM). The results indicated that the PANI/MWCNTs magnetic composites were synthesized. The application of PANI/MWCNTs magnetic composites for the removal of Pb(II) from aqueous solutions was investigated under ambient conditions. The modified PANI on MWCNT surfaces contributed to the enhancement of MWCNT adsorption capacity because the amine and imine functional groups of PANI have strong affinity with Pb(II) ions. PANI/MWCNTs magnetic composites can be separated and recovered from aqueous solution by simple magnetic separation. The results show that PANI/MWCNTs magnetic composites are promising magnetic materials for the preconcentration and separation of heavy metal contaminants from large volumes of aqueous solutions in environmental pollution cleanup.

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1. Introduction

Water pollution caused by heavy metal ions (such as Pb(II)) is a crucial worldwide environmental problem with significant effect on human health and environment [1]. The abatement of heavy metal contaminants from aqueous solution, even drinking water, has become a very pressing issue to the whole world for their great environmental toxicity. Adsorption has been recognized as a promising and cost-effective technique for the treatment of wastewater with trace levels of heavy metal contaminants.

Multiwalled carbon nanotubes (MWCNTs) and surface modified MWCNTs have been considered as very suitable materials in the removal of organic and inorganic pollutants from aqueous solutions because of their high adsorption capacity and many outstanding and remarkable properties [1–3]. However, it is difficult to separate MWCNTs from aqueous solutions by using traditional methods (such as centrifugation and filtration) because of their small size. The application of magnetic materials has attracted much attention because of their easy separation from large volumes of aqueous solutions by simple magnetic technique after usage [4].

Due to its outstanding stability in acidic solution, organic magnetic materials have attracted considerable attention and are viewed as a promising substitute for metal and metal oxide based magnetic materials. Among them, polyaniline (PANI) is one of the most attractive magnetic polymers because of its excellent chemical stability, easy synthesis [5–10], and excellent magnetic property [11]. Because the large amount of amine and imine functional groups of PANI are expected to have strong affinity with metal ions, PANI can enrich and remove heavy metal contaminants from aqueous solutions easily and effectively [10,12,13]. A great deal of attention was given to the deposition of PANI onto various materials to extend its application [14,15]. Considering the promising magnetic property of PANI and excellent adsorption capacity of MWCNTs, PANI/MWCNTs magnetic composites might be an attractive material in the removal of heavy metal contaminants from large volumes of aqueous solutions.

Comparing to conventional chemical methods, plasma technique has many advantages in surface modification of various materials. Nastase et al. [16] also modified singlewalled carbon nanotubes with PANI by using plasma induced polymerization technique and studied its electrical properties. Herein, MWCNTs were modified with PANI by using plasma induced polymerization technique to synthesize PANI/MWCNTs magnetic composites. The prepared PANI/MWCNTs magnetic composites were characterized by ultraviolet–visible (UV–vis) spectrophotometry, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis–differential thermal analysis (TGA–DTA), field-emission scanning electron microscopy (FE-SEM), and vibrating sample

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magnetometer (VSM). The prepared PANI/MWCNTs magnetic composites were applied to adsorb and to enrich Pb(II) from aqueous solutions to evaluate its application in the removal of heavy metal contaminants from large volumes of aqueous solutions in environmental pollution cleanup.

2. Experimental

2.1. Plasma induced polymerization procedure

Plasma induced polymerization of aniline molecules on MWC-NTs was composed of two successive processes, namely, the surface activation of MWCNTs and polymerization of aniline. First, 1.0g of MWCNTs was activated by using N2 plasma (gas pressure of 10 Pa, power of 100 W and voltage of 940 V) in a custom-built reactor for 40 min under continuous stirring to form active species on MWCNT surfaces. The N₂ plasma treated MWCNTs were denoted as MWCNTs-treat. Then, 80 mL of 20 g/L aniline aqueous solution (50°C) was immediately injected into the reactor, and the activated MWCNTs were reacted with aniline at 50 °C for 24 h under N₂ protection and continuous stirring. In the second process, aniline molecules were polymerized and formed PANI on MWCNT surfaces. The derived sample was repeatedly rinsed with Milli-Q water until no aniline was detected by using high performance liquid chromatography-mass spectrometry methods in the supernatant. Finally, the sample was dried in oven at 95 °C for 24 h, and thus, PANI/MWCNTs magnetic composites were obtained.

