

# Adsorption of Copper(II) from an Wastewater Effluent of Electroplating Industry by Poly(ethyleneimine)-Functionalized Silica

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**ABSTRACT:** *The poly(ethyleneimine)-functionalized silica has been developed successfully as an effective adsorbent for the adsorption removal of Cu(II) ions from electroplating wastewater. The influences of pH, contact time and initial concentration of Cu(II) ions on the adsorption capacity and the effect of adsorbent dosage on the removal efficiency of Cu(II) ions from electroplating wastewater were investigated. The adsorption behaviors and mechanisms of Cu(II) ions onto poly(ethyleneimine)-functionalized silica were also studied in details. The uptake of Cu(II) ions on poly(ethyleneimine)-functionalized silica was constant in the range of pH 4-8. The poly(ethyleneimine)-functionalized silica offered a fast rate for the adsorption of Cu(II) ions and reached an equilibrium state within 30 min. The results of static batch experiment indicated that the maximum static adsorption capacity of Cu(II) ions on PEI-functionalized silica was 31.8 mg/g. The adsorption process was found to follow a pseudo-second-order rate mechanism. Langmuir adsorption isotherms fitted well in the experimental data. The optimum dosage of poly(ethyleneimine)-functionalized silica for the removal Cu(II) ions from electroplating wastewater was 10 g/L. The removal efficiency of Cu(II) ions from electroplating wastewater was 92.6%. Some scale-up experiments were also investigated to offer the reference for water treatment. The results showed that poly(ethyleneimine)-functionalized silica could be employed as an effective adsorbent for the removal of Cu(II) ions from electroplating wastewater.*

**KEY WORDS:** *Copper, Removal, Poly(ethyleneimine), Adsorption, Electroplating wastewater.*

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1021-9986/15/2/73

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## INTRODUCTION

Most heavy metal ions are toxic or carcinogenic and present a threat to human health and the environment due to not biodegradable, and most of them accumulate in the environment causing both short term and long term adverse effects [1]. Copper is essential elements for all living organisms, which are incorporated into a number of metalloenzymes. The deficiency of copper results in severing health problems. On the other hand, copper excess is toxic [2,3]. The amount of discharged copper is increasing as electronic industries development. Electroplating industries generate large amounts of effluents containing heavy metals, such as copper. The presence of copper ions in water poses serious environmental and human health hazards because of their toxicity, tendency to bioaccumulate, and abundance and persistence in the environment [4]. Owing to toxicity of copper ions, electroplating wastewaters require a previous treatment before being discharged in surface waters and prevent environmental degradation.

Several treatment methods are used for the removal of copper ions from contaminated waters including physical and chemical treatment processes (e.g. chemical precipitation [5], membrane systems [6], electrochemical method [7], biosorption [8], ion-exchange [9] and solvent extraction [10]), but in general, these methods are commercially impractical, either because of the high operating cost or the difficulty in treating. For dilute concentrations, adsorption is one of the suitable methods for the removal of copper ions with high removal efficiencies. In the adsorption process, metal ions in the aqueous solutions may be transported through diffusion or convection to the surface of the adsorbent and then attached to the surfaces due to various physical or chemical interactions between the metal ions and the surface functional groups of the adsorbents. The synthesis of adsorbents for the removal of toxic heavy metal ions from aqueous solution is a continuing research objective of environment pollution control processes. Materials that contain functional groups to complex the dissolved metal ions in aqueous solutions can be very effective. Silica gel is an ideal support for functional groups because it is an inorganic material, stable under acidic conditions and nonswelling, and has high mass exchange characteristics and very high thermal resistance [11]. The chemical modification of silica gel has shown great promise

in improving the efficiency of adsorption due to the increase of functional groups [12]. Poly (ethyleneimine) (PEI) is a typical alkaline water-soluble functional macromolecular which contains a large quantity of N-donor atoms and can react with Cu(II) ions [13-15], because Cu(II) is regarded as a borderline Lewis acid metal in the Hard and Soft Acids and Bases classification and is expected to form strong metal complexes with borderline donor atoms such as  $\text{NH}_2$ - groups [16]. PEI-functionalized silica has been found to be a good adsorbent for Cu(II) ions [17,18]. However, the application of PEI-functionalized silica on the removal of Cu(II) ions from a wastewater effluent of electroplating industry has not been reported and few studies were designed to examine the adsorption behaviors and mechanisms of Cu(II) ions onto PEI-functionalized silica in details.

