Synthesis and Characterization of Adsorbent for Pb(II)-capture by using Glow Discharge Electrolysis Plasma

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A novel polyacrylamide grafted hydrous ferric oxide adsorbent composite has been synthesized by using glow discharge electrolysis plasma. To optimize the synthesis conditions, the following parameters were examined in detail: applied power, discharge time, post polymerization temperature, post polymerization time, amount of crosslinking agent and hydrous ferric oxide gel added and so on. The adsorbent was characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The removal percentage of the adsorbent in Pb(II) solution was examined and the data obtained showed that the adsorbent composite has a high capacity for lead ion. For the use in wastewater treatment, the thermodynamic and kinetic of Pb(II)-capture were also studied. Results indicated that the adsorption reaction was a spontaneous and an endothermic process, and it seems to be obeyed a pseudo-second-order rate model. Moreover, the adsorption isotherm of Pb(II)-capture is following the Langmuir and Freundlich isotherm models.

Key Words: Glow discharge electrolysis plasma, Lead ion, Adsorbent, Thermodynamics and kinetics, Adsorption isotherm

Introduction

Owing to Pb(II) being a non-biodegradable and enrichment substance in human-body, the Pb-pollution to environment is a serious problem, even at low concentration. Thus, the removal of lead ion from water or soil is still an important project. Commonly used methods for removing dissolvable lead ion are below: chemical precipitation, electrochemical treatment, ion exchange, filtration, electrodeposition, solvent extraction, biological systems, and adsorption, in which each has its own advantage and shortcoming.[1-4] Because the characteristic of adsorption technique for the use in water treatment is simple in operation and cheap in price, the synthesis of new adsorbent has received more interesting.

Adsorption of metal ions occurs as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present in the adsorbent surface. Thereby, adsorbents with proper functional groups play a vital role in the adsorption performance. Various functional groups such as hydroxyl, thio, iminodiacetic and amine functional groups have been adopted in adsorbents, in which the nitrogen-containing functional group has been found to be one of the most effective functionalities in the adsorption or removal of heavy metal ions.[5,6]

Glow discharge electrolysis is a kind of non-equilibrium plasma, which can provide a lot of energetic species such as ·OH, ·H, and HO$_2$·. Sengupta *et al.*[7] found that the yield of ·OH radical was more than 12 mol for the passage of per mole electron of electricity in glow discharge electrolysis. The chemical yield exceeded the theoretical value observed on the basis of Faraday's law. In other words, glow discharge electrolysis can be considered as a rich source of free radical in aqueous solution, which could be applied to induce some unusual chemical chang-

es in solution.[8,9] So far, this technique has been studied widely in the field of wastewater treatment and gotten many potential applications.[10-13] However, relatively few papers are devoted to synthetic chemistry, that is, how to use these energetic species to initiate a formation reaction. As far back as the 1970s, Harada *et al.*[14,15] found firstly the formation of some amino acids during the contact glow discharge process in aqueous solution containing aliphatic carboxylic acid or elemental carbon. Since then, Sengupta *et al.*[16] taking the technique as a new tool examined in detail the acrylamide polymerization. Gao and his co-workers[17-20] synthesized successfully the oxalic acid from formic acid and some superabsorbent composites by means of this technique rather than using chemical initiators. That is to say, the technique of glow discharge electrolysis plasma (GDEP) can be used in synthetic chemistry to initiate radical reactions. Moreover, it differs from gaseous plasma that the generation of GDEP is not need the high voltage and high vacuum apparatus and the operation very easy.

In this paper, the polyacrylamide grafted hydrous ferric oxide adsorbent composite was synthesized by aqueous solution polymerization with the glow discharge electrolysis plasma. The polymerization conditions were investigated in detail. The goal of this study was to evaluate the potential of the composite for adsorption of lead ion from solution. Thermodynamic and kinetic studies of lead ion solution were performed and the capacity data were also correlated to the standardized isotherm model.

Experimental

All chemicals used were of analytical grade or HPLC grade. Acrylamide was re-crystallized thrice from acetone. Double-distilled water was used throughout. The experimental apparatus consists of a high voltage power supply and a reactor. The power

supply was a Model of LW100J1 DC power supply (Liyou, Shanghai, China) providing the voltage of $0 \sim 1000$ V and the current of $0 \sim 1$ A. The reactor was a 250 mL four-necked flask equipped a reflux condenser and a nitrogen conduit, a platinum wire anode with a diameter of 0.5 mm sealed into a glass tube to generate glow discharge plasma in aqueous solution and a graphite cathode with a diameter of 10 mm. There was a magnetic stirring bar at the bottom of the flask to keep the solution mixed well.

Acrylamide was examined by means of a high-performance liquid chromatography (Shimadzu HPLC-LC-6A) equipped with a spectrophotometric UV/V detector (Shimadzu-SPD-6AV) and a Kromasil 100-5 C18 column (250×4.6 mm). The infrared spectra of polyacrylamide grafted hydrous ferric oxide adsorbent were recorded in the range of 4000 - 400 cm^{-1} on a DIGILAB FTS 3000 FT-IR spectrophotometer (USA) with KBr pellet. A thermostat water shaker (WHY-2S, Changzhou Chenghui Instrument Factory, China) was used at room temperature. The pH was measured by a pH meter (pHS-25 B, Shanghai Dapu Instrumental Factory, China). The information about chemical binding of Pb(II) on the surface of adsorbent was ascertained by X-ray photoelectron spectroscopy (XPS) (Physical electronics division, USA) equipped with a twin anode (Mg Kα/Al Kα) source under a 10^{-8} Pa residual pressure. Surface charging effects were corrected with C1s peak at 284.6 eV as a reference. The adsorption capacity of metal ion was obtained from the initial and the final concentration of metal ion determined by atomic adsorption spectrophotometer (Hitachi 180 - 80, Japan).

Hydrous ferric oxide gel was prepared by adding ammonia into ferric chloride solution until pH = 7.0. The resulting precipitate was dried under low temperature and then grafted with polyacrylamide using the following procedure: 5 g of acrylamide and 0.5 g of *N,N*-methylenebisacrylamide were first mixed in 70 mL of degased Na$_2$SO$_4$ solution (2 g/L) and then, 1.5g of hydrous ferric oxide gel was added to the mixture with stirring. The discharge with 540 V and 75 ± 5 mA was lasting for 14 min. Finally, the mixture was heated at 85 $^{\circ}$C under N$_2$ ambient for additional 150 min which was called the post polymerization reaction. The resulting product was dewatered and washed with methanol, and dried at 65 $^{\circ}$C for getting a constant weight. The product was milled and screened to select the particles between 100 - 900 μm for this study.