2.2. Characterization

PANI/MWCNTs magnetic composites were characterized by UV-vis, XPS, TGA-DTA, FE-SEM, and VSM in detail. A magnetic curve was obtained by using a model 155 vibrating sample magnetometer at room temperature. The morphological structures of PANI/MWCNTs were determined by SEM using a field emission scanning electron microscope (FEI Sirion 200 FEG SEM). The XPS measurements were performed with an ESCALab220i-XL surface microanalysis system (VG Scientific) equipped with an Al Ka (hv = 1486.6 eV) source. UV-vis spectrophotometer analyses were carried out by using a Shimadzu 2550 UV-vis spectrophotometer. Because MWCNTs deposited easily in water, MWCNT were first sonicated in Milli-Q water for 10 h and then UV-vis measurements were carried out. TGA-DTA measurements were examined by using a Shimadzu TGA-50 thermogravimetric analyzer from room temperature to 800 °C with heating rate of 10 °C/min and an air flow rate of 50 mL/min. Magnetic curves were obtained using a model 155 VSM at room temperature, and its measurement range is 0 to ± 20.0 kOe.

2.3. Adsorption of Pb(II) on PANI/MWCNTs and MWCNTs

In order to evaluate the effect of modified PANI on MWCNT adsorption capacity and the application of PANI/MWCNTs magnetic composites in real work, the adsorption of Pb(II) from aqueous solution on PANI/MWCNTs magnetic composites and on MWC-NTs were studied by using batch technique at $T=20\pm1$ °C. The stock suspension of adsorbents, NaClO₄, and Pb(II) solutions were added into polyethylene test tubes to achieve the desired concentrations of different components. The pH values of suspensions were adjusted by adding negligible volumes of 0.1 or 0.01 mol/L HClO₄ or NaOH. For the consistency principle, after the suspensions were shaken for 24 h, the solid phase was separated from the liquid phase by centrifugation at 18000 rpm for 60 min, and then the supernatant was filtered using 0.45 μ m membrane filters.

The concentration of Pb(II) in filtrates were analyzed by chlorophosphonazo III spectrophotometric method at 616 nm. All the experimental data were the average of duplicate determinations, and the average uncertainties were <5%. The adsorption percent (%) of Pb(II) on PANI/MWCNTs magnetic composites and MWCNTs were calculated from the difference between the initial concentration (C_0) and the final one of Pb(II) in the supernatant after centrifugation (C_e):

$$Adsorption\% = \frac{C_0 - C_e}{C_0} \times 100\%.$$
 (1)

The amount of Pb(II) adsorbed on solid phase (C_s) was calculated from the initial concentration (C_0), the final one (C_e), the volume of the suspension (V) and the mass of the adsorbent ($m_{adsorbent}$):

$$C_{\rm s} = \frac{C_0 - C_e}{m_{\rm adsorbent}} \times V. \tag{2}$$

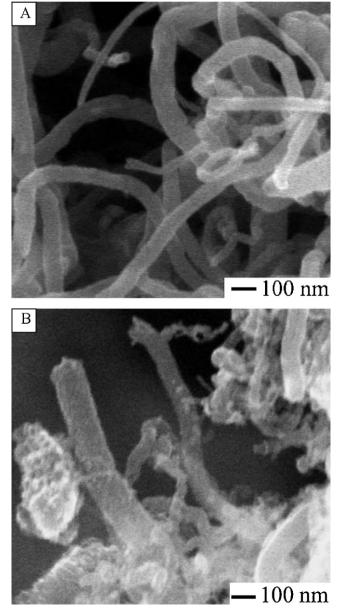


Fig. 1. SEM images of MWCNTs (A) and PANI/MWCNTs (B).