In this study, in order to determine the applicability of PEI-functionalized silica on electroplating effluent, a PEI-functionalized silica was used as new adsorbent for the removal of Cu(II) ions. The adsorption behavior and mechanisms of Cu(II) ions on PEI-functionalized silica were investigated.

## EXPERIMENTAL SECTION

### Reagents

3-Chloropropyltriethoxsilane was purchased from Jingzhou Jinghan Fine Chemical Co., Ltd. Hubei, China. Branched poly (ethyleneimine) (PEI) (molecular weight of 25,000) was obtained from Sigma-Aldrich. Silica gel (60-80 mesh) was purchased from Qingdao Ocean Chemical Co., Ltd., Shandong, China. And all the reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Deionized water was used throughout.

### Apparatus

The Fourier Transmission Infrared Spectra (FT-IR) of the samples in KBr pellets were performed by a Nicolet 6700 FT-IR spectrometer in the range from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ . The concentrations of metals in aqueous solutions were determined by an AA-6300c flame atomic absorption spectrometer (FAAS, Shimadzu Corporation, Japan) with Cu hollow cathode lamps and air-acetylene flame after appropriating dilutions and acidification to pH~2 adjusted with  $\text{HNO}_3$ .

The pH of solution was measured by a pHS-3C digital pH meter equipped with a combined electrode (Shanghai Precision & Scientific Instrument Co., LTD, Shanghai, China). The pH was maintained in a range of  $\pm 0.1$ U until equilibrium was attained.

#### **Synthesis and characterization of PEI-functionalized silica**

The PEI-functionalized silica was prepared according to the steps described in Ref. [19]. Firstly, 6 g of silica gel particles was treated for activating by refluxing in 60 mL of 33% solution of methanesulfonic acid as an activation reagent with stirring for 8 h. Secondly, 4 g of activated silica gel reacted with  $\gamma$ -chloropropyltrimethoxysilane using xylene as solvent at 80 °C for 24 h. Thirdly, 10 mL of 10% PEI aqueous solution was added, and then reaction was carried out at 80 °C for 24 h. Finally, the solid prepared was filtered, washed by ethanol and water (pH $\approx$ 7), and dried in vacuum at 60 °C for 12 h. Furthermore, the PEI-functionalized silica was sieved to obtain the particle size below 60 mesh. The chemical structure of the solid prepared after grafting was characterized by infrared spectrum in order to confirm that PEI had been grafted onto the surface of silica gel particle. The surface areas of the sample particles synthesized and silica gel particles were determined. The amino concentration of the sample particles synthesized was determined by acid–base titration analysis.

#### **General procedure for batch adsorption studies**

In order to determine the static sorption capacity of PEI-functionalized silica for Cu(II) ions as well as the effect of the contact time (5-60 min), the concentration of Cu(II) ions (50-600 mg/L), and solution pH (pH 2-9), static adsorption experiments were performed by batch equilibration because of its simplicity and reliability. For each set of experiments conducted for the optimization of conditions necessary for maximum adsorption, 25 mL of known concentration of heavy metals solution was taken in a conical flask and pH was adjusted using 0.1 mol/L HCl or 0.1 mol·L<sup>-1</sup> NaOH solutions. The pH measurements were made by pH meter. After addition of a known amount of the PEI-functionalized silica, the flask was stirred at 200 rpm for a given time while maintaining a constant temperature (25 °C). The amount of Cu(II) ions left in each of the filtrates was measured

by FAAS. The dosage of adsorbent for Cu(II) electroplating wastewater was tested. The effect of some scale-up experiments with reaction volumes of 2, 5, 10, 20 and 50 L on the removal efficiency of Cu(II) ions from electroplating wastewater were also investigated.