All experiments for the adsorption were carried out by the following procedure, unless otherwise stated. About 0.1g of adsorbent was shaken with 100 mL solution containing metal ions at 298 K and 150 rpm with a mechanical shaker. The pH of solution was adjusted by using 0.05 M solution of HNO$_3$ and NaOH. After centrifuging and separating, the metal ion in adsorbent was analyzed by using atomic absorption spectrophotometer. The adsorption capacity (Q_e) was calculated by the following equation:

$$Q_e = \frac{(C_o - C_e)}{W} \qquad (1)$$

Where C_o is the initial concentration of metal ion (mg/mL), C_e is the final concentration of metal ion (mg/mL), V is the volume of metal ion solution (mL) and W is the weight of the adsorbent (g) used. All the adsorption experiments were performed in triplicate to observe the reproducibility and the mean value was used for each set of values.

The effects such adsorbent mass, initial lead ion concentration, pH and particle size of adsorbent on adsorption for lead ion were examined. Artificial wastewater solution (500 mg/L Pb(II)) was prepared by dissolving analytical grade lead acetate in distilled water, and diluted to the desired concentration before the use. Batch adsorption tests were conducted by mixing a given weight of adsorbent and 100 mL of wastewater containing lead ion at pH = 5.0 for 240 min. The size of adsorbent particles was selected in the range from 450 to 600 μm.

In the range of 100 - 500 mg/L Pb(II), the adsorption isotherm experiments were performed by adding 0.1 g of polyacrylamide grafted hydrous ferric oxide adsorbent into the lead ion solution. The mixture was shaken for 240 min to reach equilibrium at pH 5.0 and 298 K. The mixture solution was filtered and the determination of Pb(II) content was carried out.

Thermodynamic parameters for the adsorption process were examined on the batch adsorption of 100.0 mg/L Pb(II) at the temperature ranging from 283 to 318 K, shaking for 240 min to reach equilibrium. After determining Pb(II), the percent removal was calculated. The kinetic study was carried out by using 0.1 g adsorbent in 100 mL of Pb(II) solution at pH 5.0 and 298 K during different time interval from 20 to 300 min.

Single component 1000 mg/L of stock solution was prepared by using their corresponding nitrate, such as Cu(II), Co(II), Ni(II), Ag(I), Cd(II) and Pb(II), separately. Working solution was diluted to a desired concentration before the use. Multi-component adsorption was tested by using 600 mL of the mixed solution with 0.1 g adsorbent, in which each ion concentration was 50 mg/L.
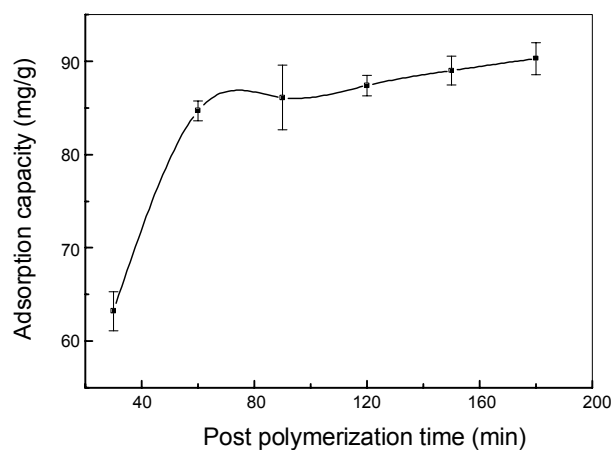
Acrylamide stock solution (3 mg/mL) was prepared by dissolving a desired amount of acrylamide in the mixed solution containing 40 mL isopropyl alcohol, 450 mL deionized water and 10 mL enthanol, and then, was diluted to working solution and stored in amber bottle. Likewise, adsorbent of 0.1 g was added to 10 mL of the above solution. After shaking for 4 h and filtering through a 0.22 mm polytetrafluoroethylene (PTFE) syringe filter, the filtrate was determined directly by HPLC. The used conditions were below: flow rate was 0.9 mLmin^{-1}; detection wavelength 205 nm.
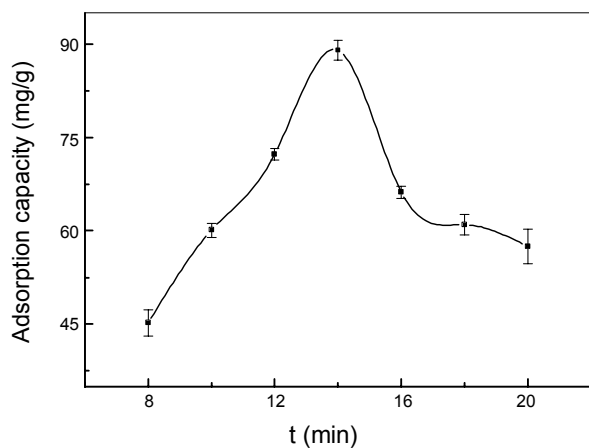
Results and Discussion