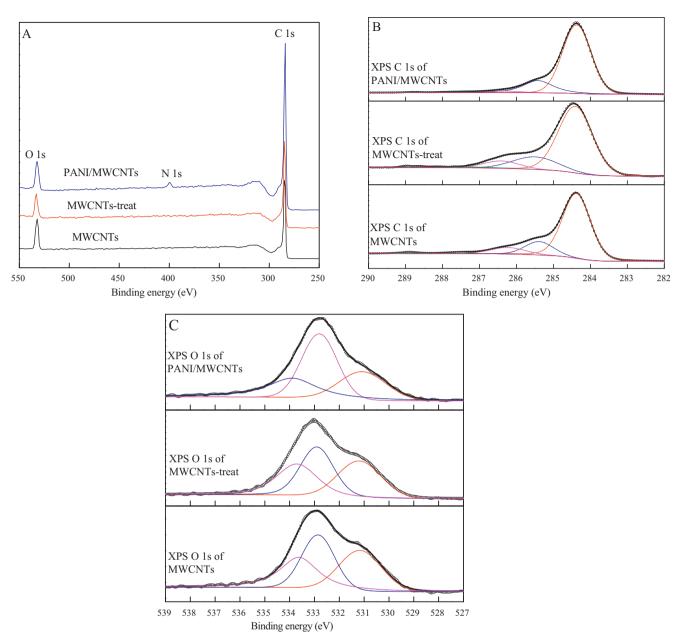


Fig. 2. XPS survey spectra (A), C 1s spectra (B), and O 1s spectra (C) of MWCNTs, MWCNTs-treat, and PANI/MWCNTs.

3. Results and discussion

3.1. Characterization of PANI/MWCNTs magnetic composites

Fig. 1 shows the typical FE-SEM images of PANI/MWCNTs magnetic composites and MWCNTs. The surfaces of MWCNTs are smooth and tidy, whereas the smooth PANI/MWCNT surfaces become rough and are attached with many new branches. This can be attributed to the modified PANI on MWCNT surfaces. Comparing to MWCNTs, PANI/MWCNTs magnetic composites have a more compact stacking morphology, which can be attributed to the strong interactions among the functional groups of modified PANI on the external wall of MWCNTs. Moreover, owing to the modified PANI, the average diameter of PANI/MWCNTs (80–100 nm) is larger than that of MWCNTs (50–70 nm), which also suggests that PANI is successfully modified on MWCNT surfaces. It is further confirmed by XPS and UV–vis characterizations.

As can be seen from Fig. 2A, it is difficult to detect the possibly introduced nitrogen atoms on MWCNT surfaces after N_2 plasma

treatment by using XPS technique. The new peak at \sim 399 eV in the XPS survey spectra PANI/MWCNTs is related to N 1s corresponding to the modified PANI on MWCNT surfaces. It is clear that aniline molecules are induced polymerization and form PANI/MWCNTs successfully after N2 plasma treatment. According to the curve fitting results of XPS C 1s spectra (multi-scan of Fig. 2A) of MWCNTs, MWCNTs-treat, and PANI/MWCNTs magnetic composites (Fig. 2B, Table 1), due to the effect of modified PANI on MWCNT surfaces, the peak fractions of hydroxyl groups (–C–OH, $286.3 \pm 0.2 \text{ eV}$) and carboxyl groups (-COO⁻, $288.8 \pm 0.2 \text{ eV}$) decrease markedly after MWCNTs are modified with PANI because plasma treatment just has an negligible effect on the peak fractions of the hydroxyl groups and carboxyl groups on MWCNT surfaces. Although parts sp²hybridized (C=C, $284.3 \pm 0.2 \text{ eV}$) [1,3] of MWCNTs are destroyed under plasma discharging conditions, the sp²-hybridized carbon of MWCNTs increases markedly after plasma induced polymerization process. It indicates that PANI is modified on the surfaces of MWC-NTs successful because PANI is a π -conjugated polymer containing an abundance of C=C bonds [5,17,18]. It is also confirmed by the

 Table 1

 Curve fitting results of XPS C 1s spectra.