The uptake of Cu(II) ions was calculated by the simple concentration difference method. The metal uptake  $Q$  (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation (Eq. 1) as follows:

$$Q = \frac{(C_i - C_f) V}{1000 W} \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations of Cu(II) ions (mg/L), respectively.  $V$  is the volume of the solution (mL);  $W$  is the mass used of adsorbents (g).

#### **Desorption and repeated reuse of PEI-functionalized silica**

To evaluate the desorption ratio, the adsorbed metal ions were desorbed by the treatment of with 1 mol/L HCl solution. The adsorbents were placed in the desorption medium and stirred continuously for 2 h. The final concentrations of Cu(II) ions in the aqueous phase were determined by FAAS. The desorption ratio was calculated as follows:

$$\text{Desorption ratio (\%)} = \frac{\text{amount of ions desorbed to the elution medium (mg)}}{\text{amount of ions adsorbed onto the sorbent (mg)}} \times 100 \quad (2)$$

The adsorption/desorption cycle was performed up to five times to evaluate the possibility of repeated reuse of PEI-functionalized silica. The Cu(II) ions were removed from the adsorbents by washing with 1 mol·L<sup>-1</sup> HCl solution for 2 h. The adsorbents were rinsed several times with deionized water and dried under vacuum at 70 °C overnight before another extraction cycle. The adsorption ratio of each cycle was calculated as a percentage of the uptake at the first adsorption.

For all samples, the experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. All statistical analysis were done using Microsoft Excel 2003, Version office XP.

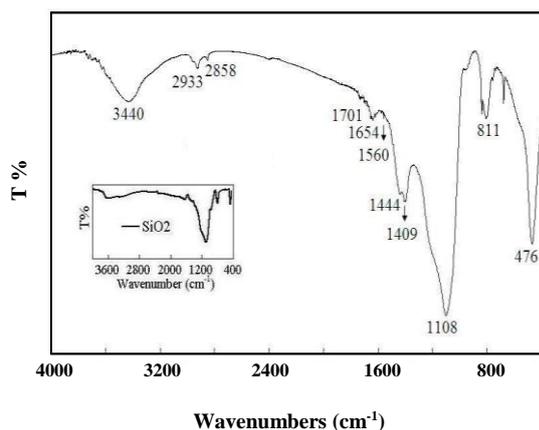


Fig. 1: IR spectra of PEI-functionalized silica and silica gel.

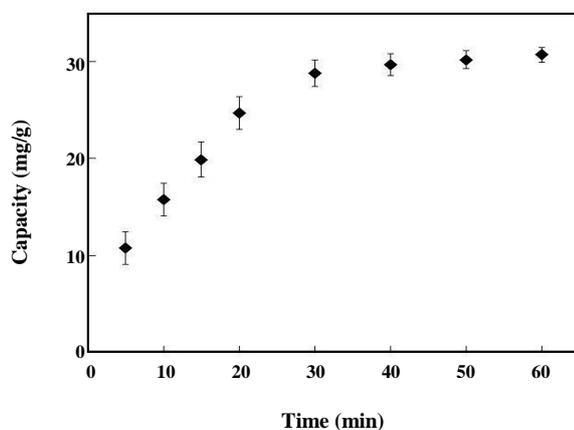


Fig. 2: Effect of contact time on the adsorption equilibrium for Cu(II) ions: Concentration of Cu(II) ions = 400 mg/L, pH = 5, temperature = 25 °C.