Because the adsorbent was prepared by glow discharge electrolysis plasma rather than chemical initiator, the optimum conditions should be re-selected again. Generally, the variables affecting the polymerization could be divided roughly into two parts, in which one comes from the plasma source such as applied power and discharge time; others are alike the common polymerization, i.e., post polymerization temperature, post polymerization time, amount of cross linking-agent and hydrous ferric oxide gel added and so on. Here the adsorption capacity was chosen as a quality standard to evaluate the polymerization reaction. It is not easy to offer an accurate explanation for every test, because there are a lot of energetic species in the plasma. In other words, it is not only a radical polymerization reaction.
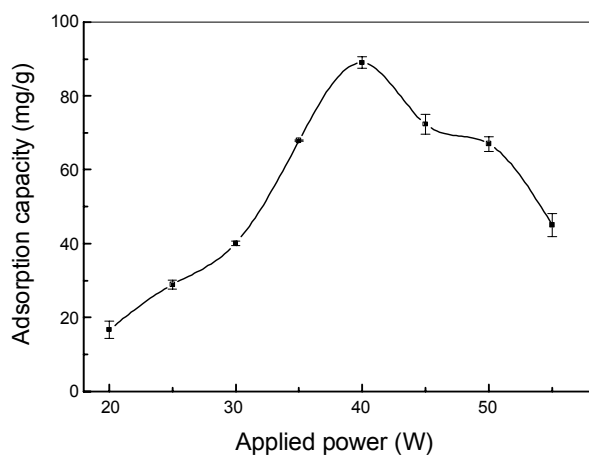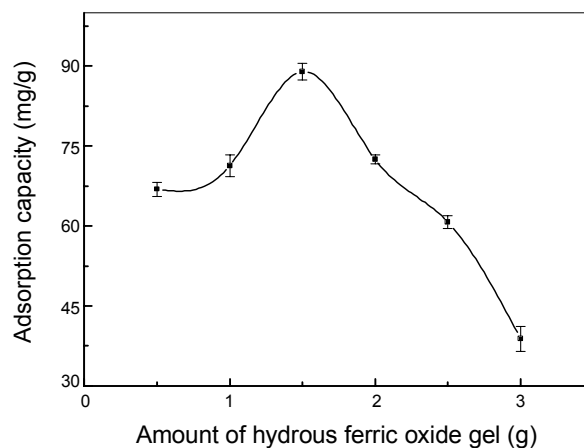
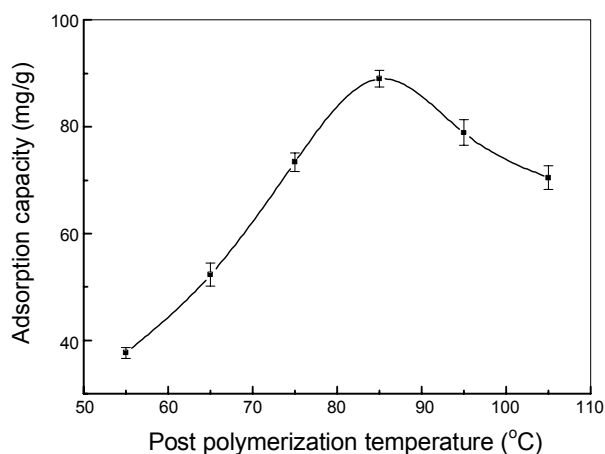**Figure 1.** Effect of applied power

Figure 2. Effect of discharge time

Figure 3. Effect of post polymerization temperature

Figure 4. Effect of post polymerization time

Figure 5. Effect of the amount of hydrous ferric oxide gel

Just as shown in Fig. 1, the adsorption capacity increases sharply with the increase of the applied power up to 40 W, and then decreases gradually. This is attributed to the fact that at the beginning the increase of energetic species is benefit to polymerization of acrylamide monomer. With reaction time prolonging the amount of acrylamide monomer was decreased, offering more collision between energetic species and polymer to destroy the polymer. Thereby, 40 W of power was chosen in this study.

It can be seen from Fig. 2, the adsorption capacity of adsorbent composite increases with increasing discharge time from 8 min to 14 min. Over 14 min, the adsorption capacity decreases. The reason may be as same as explanation in section Fig. 1.

It is well-known that raising temperature can speed the polymerization as showing in Fig. 3. Over 85 ^{o}C the adsorption capacity decreases due to perhaps the change of polymer structure, for example, a compact structure with smaller pores. However, the longer the post polymerization time, the larger the adsorption capacity is (see Fig. 4). To economize resource, 150 min was enough in this work. Due to the limit of solubility of hydrous ferric oxide gel in aqueous, the graft polymerization with polyacrylamide seems to be a heterogeneous reaction. Just as Fig. 5 shown the excess of hydrous ferric oxide gel is not suitable for polymerization. Commonly, the adsorbent should exhibit somewhat both rigidity and swelling for removing metal ions from aqueous solution. This character relies strongly on the amount of cross linking-agent used in the polymerization reaction. More than or less than a critical amount of cross linking-agent would decrease the adsorption capacity of adsorbent composite. It can be seen from Fig. 6 that 0.6 g cross linking-agent was appro-
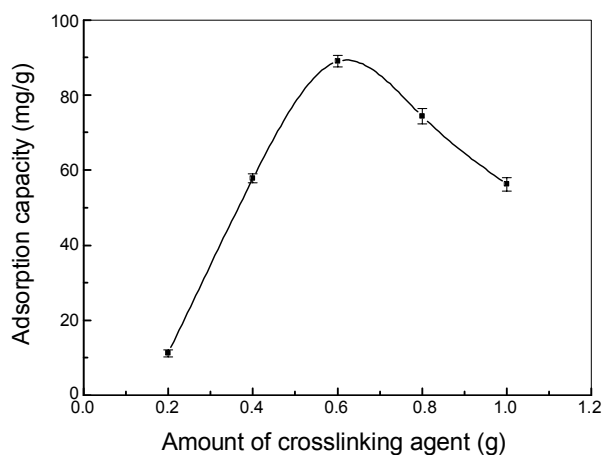
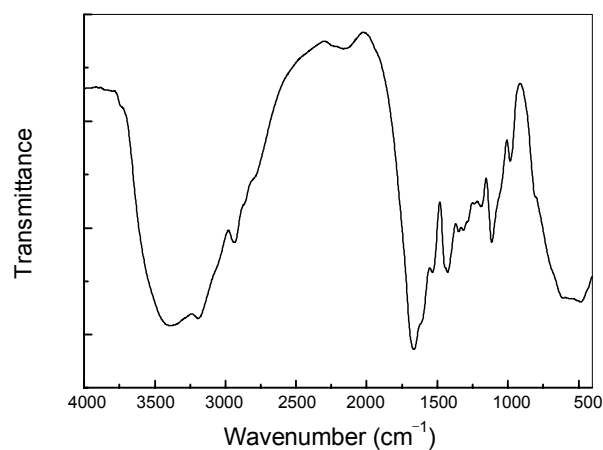**Figure 6.** Effect of the amount of cross linking agent

