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Adsorption of phenol on a novel adsorption material PEI/SiO_2

Fuqiang An *, Baojiao Gao

Department of Chemical Engineering, North University of China, Taiyuan 030051, People' s Republic of China

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Abstract

In this paper, functional macromolecule polyethyleneimine (PEI) was grafted onto the surfaces of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane (CP), and the novel adsorption material PEI/SiO_2 with strong adsorption ability for phenol was prepared. The adsorption properties of PEI/SiO_2 for phenol were researched by both static and dynamic methods. The experimental results show that PEI/SiO_2 possesses very strong adsorption ability for phenol, and the saturated adsorption amount could reach to 160 mg g^{-1}. The empirical Freundlich isotherm was found to describe well the equilibrium adsorption data. pH and grafting amount of PEI have great influence on the adsorption amount. Diluted sodium hydroxide solution is used as eluent, and the adsorbed phenol is eluted easily from PEI/SiO_2.

Keywords: Polyethyleneimine; Silica gel; Adsorption; Phenol

1. Introduction

Phenol has great harmful effect for public health and environmental quality, and more and more rigorous limits on the letting amount of phenol have been established. Especially, wastewater containing phenol brings a series of serious environmental problem because of high toxicity and accumulation of phenol in the environment [13,9,10]. For treatment of wastewater containing phenol, adsorption with various adsorption materials, such as activated carbon and bentonite and so on [12,8,17,3], and degradation with various microorganisms [15,2,6] were studied extensively, but there are some problems, such as lower adsorption capacity, high cost, being incapable of reuse and so on. In recent years, functional polymers containing amide groups have been increasingly studied by using as adsorbents for efficient removal of phenol from wastewater [10,5] because a strong adsorption force, hydrogen bond interaction, can be produced between the nitrogen atoms of those mentioned polymers and phenol.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there are a great number of nitrogen atoms of amino groups on its macromolecular chains, very strong hydrogen bond interaction can produce between PEI and phenol. In our previous study, the adsorption properties of surface-modified diatomite with PEI for phenol [7] were researched, in which PEI was coated physically onto diatomite particles. In that work, although the physically modified diatomite with PEI had stronger adsorption ability for phenol and the adsorption capacity could attach to 92 mg g^{-1}, there were some drawbacks. On one hand, the amount of coated PEI on diatomite particle surfaces is less and the adsorption property of diatomite for phenol was limited; on the other hand, wrapped PEI macromolecules were easy to fall off. Obviously, the adsorption efficiency is lower. In this study, PEI macromolecules were bond covalently onto the surface of silica gel particles by coupling grafting, and a novel composite adsorption material, PEI/SiO_2, was prepared. PEI/SiO_2 displayed excellent adsorption property for phenol, and the adsorption capacity can get up to 160 mg g^{-1}. The adsorption material combines well the strong adsorption property of PEI for phenol with high specific area and fine mechanical strength of silica gel, and it is promising route for the preparing adsorption materials to graft functional polymer onto inorganic particles.

2. Experimental

2.1. Materials and instruments

Silica was purchased from Ocean Chemical Limited Company (120–160 mesh, about 125 μm in diameter, pore size:

* Corresponding author. Tel.: +86 351 3921414; fax: +86 351 3922118.
E-mail address: anfuqiang@nuc.edu.cn (F. An).

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6 nm, pore volume: 1.0 mL/g, surface area: 350 m^2/g. Qingdao, China). PEI was purchased from Qianglong Chemical Limited Company (Wuhan, China, AR grade). γ-Chloropropyl trimethoxysilane was purchased from Yongchang Chemical Limited Company (Naking, China, AR grade). Phenol and other chemicals were purchased from Beijing Chemical Plant (AR grade).

Used instruments in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, American), Perkin-Elmer1700 infrared spectrometer (Perkin-Elmer Company, American), DDS-11Ar digit conductivity meter (Leici Instrument Limited Company of Shanghai, China), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), 721 spectrophotometer (The Third analytical Instrument Factory of Shanghai, China).

2.2. Preparation and characterization of adsorbent PEI/SiO_2

The adsorption material PEI/SiO_2 was prepared and characterized according to the process described in previous study [5], and the typical procedures are as follows. Firstly, silica gel particles were treated for activating by using aqueous solution of methane sulfonic acid as activation reagent; secondly, activated silica gel reacted with γ-chloropropyl trimethoxysilane (CP) at 80 °C by using xylene as solvent into which a little water was added, and chlopropylation silica (CP-SiO_2) was prepared; finally, CP-SiO_2 was added into PEI aqueous solution with a certain concentration, reaction was carried out at 90 °C for 6 h, PEI was grafted onto silica gel surface in coupling manner, and the novel composite adsorption particles of PEI/SiO_2 were prepared. The chemical structures of CP-SiO_2 before and after grafting were characterized by infrared spectrum in order to confirm that PEI had been grafted onto silica particle surface. The amount of amino groups on PEI/SiO_2 was determined with conductivity titration method by using hydrochloric acid as titrant, and the grafting amount (g/100 g) of PEI was calculated further. Through varying the concentration of PEI solution during grafting reaction, PEI/SiO_2 with different grafting amount of PEI were prepared.