## RESULTS AND DISCUSSION

### Characterization

In order to confirm the presence of PEI in the functionalized silica adsorbents, the FT-IR spectra of silica gel and PEI-functionalized silica are shown in Fig. 1. The absorption bands at 3629–3731  $\text{cm}^{-1}$  and 1701  $\text{cm}^{-1}$  are the stretching vibration and bending vibration of N-H bond, respectively. The absorption band at 3440  $\text{cm}^{-1}$  is attributed to stretching vibration of O-H groups on the surface silanol groups with hydrogen bond and the remaining adsorbed water molecules. The absorption band at 1653  $\text{cm}^{-1}$  is due to the deformation vibrations of adsorbed water molecules. The absorption bands at 2933 and 2857  $\text{cm}^{-1}$  are ascribed to the asymmetric stretching vibrations of  $-\text{CH}_2-$  groups, while the absorption

peaks at 1444 and 1409  $\text{cm}^{-1}$  are related to the bending vibrations of  $-\text{CH}_2-$  groups. The band at 1560  $\text{cm}^{-1}$  is the stretching vibration absorption of C-N bond. The absorption bands at 1108  $\text{cm}^{-1}$  and 811  $\text{cm}^{-1}$  are due to the Si-O-Si and Si-O stretching vibrations, respectively. The absorption peak at 476  $\text{cm}^{-1}$  is assigned to the bending vibrations of Si-O-Si groups. The content of amino groups onto PEI-functionalized hybrid silica was 3.1 %. These indicated that PEI had been grafted on the surface of silica. Similar result was reported previously [20].

BET surface areas of silica gel, PEI-functionalized silica were 122 and 75  $\text{m}^2\cdot\text{g}^{-1}$ , respectively. The surface area of PEI-functionalized silica adsorbents dramatically reduced with the increase of the grafting efficiency of PEI because the silylation covered the pore openings on the surface of silica gel.

### Effect of contact time

The effect of equilibration time on the adsorption of Cu(II) ions was analyzed kinetically over a range of 5–60 min. The reaction was carried out with initial metal solution concentration of 400  $\text{mg}\cdot\text{L}^{-1}$  at pH 6. Fig. 2 indicates that more than 95 % of the total adsorption capacity occurred within 30 min, after that the removal further increased but with a much slower rate. This shorter-time indicates easier approachability of the binding sites for metal ions at the surface of PEI-functionalized silica. Based on the kinetic results, an equilibration time of 45 min was selected for the further experiment.

### Effect of pH

The adsorption of Cu(II) ions from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent. To investigate the relationship between pH and adsorption amount, the adsorption amount of Cu(II) ions with pH value was observed from pH 2 to 9 as shown in Fig. 3. The adsorption amount increased rapidly with increasing pH from pH 2 to 4, and remained constant in the range of pH 4–8, and decreased over pH 8. At lower pH, the functional groups of PEI-functionalized silica responsible for uptake of Cu(II) are protonated by  $\text{H}_3\text{O}^+$  ions. Due to electrostatic repulsion of  $\text{H}_3\text{O}^+$  and Cu(II) ions, a lower uptake has been observed at lower pH. On the other hand, on increasing pH values, the electrical repulsion force becomes weaker and the Cu(II) ions interactions with the PEI-functionalized silica become stronger. Over pH 8,

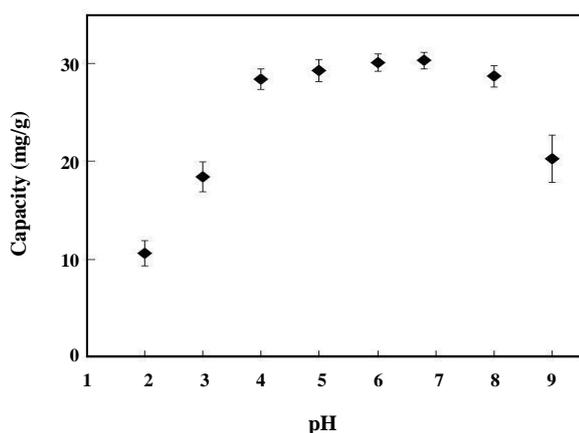


Fig. 3: Effect of pH on the adsorption capacity of PEI-functionalized silica for Cu(II) ions: Concentration of Cu(II) ions = 400 mg/L, time = 45 min, temperature = 25 °C.

small adsorption capacity has been observed due to the formation of Cu(II) hydroxide precipitation. The optimum pH range for the removal of Cu(II) was from 4 to 8.