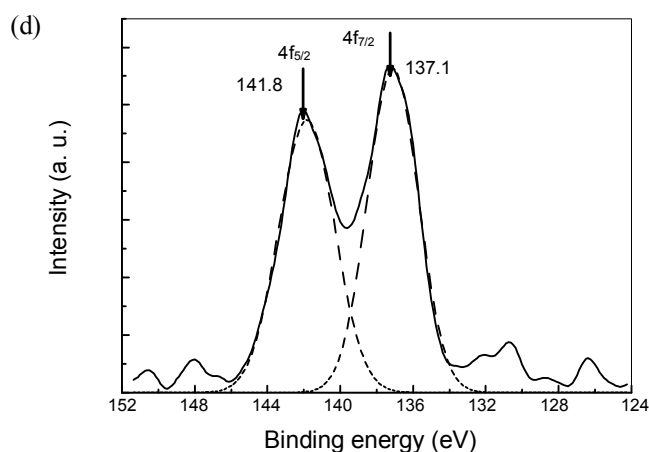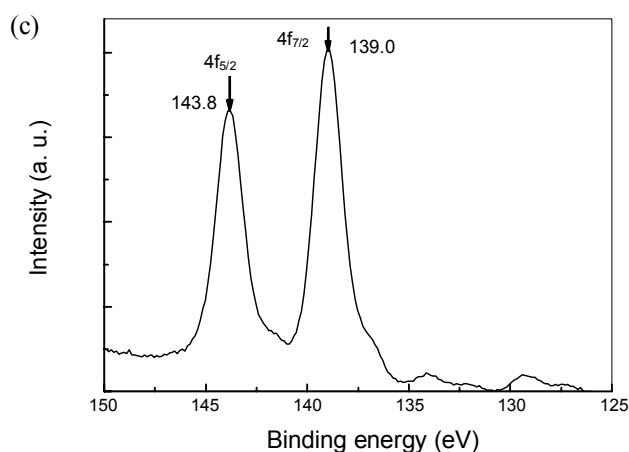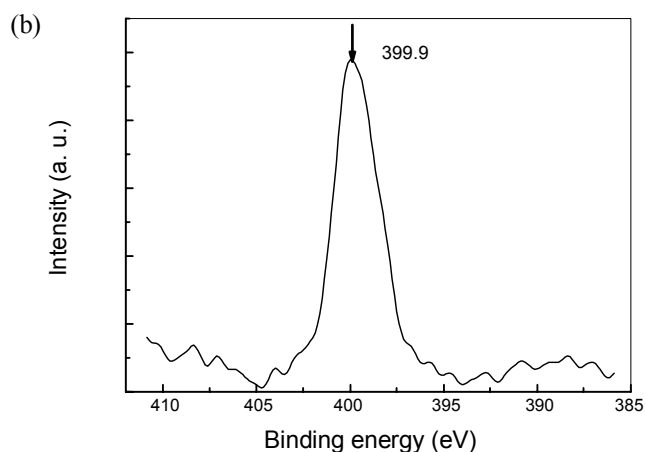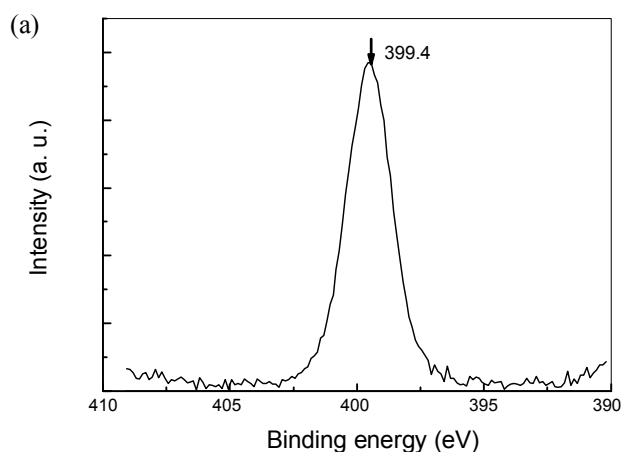**Figure 7.** FT-IR spectra of polyacrylamide grafted hydrous ferric oxide adsorbent

Figure 8. (a) N1s XPS spectrum of the adsorbent before Pb(II) adsorption; (b) N1s XPS spectrum of the adsorbent after Pb(II) adsorption; (c) Pb $4f_{7/2}$ and Pb $4f_{5/2}$ XPS spectrum of pure lead acetate; (d) Pb $4f_{7/2}$ and Pb $4f_{5/2}$ XPS spectrum of the adsorbent after Pb(II) adsorption.

priate.

The FT-IR spectrum of polyacrylamide grafted hydrous ferric oxide adsorbent was recorded in the range of 4000 - 400 cm^{-1}, showing in Fig. 7. The broad spectrum around 3388 cm^{-1} represents the overlap of O-H, which is the sum of contribution from water and hydroxyl bonding to ferric oxide, and N-H sym-

metric stretching vibrations absorption in an acyl (-$CONH_2$) group. The peak at 1113 cm^{-1} is assigned to C-O stretching vibration. The characteristic absorption peak at 1665 cm^{-1} is corresponding to the C=O stretching vibration in amide group. Furthermore, the absorption peak at 2937 cm^{-1} is attributed to the methylene (C-H) group. The disappearance of the absorption

peak of C = C indicated that the polymerization was completed fully.

To understand the characteristic of adsorption, XPS spectra were used to analyze the change of binding energy before and after adsorption, which were shown in Fig. 8. Fig.8a and 8b were separately developed the N 1s core-level spectra of the adsorbent before and after Pb(II) adsorption, in which the binding energy of 399.4 eV can be assigned to nitrogen in the amino groups on the adsorbent surface.[21] After Pb(II) adsorption, the binding energy of N 1s electron becomes 399.9 eV, implying that it shifts upward to be 0.5 eV. In general, it can be considered as the shift of electronic cloud from nitrogen atom to Pb(II) ion.[22]

Fig. 8c and 8d show the binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ in the pure lead acetate and in the adsorbent after Pb(II) adsorption. The former was 139.0 and 143.8 eV and the latter was 137.1 and 141.8 eV, respectively. That is to say, the binding energies both Pb $4f_{7/2}$ and Pb $4f_{5/2}$ shift down to the lower energy region, reflecting the increase of the electronic density around Pb(II) ion and the formation of Pb(II)-N coordinate bond.

The binding ability of the adsorbent for metal cations was depended on the amino group (-NH$_2$) of the polymer chain.[23] *N,N*-methylenebisacrylamide as a crosslinking agent in polymerization reaction could provide more amino groups. Thereby, it is benefit to metal ion adsorption onto polyacrylamide.

The most important single parameter influencing the sorption capacity is the pH of adsorption medium. The initial pH of adsorption medium is related to metal species in solution and the surface properties of the adsorbents in terms of dissociation of functional groups and surface charge.[24] So it not only affects the adsorption mechanism onto the adsorbent surface, but also influences the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbent.

In the following experiments, the used concentration of lead ion is 100 mg/L, i.e. [Pb^{2+}] equals to 4.83×10^{-4} mol/L, which represents the molarity of lead ion. Due to the solubility product of lead hydroxide being 1.2×10^{-15}, if the [OH$^-$] was beyond the limit of 1.57×10^{-6} mol/L, the precipitation of Pb(OH)$_2$ would be observed (pH ~ 8.2). However, the adsorption to Pb(II) is very poor at acidic solution (e.g. pH < 2). If the adsorption of polyacrylamide to Pb(II) ion belongs to chelation, the lower pH is benefited to the protonation of absorbent rather than chelation to Pb(II) ion, and the higher pH is in favor of the de-protonation and chelation. In addition, due to hydroxide precipitation of metal ion at basic solution, the optimum pH must be carefully chosen in acidic solution at first. In this study, the optimum pH was found to be about 5.0 showing in Fig. 9.