The grafting degree of PEI was determined by using conductivity titration method, the surface structure of PEI/SiO_2 was characterized by infrared spectrum, and the grafting of PEI on the surface of SiO_2 was confirmed.

2.3. Static adsorption of phenol on PEI/SiO_2

2.3.1. Measurement of kinetic adsorption curve

About 0.2 g of PEI/SiO_2 were introduced into a conical flask directly. Hundred millilitres of aqueous phenol solution with a initial concentration (C_0) of 200 mg L^{-1} was then added into conical flasks. This conical flask was placed in a shaker at a presettled temperature and pH and shaken. At different times, the concentration (C_t) of phenol solution was determined by using 4-aminoantipyrine-spectrophotometric method at 460 nm [18]. The adsorption amount (Q) was calculated according to Eq. (1).

$$Q = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where Q (mg g^{-1}) is the adsorption amount; V (L) the volume of the phenol solution; m (g) is the weight of the absorbent PEI/SiO_2.

2.3.2. Measurement of adsorption isotherm with static method

About 0.2 g of PEI/SiO_2 was introduced into a conical flask directly. Hundred millilitres aqueous solution of phenol with concentration (C_0) of 20, 40, 60, 80, 100, until 200 mg L^{-1} were then added into each conical flask. The conical flasks were placed in a shaker at a presettled temperature and pH and shaken. After the adsorption reached equilibrium, the concentration (C_e) of phenol solution was determined. The equilibrium adsorption amount (Q_e) was calculated according to Eq. (2).

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

2.4. Examination of influences of various factors on adsorption property of PEI/SiO_2

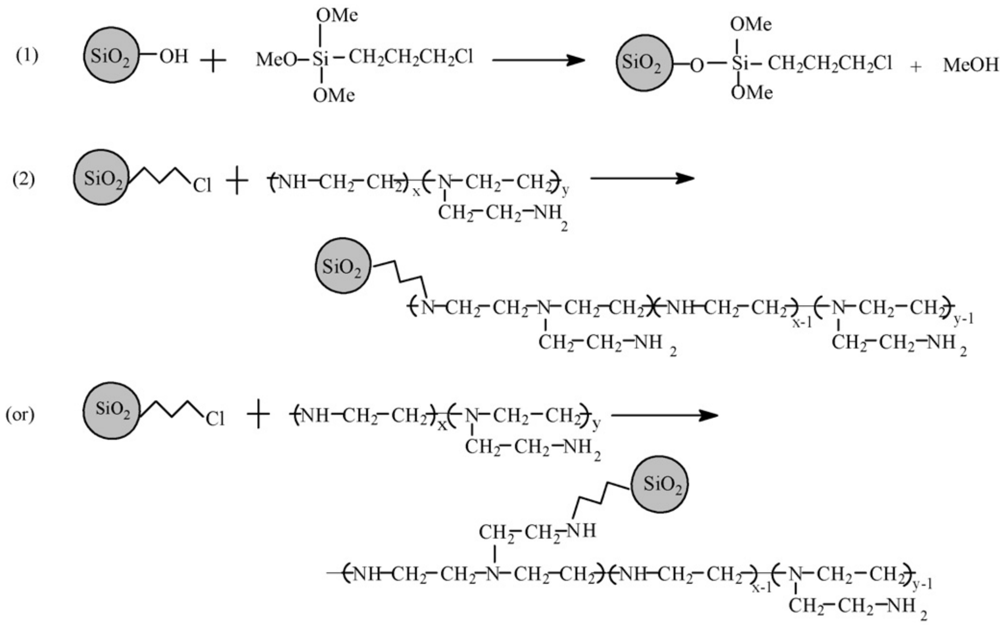
Varying the pH of each sample solution by buffer solutions (NH_4NO_3–$NH_3 \cdot H_2O$ and NaAc–HAc), the influence of pH on the adsorption property of PEI/SiO_2 was examined. Varying the grafting amount of PEI on silica gel, the influence of grafting amount on the adsorption property of PEI/SiO_2 was examined.