#### Adsorption capacity

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. To measure the static adsorption capacity, 100 mg of PEI-functionalized silica was equilibrated with 25 mL of various concentrations of Cu(II) solutions at pH 5. As shown in Fig. 4, the adsorption amount increased with increasing initial concentrations of Cu(II) ions until the saturation of available adsorption site. The maximum static adsorption capacity of PEI-functionalized silica for Cu(II) ions was 31.8 mg/g.

#### Kinetic studies

To investigate the adsorption kinetic of Cu(II) ions onto PEI-functionalized silica, pseudo-first-order and pseudo-second-order kinetic models have been applied. The linear equation for the pseudo-first-order of the kinetic model is expressed as [21]:

$$\lg(q_e - q_t) = \lg q_e - k_1 t / 2.303 \quad (3)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first adsorption.  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities at equilibrium and at time  $t$  (min), respectively. The rate constants  $k_1$ ,  $q_e$  and correlation coefficients  $r^2$  were calculated using the slope and intercept of plots of  $\lg(q_e - q_t)$  versus  $t$  (Fig. 5).

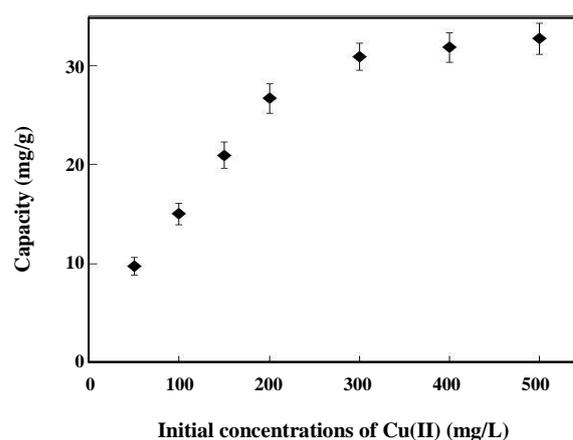


Fig. 4: Adsorption capacity of PEI-functionalized silica for Cu(II) ions: pH = 5, time = 45 min, temperature = 25 °C.

The pseudo-second-order rate expression is linearly expressed as [22]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where  $q_e$  and  $q_t$  ( $\text{mg/g}$ ) are the adsorption capacity at equilibrium and time  $t$ ,  $k_2$  ( $\text{g/mg-min}$ ) is the rate constant of the pseudo-second-order adsorption. The rate constants  $k_2$ ,  $q_e$  and correlation coefficients  $r^2$  were calculated from the linear plots of  $t/q_t$  versus  $t$  (Fig. 5).

The calculated value (37.9 mg/g) of  $q_e$  obtained from Eq.(4) complied well with the experimental value (31.8 mg/g) and also  $r^2$  value was significant in this case, which showed that adsorption kinetics of Cu(II) ions using PEI-functionalized silica followed a pseudo-second-order kinetic model. This implied that adsorption in this case took place through chemical bond formation (chemisorption).

#### Adsorption isotherms

In order to understand the design of an adsorption system, it is important to perform the study of equilibrium curves. In the present study, two adsorption isotherms such as Langmuir and Freundlich adsorption isotherm models were used to describe the obtained equilibrium data.

Langmuir isotherm can be arranged in its linear form as following [23]:

$$C_{eq}/q_{eq} = 1/(q_{max} b) + C_{eq}/q_{max} \quad (5)$$

where  $q_{eq}$  is the amount of adsorbed metals in the adsorbent ( $\text{mg/g}$ ),  $C_{eq}$  is the equilibrium ion

concentration in solution (mg/L),  $b$  (L/mg) is the equilibrium constant related to the adsorption energy, and  $q_{\max}$  is the maximum adsorption capacity (mg/g). A linear plot is obtained when  $C_{\text{eq}}/q_{\text{eq}}$  is plotted against  $C_{\text{eq}}$  over the entire concentration range of metal ions investigated (as shown in Fig. 6a).

The Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [24]. The adsorption data were also fitted to Freundlich isotherm, which is described by the linear form following the equation [24]:

$$\log q_{\text{eq}} = \log K_F + (1/n) \log C_{\text{eq}} \quad (6)$$

where  $K_F$  and  $n$  are the Freundlich constants;  $C_{\text{eq}}$  is the equilibrium ion concentration in solution (mg/L). According to Eq.(6), the values of  $K_F$  and  $n$  can be determined experimentally by plotting  $\log q_{\text{eq}}$  versus  $\log C_{\text{eq}}$  (as shown in Fig. 6b).

The high value of the regression correlation coefficient of Langmuir adsorption isotherm ( $r^2 = 0.9946$ ) was obtained, which indicated a good agreement between the experimental values (31.8 mg/g) and isotherm parameters (36.8 mg/g), and also confirmed the adsorption of Cu(II) ions onto PEI-functionalized silica followed the Langmuir adsorption isotherm.

### Desorption and regeneration

In this study, desorption of the adsorbed metals ions from PEI-functionalized silica was also studied in a batch experimental set-up. When 1 mol/L HCl solution was used as a desorption agent, Cu(II) ions were released from 0.5 g of PEI-functionalized silica into 25 mL of desorption medium. The desorption time was found to be 2 h and desorption ratios were very high (up to 95%).

Regeneration of any exhausted adsorbent is an important factor in the adsorption process for improving the process economics [25]. Regeneration allows for the repeated use of the adsorbent and decreasing costs. The same sample of the adsorbent was used for the adsorption of Cu(II) ions from solutions after five stripping cycles. After the fifth adsorption/desorption cycle, the adsorption capacity of Cu(II) ions was found to about 85 % of the fresh adsorbent. The result indicated that PEI-functionalized silica owned good regeneration ability.

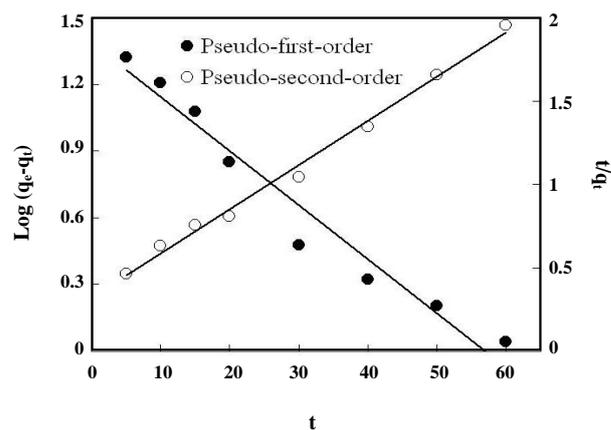


Fig. 5: The plots of pseudo-first-order and pseudo-second-order kinetic for the adsorption of Cu(II) ions onto PEI-functionalized silica..