Effect of adsorbent dose on removal percentage of lead ion was listed in Table 1. Percentage of lead ion removal increases from 13 to 96% when the adsorbent dose per 100 mL of solution with 100 mg/L lead ions concentration increases from 0.02 to 0.20 g. The number of adsorption sites or surface area increases with the amount of adsorbent and hence results in a higher percent of metal removal at a high dose. However, the amount of metal ions adsorbed per unit weight of adsorbent (mg/g) decreases with increasing the adsorbent dose. This is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower unit adsorption capacity indicating the adsorption sites
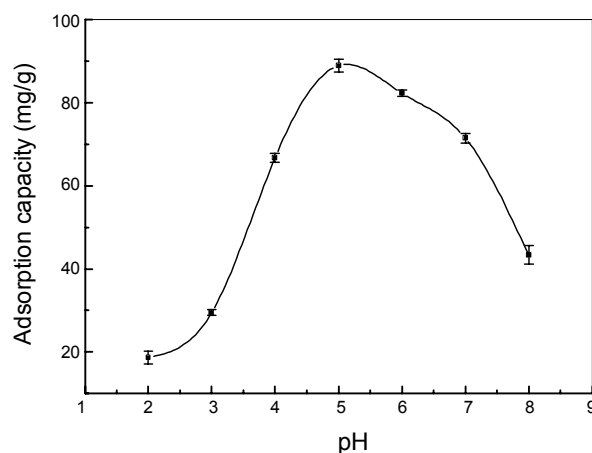

Figure 9. Effect of pH.

Table 1. Effect of adsorbent dose

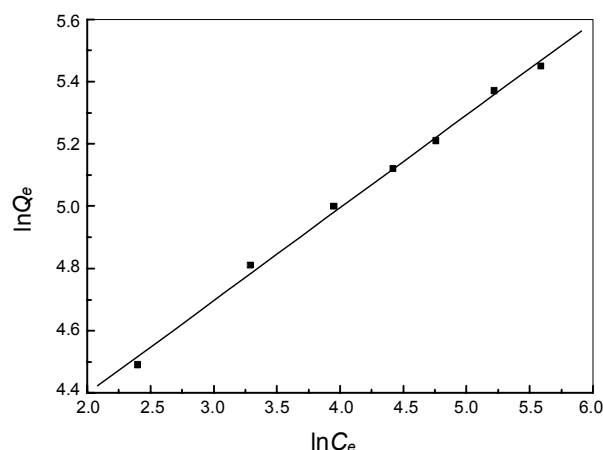| adsorbent dose (g)	percentage of lead ion removal (%)	unit adsorption capacity (mg/g)
0.02	22	110
0.05	47	94
0.10	89	89
0.15	93	62
0.20	96	48

remain unsaturated.

Singling out 20 ~ 30, 30 ~ 40, 70 ~ 80 and 100 ~ 150 meshes of sieves, prepared adsorbent is sieved to collect particles with 0.90 ~ 0.60 mm, 0.60 ~ 0.45 mm, 0.22 ~ 0.18 mm and 0.15 ~ 0.10 mm of average diameter, respectively. Due to the surface area of the adsorbent being an important parameter for adsorption, thereby, the larger surface area of adsorbent would be expected always. The smaller the particle size the larger the surface area per unit weight of adsorbent and hence higher percentage of metal removal would be reached. Results showed that the following size particles, such as 0.90 ~ 0.60 mm, 0.60 ~ 0.45 mm, 0.22 ~ 0.18 and 0.15 ~ 0.10 mm, correspond to the percentages of lead ion removal being 71%, 89%, 91% and 92%, respectively. To filter conveniently, the collected particles with a diameter 0.60 ~ 0.45 mm were selected for other experiments. Of course, the internal surface is also an effective parameter. As the examination is very difficult to do, we could not obtain this data.
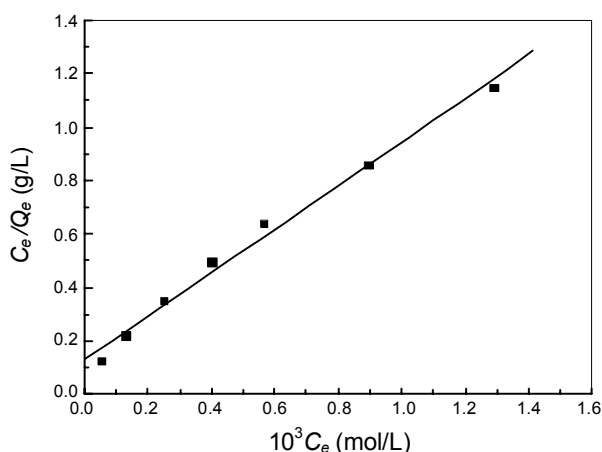
Sorption isotherm describes the behavior interacted between the Pb(II) ion and adsorbent. The equilibrium data by either theoretical or empirical equations is essential for practical design and operation of adsorption systems. Fig. 10 shows sorption isotherm of Pb(II) ion on polyacrylamide grafted hydrous ferric oxide adsorbent, and it presents a plot of the adsorption amount (Q_e, mg/g) versus the equilibrium Pb(II) concentration in the solution (C_e, mg/L). Commonly, the gas sorption equilibrium data can be applied to two common isotherm models: the Freundlich and Langmuir model. Although the two isotherm approaches have been widely used to interpret adsorption equilibrium in solution adsorption, the equation is still an empirical in nature.[25,26]
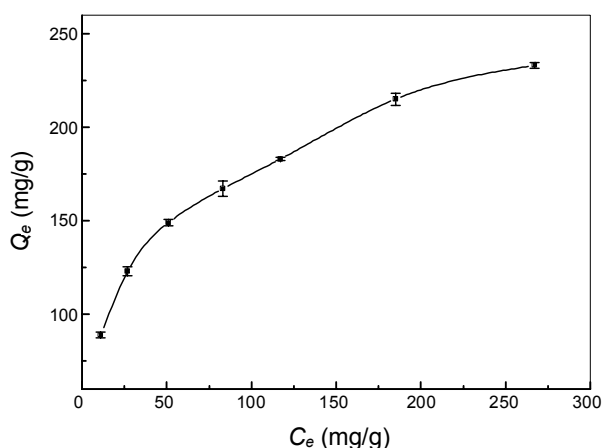
Figure 10. Sorption isotherm of initial concentration of Pb(II): 100 mg/L-400 mg/L; pH = 5.0; temperature: 298 K.