Peak	BE ^a (eV)	$FWHM^{b}\left(eV ight)$	%
C=C	284.37	0.90	78.1
C—C	285.42	0.95	18.7
—С—ОН	286.33	1.10	2.19
>c=0	287.51	0.80	0.66
COO	288.81	0.50	0.39
C=C	284.41	1.08	71.6
с—с	285.50	1.43	17.3
—С—ОН	286.40	1.14	8.17
>c=0	287.40	2.22	2.01
COO	288.78	0.76	0.96
C=C	284.38	0.89	73.5
с—с	285.38	0.90	15.1
—С—ОН	286.23	1.13	8.88
>c=0	287.53	0.77	1.20
COO	288.85	1.00	1.29
	C=C C−C −C−OH >C=0 −C00 ⁻ C=C C−C −C−OH >C=0 −C00 ⁻ C=C C=C C−C −C−OH >C=0	C=C 284.37 C=C 285.42 -C=OH 286.33 >C=O 287.51 -COO ⁻ 288.81 C=C 284.41 C=C 284.41 C=C 285.50 -C=OH 286.40 >C=O 287.40 -COO ⁻ 288.78 C=C 284.38 C=C 284.38 C=C 284.38 C=C 285.38 -C=OH 286.23 >C=O 287.53	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a Binding energy.

^b Full widths at half maximum.

Table 2

Curve fitting results of XPS O 1s spectra.

	peak	BE (eV)	FWHM (eV)	%
PANI/MWCNTs	COO	531.08	2.23	26.3
	>c=0	532.80	1.68	45.2
	—С—ОН	533.89	2.4	28.5
MWCNTs-treat	COO	531.20	2.06	32.6
	>c=0	532.90	1.58	36.1
	—С—ОН	533.70	1.94	31.3
MWCNTs	COO-	531.17	2.01	33.2
	>c=0	532.85	1.56	34.5
	—С—ОН	533.62	1.83	32.3

curve fitting results of XPS O 1s spectra (multi-scan of Fig. 2A) of MWCNTs, MWCNTs-treat, and PANI/MWCNTs. As can be seen from Fig. 2C and Table 2, the peak at 531.1 ± 0.2 eV related to carboxyl groups (COO⁻) and the peak at 533.7 ± 0.2 eV related to hydroxyl groups decrease slightly after plasma treatment and also decrease markedly after MWCNTs are modified with PANI.

UV-vis characterization of PANI/MWCNTs (Fig. 3) further confirms that PANI is modified onto MWCNTs and forms PANI/MWCNTs magnetic composites successfully. The

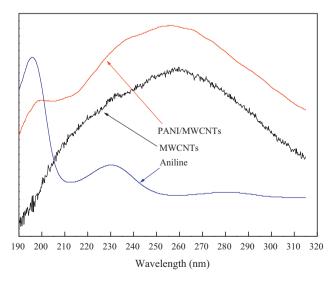


Fig. 3. UV-vis spectra of MWCNTs, aniline, and PANI/MWCNTs.

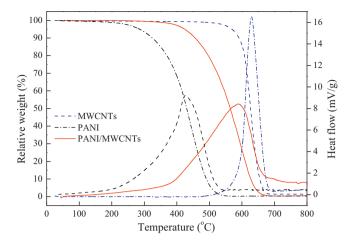


Fig. 4. TGA-DTA curves of MWCNTs, PANI, and PANI/MWCNTs.

characteristic peaks at ~198 and ~237 nm in the spectrum of PANI/MWCNTs are related to the absorbance of PANI, and the characteristic peak at ~258 nm is related to the absorbance of MWCNTs. Aniline molecule has intrinsic absorption bands in near-ultraviolet region: an intense absorption band at ~200 nm and a moderately intense absorption band at ~230 nm [19]. The characteristic peak at ~237 nm of PANI/MWCNTs is higher than that of aniline at ~230 nm, which can be due to the substitution reaction in aniline molecule [20], because the peak at ~230 nm is attributed to the intramolecular charge transfer accompanied by partial electron transfer from amino group to benzene ring in aniline molecule [19].