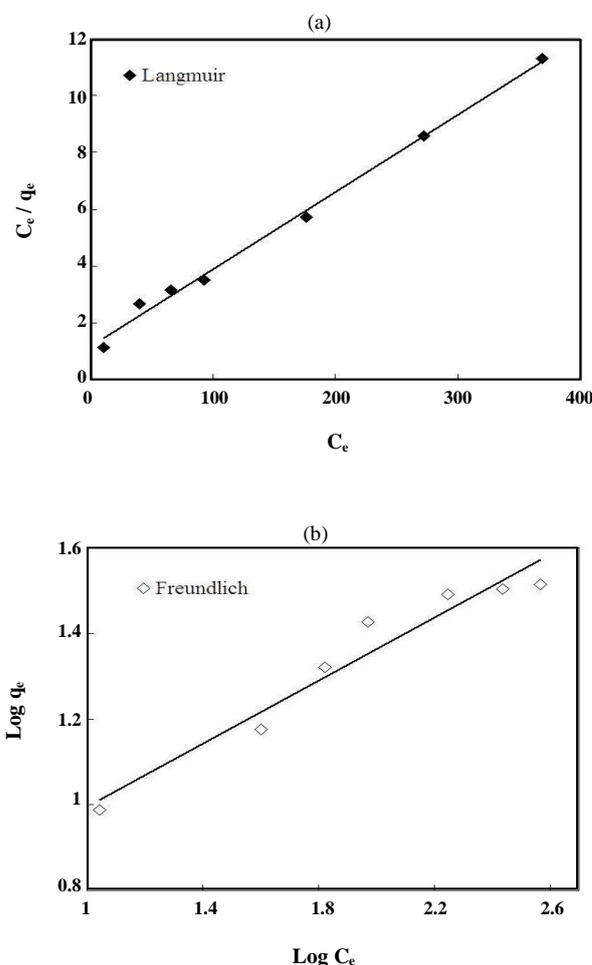


Fig. 6: The plots of Langmuir and Freundlich isotherms for adsorption of Cu(II) ions onto PEI-functionalized silica.

**Table 1: Calculated kinetic parameters for the adsorption of Cu(II) onto PEI-functionalized silica.**

Pseudo-first-order model	Pseudo-second-order model
$k_1 = 0.0557 \text{ min}^{-1}$	$k_2 = 2.17 \times 10^{-3} \text{ g/mg}\cdot\text{min}$
$q_{\text{eq}}(\text{cal}) = 24.2 \text{ mg/g}$	$q_{\text{eq}}(\text{cal}) = 37.9 \text{ mg/g}$
$r^2 = 0.9600$	$r^2 = 0.9928$

**Table 2: Isotherms parameters for the adsorption of Cu(II) by PEI-functionalized silica.**

Langmuir adsorption isotherm	Freundlich adsorption isotherm
$q_{\text{max}} = 36.8 \text{ mg/g}$	$K_F = 4.24$
$b = 0.024 \text{ L/mg}$	$n = 2.72$
$r^2 = 0.9946$	$r^2 = 0.9442$

**Table 3: Properties of Cu(II) electroplating wastewaters.**

Measured parameters	Concentrations
Potassium as $\text{K}^+$	35 mg/L
Sodium as $\text{Na}^+$	354 mg/L
Calcium as $\text{Ca}^{2+}$	76 mg/L
Magnesium as $\text{Mg}^{2+}$	54 mg/L
Copper as $\text{Cu}^{2+}$	193 mg/L
Cadmium as $\text{Cd}^{2+}$	2.4 mg/L
Nickel as $\text{Ni}^{2+}$	1.7 mg/L
Zinc as $\text{Zn}^{2+}$	9.8 mg/L
Lead as $\text{Pb}^{2+}$	0.7 mg/L
Iron as $\text{Fe}^{3+}$	6.2 mg/L
Sulphate as $\text{SO}_4^{2-}$	629 mg/L
Chloride as $\text{Cl}^-$	153 mg/L
Turbidity NTU	84 NTU
Dissolved organic carbon	78 mg C/L
N- $\text{NH}_4^+$	46.2 mg/L
N- $\text{NO}_3^-$	107 mg/L
Total P	8.7 mg/L
pH	4.7