Figure 11. Langmuir isotherms of Pb(II) adsorption on polyacrylamide grafted hydrous ferric oxide adsorbent at 298 K.

The Langmuir sorption isotherm assumes that the adsorbed layer is monomolecular layer and a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, resulting in equal free energies and enthalpies of adsorption. This equation for the Langmuir isotherm is as follows:

$$Q_e = \frac{bQ_oC_e}{1 + bC_e} \tag{2}$$

Linear form of this equation is:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \tag{3}$$

Where b is the Langmuir isotherm constant relative to adsorption energy, Q_o is the amount of adsorbate at complete monolayer coverage (mol g^{-1}), Q_e is the amount of Pb(II) adsorbed per mass unit of adsorbent at equilibrium (mol g^{-1}) and C_e is the equilibrium concentration of remaining lead ions in the solution (mol/L). The Langmuir isotherm equation was pre-tested in this

Figure 12. Freundlich isotherms of Pb(II) adsorption on polyacrylamide grafted hydrous ferric oxide adsorbent at 298 K.

study. The linear relationship of the Langmuir isotherm plot for sorption of Pb(II) on polyacrylamide grafted hydrous ferric oxide adsorbent was shown in Fig. 11 by plotting C_e / Q_e versus C_e. The Langmuir isotherm parameter was determined by least square fit of the sorption data in Fig. 11. Q_o and b were determined from the slope, intercept of the Langmuir isotherm plot. The Langmuir maximum adsorption capacity Q_o and the Langmuir isotherm constant b were found to be 1.23×10^{-3} mol/g (254.6 mg/g) and 6177 at 298 K, respectively. As it may be observed a statistically significant linearity using the Langmuir model to describe lead ions ($R^2 = 0.99504$) sorption process (Fig. 11). R^2 is linear correlation coefficient.

The Freundlich isotherm was derived by assuming an exponential decay energy distribution function inserted in the Langmuir equation. The Freundlich equation is applicable to highly heterogeneous surfaces, and an adsorption isotherm lacking stabilization indicates a multi-layer adsorption.[27] The Freundlich equation may be represented by

$$Q_e = K_F C_e^{1/n} \tag{4}$$

Q_e is the adsorption amount (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L). A linear relationship of the Freundlich equation will give the constants K_F and n.

$$\ln Q_e = \frac{1}{n}\ln C_e + \ln K_F \tag{5}$$

Based on Eq. (5), a straight line was obtained by plotting $\ln Q_e$ versus $\ln C_e$, showing in Fig.12, which was a logarithmic plot of the Freundlich isotherm for the adsorption of Pb(II). It was clearly that the Freundlich isotherm provides a good representation for this study ($R^2 = 0.99811$). K_F and n are empirical coefficients determined from the intercepts and slopes by the least square method, obtaining to be 44.8 and 3.35, respectively. Although both isotherm models were of linear relationship, the Freundlich model may be a better fit than the Langmuir model, according to the correlation coefficients at 298 K.

A comparative study with other adsorbents for the maximum removal amount of Pb(II) was listed in Table 2. Results showed

Table 2. Removal capacities (Q_o) of Pb(II) ion by various adsorbents

Adsorbent	Q_o (mg/g)	Reference
PHEMA/chitosan membranes	68.81	[28]
Wheat bran	87	[29]
Penicillium simplicissimum	152.6	[30]
Palm shell activated carbon	95.2	[31]
Activated phosphate	155	[32]
HAp (50 wt %)/PAAm gel	178	[33]
Polyacrylamide/zeolite composite	58	[34]
HAp (50 wt %)/PU composite foam	150	[35]
Polyacrylamide grafted hydrous ferric oxide adsorbent	254.6	present work
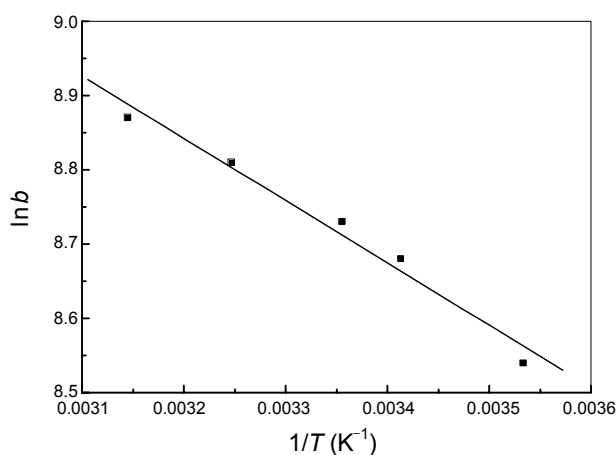
Figure 13. Plot of ln b against reciprocal temperature for Pb(II) adsorption on polyacrylamide grafted hydrous ferric oxide adsorbent.

that polyacrylamide grafted hydrous ferric oxide is, indeed, an excellent adsorbent for removing Pb(II) ion from wastewater.

To understand easily the effect of temperature on the adsorption of Pb(II) ion, the thermodynamic parameters have been studied at 283, 293, 298, 308 and 318 K, respectively, using the following equations in which b is the Langmuir constant, ΔG is the standard Gibbs energy change, ΔH is the standard enthalpy change and ΔS the standard entropy change.

$$\Delta G = -RT \ln b \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

Where, ΔG, ΔH and ΔS can be also calculated from graphical interpretation based on the experimental data. That is, using the slope and intercept by plotting ln b versus $1/T$ (Van't Hoff equation), showing in Fig. 13 to calculate ΔH and ΔS. Results show that in the narrow temperature range of 283 - 318 K the free energy change (ΔG) is vary little and no changes in ΔH (6.96 kJ/mol) and ΔS (95.79 J/mol K), implying that both physical and chemical absorptions are existed in this study.
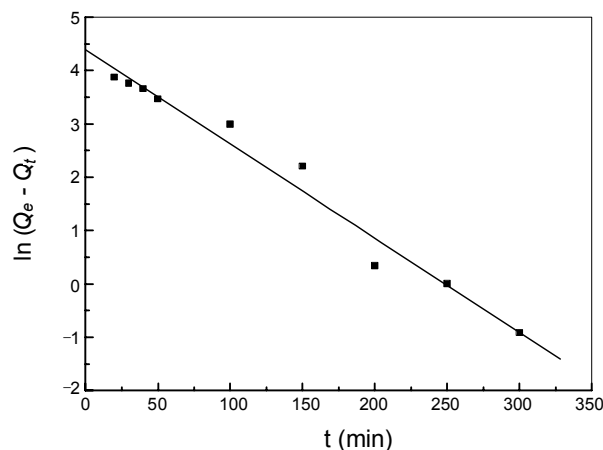
Figure 14. Lagergren first-order kinetic plots for the adsorption of Pb(II) on polyacrylamide grafted hydrous ferric oxide adsorbent at 298 K.