In order to calculate the weight percent of PANI in PANI/MWCNTs magnetic composites, MWCNTs, PANI, and PANI/MWCNTs are characterized by TGA-DTA analysis (Fig. 4). According to the TGA-DTA curves of MWCNTs, the carbon impurity (such as amorphous carbon) in MWCNTs is negligible. MWCNTs mainly decompose at 480-680 °C: MWCNTs begin to decompose at \sim 480 °C, and the weight residual of MWCNTs after 680 °C (\sim 1.52%) is close to that after 800 °C (~1.37%). Meanwhile, PANI mainly decomposes in the temperature range of ~190-580 °C [21], and the weight residual of PANIs after 580 $^{\circ}$ C (\sim 0.20%) is negligible. The TGA-DTA curves of PANI/MWCNTs show the characteristic decomposition peaks of PANI and MWCNTs. According to the TGA-DTA curves of PANI/MWCNTs, the weight loss (<0.01%) below 120 °C attributed to the loss of moisture is negligible. PANI/MWCNTs mainly decompose at \sim 260–680 °C. The weight residual is \sim 40.1% at \sim 580 °C and <0.53% after 680 °C. Considering that the weight loss of MWCNTs is \sim 6.9% before 580 °C and the complete degradation and decomposition of PANI are at \sim 580 °C, the weight percent of modified PANI in PANI/MWCNTs is calculated to be ~56.3%.

The magnetic property of PANI is critical for the separation and recovery of PANI and PANI based materials from large volumes aqueous solutions by simple magnetic technique after usage. The saturation magnetization of PANI/MWCNTs magnetic composites at room temperature (Fig. 5) reaches up to 1.31 emu/g (magnetic field: 30 kOe) by measuring the magnetization curve. The excellent magnetic property of PANI/MWCNTs magnetic composites can be due to the potentially strong exchange interactions occurring among the π -conjugated backbone of PANI, which can couple in a ferromagnetic fashion [11]. Wienk and Jansen [22] specifically identified PANI with its meta- and para-aniline oligomers as the building blocks for its ferromagnetic exchange. It is reasonable that aniline monomers are polymerize and form magnetic PANI on MWCNT surfaces after plasma activation process.

Fig. 6 shows that the PANI/MWCNTs magnetic composites are attracted quickly toward the common permanent magnet with a

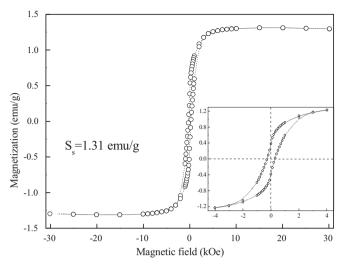


Fig. 5. Magnetization curves of PANI/MWCNTs.

magnetic field of 5000 Gauss; and clear solution can be obtained in 5 min, which can be easily removed by pipet or decanted off. Moreover, the possible residual PANI/MWCNTs in the clear solution are negligible and cannot be detected by combustion methods combined with gas chromatography. Furthermore, the possible free aniline formed from the degradation of PANI in the supernatant of PANI/MWCNTs aqueous solution placed for 12 months cannot be detected from by using high performance liquid chromatography-mass spectrometry methods, and the related PANI/MWCNTs can be separated and recovered thoroughly from aqueous solution by simple magnetic separation. The result is very interesting because the potential decomposition of PANI/MWCNTs during application can be negligible. It proves that PANI/MWCNTs magnetic composites possess excellent magnetism and can be safely used as a magnetic adsorbent to remove pollutants from large volumes of aqueous solutions, which is crucial for their application for the enrichment and removal of pollutants from large volumes of aqueous solutions in large scale in real work.

3.2. Adsorptions of Pb(II) on PANI/MWCNTs and MWCNTs.

In order to evaluate the application of PANI/MWCNTs magnetic composites in the elimination of heavy metal contaminants from large volumes of aqueous solutions, the adsorption of Pb(II) on PANI/MWCNTs magnetic composites, PANI, MWCNTs, and plasma treated MWCNTs are studied by using batch technique. The adsorption isotherms of Pb(II) from aqueous solution are shown in Fig. 7.

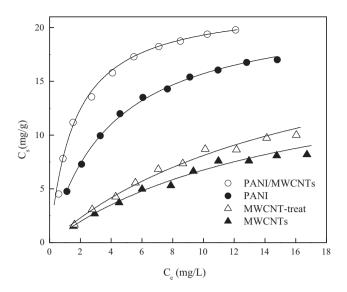


Fig. 7. Adsorption isotherms of Pb(II) from aqueous solution on PANI/MWCNTs, on PANI, on MWCNT-treat, and on MWCNTs. $T=20 \pm 1$ °C, equilibrium time 24 h, m/V = 0.20 g/L, pH 5.00 \pm 0.05, C[NaClO₄] = 0.01 mol/L.