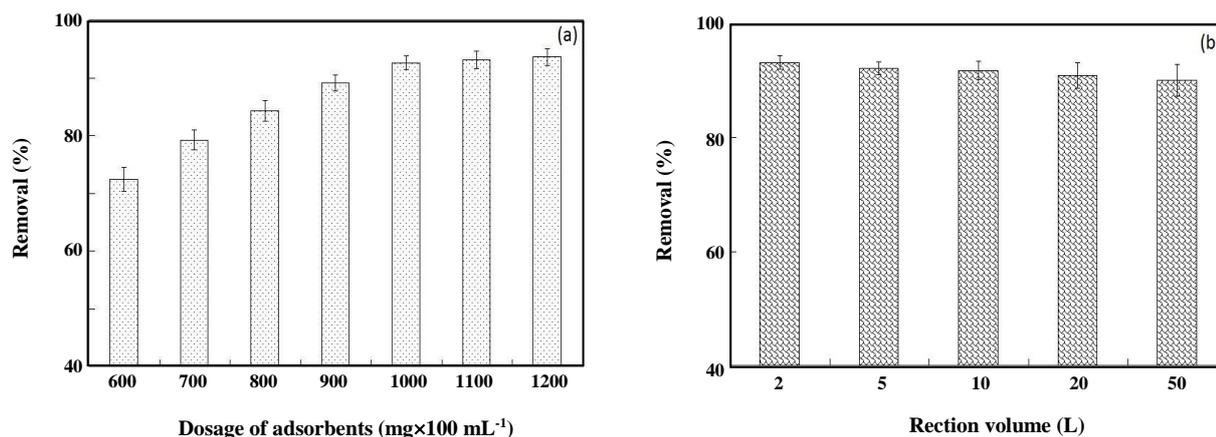


Fig. 7: Effect of dosages adsorbents (a) and reaction volumes (b) on the removal efficiency of Cu(II) from ions electroplating wastewater: pH = 4.7, time = 45 min, temperature = 25 °C.

### Application

The properties of Cu(II) electroplating wastewater are given in Table 3. The value of Cu(II) present in the electroplating wastewater is 493 mg/L. The difference of dosage between batch mode studies using synthetic solution of Cu(II) and electroplating wastewater was due to the presence of other metal ions (such as Fe(III), Pb(II), Cd(II), Zn(II)) in electroplating wastewater. To achieve maximum removal efficiency, the dosage of adsorbent for Cu(II) electroplating wastewater should be indicated in Fig. 7a. Results showed that the removal efficiency increased with increase of adsorbent dosage, attained maximum value of  $92.6 \pm 1.2\%$  at  $10 \text{ g} \cdot \text{L}^{-1}$ , while, there was no significant change for the removal efficiency with further increase of the adsorbent dosage due to the complexation of organic ligands such as dissolved organic carbon,  $\text{N-NH}_4^+$  with Cu(II) in electroplating wastewater [26]. As shown in Fig. 7b, the removal efficiencies of Cu(II) from electroplating wastewater with the reaction volumes of 2, 5, 10, 20 and 50 L were  $93.2 \pm 1.4\%$ ,  $92.2 \pm 1.1\%$ ,  $91.8 \pm 1.6\%$ ,  $90.9 \pm 2.2\%$  and  $90.1 \pm 2.8\%$ , respectively. There was no significant change for the removal efficiency of Cu(II) from electroplating wastewater with the increase of reaction volumes. This result indicated that the PEI-functionalized silica adsorbent was an effective adsorbent for the removal of Cu(II) ions from electroplating wastewater.

### CONCLUSIONS

Our work demonstrated the potential of the PEI-functionalized silica for the removal of Cu(II) ions from electroplating wastewater. The prepared PEI-

functionalized silica exhibited good characteristics, such as fast adsorption kinetics, moderate adsorption capacity, and good regeneration ability. The kinetic data showed well fitted pseudo-second-order kinetic model. The adsorption of Cu(II) ions on PEI-functionalized silica followed the Langmuir model. It was concluded that PEI-functionalized silica was a promising adsorbent for the removal of Cu(II) ions from wastewater effluent of electroplating industry.

### Acknowledgements

This work was sponsored by the Scientific Research Foundation of Educational Department of Liaoning Province (grant no. L2012102), Administration Foundation of Science & Technology of Anshan, Liaoning Province (grant no. 2011MS13), and Special Foundation of University of Science and Technology Liaoning (grant no. 2012CX03).

Received : Nov. 23, 2013 ; Accepted : Oct. 27, 2014

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