The positive of ΔH indicates an endothermic for the adsorption process; whereas the negative of ΔG means a spontaneous process of Pb(II) adsorption. The positive of ΔS indicates a more random state owning to the liberation of water molecule during chelation process.[36]

The kinetics for the adsorption of Pb(II) on polyacrylamide grafted hydrous ferric oxide adsorbent has been studied in aqueous solution containing 100 mg/L Pb(II) ion at pH 5.0 with time ranging from 20 to 300 min. The rate of sorption process was affected by several parameters such as the structural of adsorbent, properties and concentration of the metal ion, chelate formation between metal ion and adsorbent, and so on. The adsorption kinetics of Pb(II) on polyacrylamide grafted hydrous ferric oxide adsorbent was obeyed to the Lagergren first-order and pseudo-second-order, according to Eqs (9) and (10), respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{9}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{10}$$

Where Q_e and Q_t (mg g^{-1}) are the amounts of Pb(ii) adsorbed on the adsorbent at equilibrium and at various times t. k_1 (min^{-1}) is the rate constant of the Lagergren-first-order model and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second-order model for adsorption process. The plot of $\ln(Q_e - Q_t)$ against t was fitted the Lagergren-first-order model (see Fig.14) and the plot of t/Q_t vs t for the pseudo-second-order model (see Fig.15), in which the rate constant for former was $k_1 = 1.77 \times 10^{-2}$ min^{-1} and for the latter $k_2 = 2.76 \times 10^{-4}$ g mg^{-1} min^{-1}, respectively. However, the value of correlation coefficient R^2 for the former (0.99864) was better than the latter (0.98789). The pseudo second-order model was based on the assumption that the rate-limiting step could be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. Thereby, it could reflect the adsorption behavior involving the valence forces through sharing electrons between metal ion and adsorbent.[37]
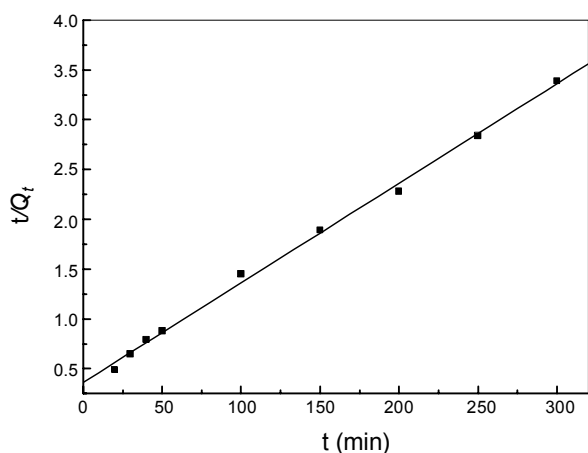
Figure 15. Pseudo-second-order kinetic plots for the adsorption of Pb (II) on polyacrylamide grafted hydrous ferric oxide adsorbent at 298 K.
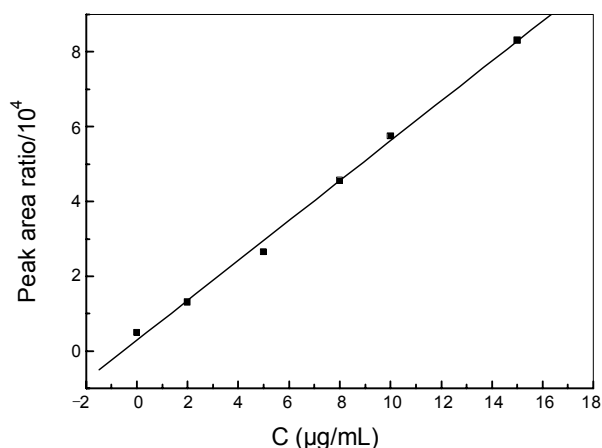
Figure 16. The calibration curve ($y = ax + b$) is constructed by plotting the peak area ratio (y) of the standards versus the amount of acrylamide (x). The linear fit equation for is: *y = 5338.6x + 2832.1.*

In general, the content of metal ion in industrial wastewater was less than 50 mg/L. Thus, in this work a solution of 50 mg/L metal ion was used to examine the removal percentage for Ag^+, Cd^{2+}, Pb^{2+} Co^{2+}, Ni^{2+}, and Cu^{2+} ions in which 0.1g of polyacrylamide grafted hydrous ferric oxide adsorbent was used. Results showed that for Ag^+, Cd^{2+}, Pb^{2+} ions the removal percentage were near to 100%, and for Co^{2+}, Ni^{2+}, Cu^{2+} ions were 96%, 94%, and 98%, respectively.

Place 0.1g of polyacrylamide grafted hydrous ferric oxide adsorbent into 600 mL of mixed solution containing Ag^+, Co^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} and Cu^{2+} ions in which every ion concentration was chosen as 50 mg/L. The adsorption amounts were found to be Ag^+ 27.3 mg/g, Co^{2+} 16.8 mg/g, Cd^{2+} 28.2 mg/g, Pb^{2+} 31.1 mg/g, Ni^{2+} 14.7 mg/g, and Cu^{2+} 15.9 mg/g. It can be seen roughly that the adsorption behavior was relative to the property of metal ion; that is, highly positive charge and smaller ionic radii would be benefit to the adsorption.[38]

Due to acrylamide being is a toxic monomer,[39] its residual amount in polymer must be strictly controlled. The commonly used technique is chromatography for determination of acryl-

amide.[40] The calibration curve of acrylamide by HPLC with UV detector at 205 nm was given in Fig.16. In the range of 1 - 15 μg/mL the regression equation $y = 5338.6x + 2832.1$ exhibits a well linear relationship with a correlation coefficient of 0.9982. Using this method to detect the product, the amount of acrylamide was less than 1.36 μg/mL, i.e. 0.0136%. This result showed again that the polyacrylamide grafted hydrous ferric oxide adsorbent by the proposed technique has an excellent property and could be applied in wastewater treatment.