As can be seen from Fig. 7, the adsorption isotherm of Pb(II) on PANI/MWCNTs magnetic composites are much higher than those of Pb(II) on MWCNTs and on plasma treated MWCNTs. As it is well known. PANI carries large amounts of amine and imine functional groups simultaneously [5,10]. The nitrogen of coexisting amine and imine functional groups is expected to have strong affinity to metal ions, such as Hg(II) [10,12], As(V) [12], and Fe(III), etc. [5]. Furthermore, PANI has been effectively used to preconcentrate and separate noble metal ions [23] and heavy metal ions [24] before instrumental analysis. It is reasonable that the amine and imine functional groups of PANI/MWCNTs magnetic composites can form strong complexes with metal ions on PANI/MWCNT surfaces, and thereby enhance the adsorption capacity of PANI/MWCNTs obviously. As it is well known, the surface defects on MWCNT surfaces increase after plasma treatment, which can also improve MWCNTs adsorption capacity partly in the removal of Pb(II) from aqueous solutions.

The adsorption data of Pb(II) on PANI/MWCNTs magnetic composites, MWCNTs, and plasma treated MWCNTs are simulated by Langmuir model [1–3] very well:

$$C_{\rm s} = \frac{bC_{\rm s\,max}C_e}{1+bC_e} \tag{3}$$

where C_{smax} is maximum adsorption capacity and *b* is Langmuir constant. The maximum adsorption capacities (C_{smax}) of Pb(II)

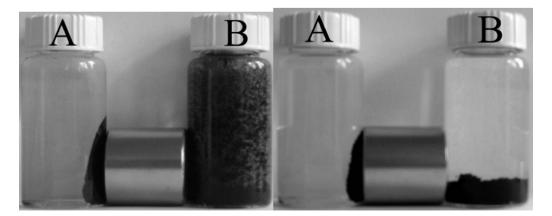


Fig. 6. Magnetic separation of PANI/MWCNTs (A) and MWCNTs (B) from Milli-Q water using a permanent magnet after 1 (left) and 5 min (right).

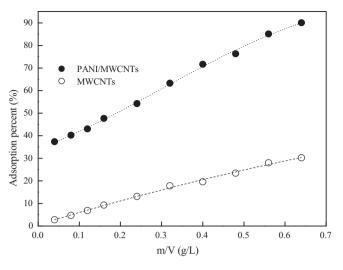


Fig. 8. Effect of solid content on the removal of Pb(II) from aqueous solution on PANI/MWCNTs and on MWCNTs. $T = 20 \pm 1 \,^{\circ}$ C, equilibrium time 24 h, C[Pb(II)]_{initial} = 10.0 mg/L, pH 5.00 ± 0.05, C[NaClO₄] = 0.01 mol/L.

calculated from the Langmuir model are $\sim 12.6 \text{ mg/g}$ for MWC-NTs, $\sim 13.3 \text{ mg/g}$ for MWCNTs-treat, $\sim 21.0 \text{ mg/g}$ for PANI, and $\sim 22.2 \text{ mg/g}$ for PANI/MWCNTs under the experimental conditions. The results indicate that the adsorption capacity of PANI/MWCNTs is ~ 1.8 times higher than that of MWCNTs in the removal of Pb(II) from aqueous solutions.

Under the effective removal percent uncertainties, the less the amount of sorbent is used, the lower cost is applied. The effect of sorbent content on the removal of Pb(II) is shown in Fig. 8. The adsorption percentage increases with increasing sorbent content. The adsorption percentages of Pb(II) on PANI/MWCNTs are markedly higher than those of Pb(II) on MWCNTs. Under the experimental conditions applied, the adsorption percentage of Pb(II) from solution increased from ~37% to ~90% with PANI/MWCNT contents increasing from 0.04 g/L to 0.64 g/L, whereas the adsorption percentage of Pb(II) from solution increased from ~5% to ~59% with MWCNT contents increasing from 0.04 g/L to 0.64 g/L. This is very important in the application of PANI/MWCNTs in the removal of Pb(II) from large volume of aqueous solutions. If the same amounts of PANI/MWCNTs is much higher than that of MWCNTs.