Conclusion

In this study, polyacrylamide grafted hydrous ferric oxide adsorbent composite has been synthesized by using glow discharge electrolysis plasma. The following parameters would be the optimization conditions: applied power 40 W, discharge time 14 min, post polymerization temperature 85 °C, post polymerization time 150 min, 1.5 g of hydrous ferric oxide gel and 0.6 g of crosslinking agent. The adsorption of Pb(II) onto polyacrylamide grafted hydrous ferric oxide adsorbent could be a chelate process. Langmuir and Freundlich adsorption isotherm models were employed to describe the Pb(II) adsorption onto polyacrylamide grafted hydrous ferric oxide adsorbent at 298 K. According to the Langmuir isotherm, the maximum adsorption capacity for Pb(II) of the adsorbent was 254.6 mg/g. The Freundlich model fits the experimental data better than the Langmuir model. Thermodynamic parameters suggested that the adsorption process was a spontaneous process and endothermic in nature. The pseudo-second-order rate model accurately describes the kinetics of adsorption.

References

1. Smara, A.; Delimi, R.; Chainet, E.; Sandeaux, J. *Sep. Purif. Technol.* **2007**, *57*, 103.
2. Chen, A. H.; Liu, S. C.; Chen, C. Y.; Chen, C. Y. *J. Hazard. Mater.* **2008**, *154*, 184.
3. Matsumoto, N.; Uemoto, H.; Saiki, H. *Water Res.* **2007**, *41*, 2541.
4. Ng, J. C. Y.; Cheung, W. H.; McKay, G. *Chemosphere* **2003**, *52*, 1021.
5. Deng, S. B.; Bai, R. B.; Chen, J. P. *Langmuir* **2003**, *19*, 5058.
6. Al-Faqih, L.; Johnson, P. D.; Allen, S. J. *Bioresour. Technol.* **2008**, *99*, 1394.
7. Sengupta, S. K.; Singh, R.; Srivastava, A. K. *Indian J. Chem. Sect. A* **1998**, *37*, 558.
8. Gao, J. Z.; Wang, A. X.; Fu, Y.; Wu, J. L.; Ma, D. P.; Guo, X.; Li, Y.; Yang, W. *Plasma Sci. Technol.* **2008**, *10*, 30.
9. Gao, J. Z.; Guo, X.; Ma, D. P.; Yang, W. *Plasma Sci. Technol.* **2007**, *9*, 431.
10. Gao, J. Z. *Pak. J. Biol. Sci.* **2006**, *9*, 323.
11. Tezuka, M.; Iwasaki, M. *Plasma & Ions* **1999**, *1*, 23.
12. Lu, Q. F.; Yu, J.; Gao, J. Z. *J. Hazard. Mater.* **2006**, *136*, 526.
13. Gao, J. Z.; Yu, J.; Lu, Q. F.; He, X. Y.; Yang, W.; LI, Y.; Pu, L. M.; Yang, Z. M. *Dyes & Pigments* **2008**, *76*, 47.
14. Harada, K.; Iwasaki, T. *Nature* **1974**, *250*, 426.

15. Harada, K.; Suzuki, S. *Nature* **1977**, *266*, 275.
16. Sengupta, S. K.; Sandhir, U.; Misra, N. *J. Polym. Sci. Part A* **2001**, *39*, 1584.
17. Wang, A. X.; Gao, J. Z.; Yuan, L.; Yang, W. *Plasma Chem. Plasma Process* **2009**, *29*, 387.
18. Gao, J. Z.; Fu, Y.; Wang, A. X.; Wu, J. L.; Li, Y.; Yang, W. *Chem. J. Internet* **2008**, *10*, 41.
19. Gao, J. Z.; Wang, A. X.; Li, Y.; Fu, Y.; Wu, J. L.; Wang, Y. D.; Wang, Y. J. *React. Funct. Polym.* **2008**, *68*, 1377.
20. Gao, J. Z.; Wang, Y. D.; Wang, A. X.; Wang, Y. J.; Li, Y.; Fu, Y.; Wu, J. L. *Chin. J. Appl. Chem.* (*Ch*) **2009**, *26*, 282.
21. Sun, S. L.; Wang, L.; Wang, A. Q. *J. Hazard. Mater.* **2006**, *136*, 930.
22. Guan, H. M.; Cheng, X. S. *Polym. Adv. Technol.* **2004**, *15*, 89.
23. Dambies, L.; Guimon, C.; Yiacoumi, S.; Guibal, E. *Colloids and Surf. A* **2001**, *177*, 203.
24. Sheng, P. X.; Ting, Y. P.; Chen, J. P.; Hong, L. *J. Colloid Interface Sci.* **2004**, *275*, 131.
25. Deng, S. B.; Ting, Y. P. *Water Res.* **2005**, *39*, 2167.
26. Amarasinghe, B. M.; Williams, R. A. *Chem. Eng. J.* **2007**, *132*, 299.
27. Li, Y. H.; Di, Z. C.; Ding, J.; Wu, D. H.; Luan, Z. K.; Zhu, Y. Q. *Water Res.* **2005**, *39*, 605.
28. Genc, O.; Soysal, L.; Bayramoglu, G.; Arica, M. Y.; Bektas, S. *J. Hazard. Mater.* **2003**, 97, 111.
29. Bulut, Y.; Baysal, Z. *J. Envfer. Manage.* **2006**, *78*, 107.
30. Li, X. M.; Liao, D. X.; Xu, X. Q.; Yang, Q.; Zeng, G. M.; Zheng, W.; Guo, L. *J. Hazard. Mater.* **2008**, *159*, 610.
31. Issabayeva, G.; Aroua, M. K.; Sulaiman, N. M. N. *Bioresour. Technol.* **2006**, *97*, 2350.
32. Mouflih, M.; Aklil, A.; Sebti, S. *J. Hazard. Mater.* **2005**, *119*, 183.
33. Jang, S. H.; Jeong, Y. G.; Min, B. G.; Lyoo, W.S.; Lee, S. C. *J. Hazard. Mater.* **2008**, *159*, 294.
34. Ulusoy, U.; Simsek, S. *J. Hazard. Mater.* **2005**, *127*, 163.
35. Jang, S. H.; Min, B. G.; Jeong, Y. G.; Lyoo, W. S.; Lee, S. C. *J. Hazard. Mater.* **2008**, *152*, 1285.
36. Malkoc, E.; Nuhoglu, Y. *Sep. Purif. Technol.* **2007**, *54*, 291.
37. Chen, A. H.; Liu, S. C.; Chen, C. Y. *J. Hazard. Mater.* **2008**, *154*, 184.
38. Manju, G. N.; Krishnan, K. A.; Vinod, V. P.; Anirudhan, T. S. *J. Hazard. Mater.* **2002**, *91*, 221.
39. Gertz, C.; Klostermann, S. *Eur. J. Lipid Sci. Technol.* **2002**, *104*, 762.
40. Paleologos, E. K.; Kontominas, M. G. *J. Chromatogr. A* **2005**, *1077*, 128.