In the application of PANI/MWCNTs to remove Pb(II) ions in environmental pollution management, the pH value of aqueous solutions is also crucial because the adsorption of metal ions on solid particles is generally affected by the pH values. Moreover, the amine and imine functional groups of PANI [10,25] and the oxygen containing functional groups of MWCNTs [3] on PANI/MWCNT surfaces are protonated at low pH. The functional groups of PANI/MWCNTs are protonated easily at low pH, causing PANI/MWCNTs carry positive charges. Moreover, at low pH, the functional groups on PANI/MWCNT surfaces are competitively bound by the protons in aqueous solutions, which can restrict the enrichment of Pb(II) onto PANI/MWCNTs. The protonation of functional groups on PANI/MWCNT surfaces decreases with increasing pH, which results in the less positively charged PANI/MWCNTs. It is reasonable that the competitive binding for the functional groups on PANI/MWCNT surfaces between protons and Pb(II) will decrease. The removal of Pb(II) on MWCNTs and PANI/MWCNTs as a function of pH is dependent on pH values (Fig. 9). As can be seen from Fig. 9, the adsorption of Pb(II) on PANI/MWCNTs and MWC-NTs increases with increasing pH at the whole pH values under the experimental conditions.

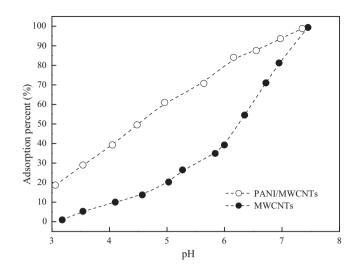


Fig. 9. Effect of pH on the removal of Pb(II) from aqueous solution on PANI/MWCNTs and on MWCNTs. $T=20 \pm 1$ °C, equilibrium time 24 h, C[Pb(II)]_{initial} = 10.0 mg/L, m/V = 0.20 g/L, C[NaClO₄] = 0.01 mol/L.

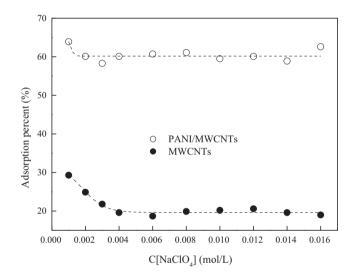


Fig. 10. Effect of ionic strength on the removal of Pb(II) from aqueous solution on PANI/MWCNTs and on MWCNTs. $T=20\pm1$ °C, equilibrium time 24 h, C[Pb(II)]_{initial} = 10.0 mg/L, m/V = 0.20 g/L, pH 5.00 \pm 0.05.

The effect of ionic strength on the sorption of Pb(II) to PANI/MWCNTs is also important because of the presence of different cations and anions in the environment and the salt concentration in wastewater may be different for different sites. The effect of ionic strength on the adsorption of Pb(II) on PANI/MWCNTs and MWCNTs is shown in Fig. 10. As can be seen from Fig. 10. the adsorption percentage of Pb(II) on PANI/MWCNTs is independent of NaClO₄ concentrations under the experimental conditions (<0.02 mol/L). The weakly ionic strength independent adsorption of Pb(II) on PANI/MWCNTs at ionic strength >0.01 mol/L is critical for the evaluation of PANI/MWCNTs in wastewater cleaning management. It is well known that the concentration of different salts in wastewater is generally higher than 0.01 mol/L. In the application of PANI/MWCNTs in the preconcentration of Pb(II) from large volumes of aqueous solutions, it is not necessary to consider the salt concentration in real work.

4. Conclusions

PANI/MWCNT magnetic composites were synthesized by using plasma induced polymerization technique. The analysis results of UV–vis spectra, XPS, TGA, and FE-SEM characterizations indicate that PANI has been modified onto MWCNTs. PANI/MWCNTs magnetic composites have very high adsorption capacities in the removal of Pb(II) ions from large volumes of aqueous solutions, and PANI/MWCNTs magnetic composites can be separated and recovered from solution by simple magnetic separation. The results of this research highlight the potential application of the magnetic composites of PANI/MWCNTs for heavy metal contaminants cleanup in the natural environment. The content in this paper is relevant and important for the applications of plasma technique, magnetic separation method, and MWCNTs in environmental pollution cleanup.

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