2.5. Adsorption dynamics and elution experiment

1.41 g of PEI/SiO_2 were filled in a glass column with 8 mm of diameter, and the bed volume was 2 mL. The phenol solution with concentration of 1 g/L and pH 7 was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV/h). The effluent with one bed volume was collected, the concentration of the phenol was determined, and the dynamics adsorption curve was measured. The leaking adsorption amount and the saturated adsorption amount were also calculated. Elution experiment were performed by using sodium hydroxide solution with concentration of 0.01 mol/L as eluting agent, and the flow rate of the eluting agent was controlled at 1 BV/h. The eluent with one bed volume was collected, the concentration of the phenol was determined, and the elution curve was plotted (Table 1).

Table 1
The n and k value

pH	n	k
4	1.03	0.4257
6	1.03	0.9638
7	0.9807	1.1725
8	1.0827	0.5169
10	0.9291	0.3288
12	1.0152	0.0474



Scheme 1. Synthesis process of composite material PEI/SiO_2.

3. Results and discussion

3.1. Preparing process and structure characterizing of PEI/SiO_2

The molecules of commercial PEI often have branch chains (branched PEI), and it contains primary, secondary and ternary amino groups in a ratio of approximately1:2:1 [4] (its chemical structure can be seen from Scheme 1).γ-Chloropropyl trimethoxysilane was chosen as coupling agent to link silica gel and functional macromolecular PEI. After activating treatment, a great deal of silanol groups produce on silica gel particle surfaces, and γ-chloropropyl trimethoxysilane reacts with silanol groups to form modified silica gel (it can be called chloropropylation silica gel, CP-SiO_2). The chloropropyl groups on CP-SiO_2 react further with amine groups on PEI chains, macromolecule PEI is grafted onto silica surface in coupling mode, so that the composite particles of PEI/SiO_2 are formed finally. The coupling grafting reactions occur possibly on all of the active sites of the primary amine groups and secondary amine groups in PEI molecule, so there are two types of coupling grafting reactions. The reaction processes to prepare the composite material PEI/SiO_2 can be expressed in Scheme 1.

The infrared spectrums of PEI/SiO_2 are shown in Fig. 1. The characteristics absorptions of flex vibration and bend vibration of N–H bond appear at 3641 and 1701 cm^{-1}, respectively, and the characteristics absorptions of bend vibration of C–N bond appear at 1488 and 1560 cm^{-1}. The appearances of these absorption bands show that PEI macromolecules have been grafted onto silica gel surface, and PEI/SiO_2 particles have been formed.

3.2. Kinetic adsorption curve of PEI/SiO_2 for phenol

The kinetic adsorption curve is shown in Fig. 2. The adsorption rate of PEI/SiO_2 towards the phenol is fast, and the adsorption reaches to equilibrium in 100 min. It was implied that PEI/SiO_2 possesses very strong adsorption ability for phenol.

3.3. Adsorption isotherm of PEI/SiO_2 for phenol

The adsorption isotherms of PEI/SiO_2 for phenol are shown in Fig. 3. It can be seen that the equilibrium adsorption amount of phenol increases rapidly with the increase of equilibrium concentrations, there appears a maximum value (160 mg/g), and subsequently the adsorption amount decreases again. To our knowledge, the adsorption capacity of 160 mg/g is very high compared with those values (3–40 mg/g) reported in references and at least there is an enhancement of three times [1,11,16]. Obviously, the novel composite material PEI/SiO_2 has very strong adsorption ability for phenol. Besides, the adsorption isotherm type characterized by a plateau after an initial sharp

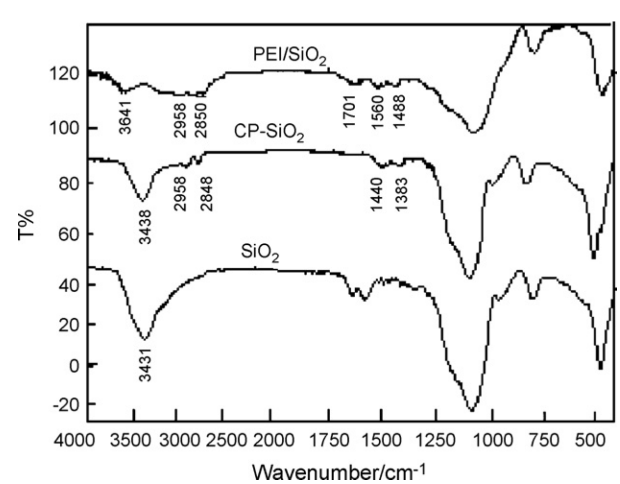


Fig. 1. FTIR spectrum of PEI/SiO_2.

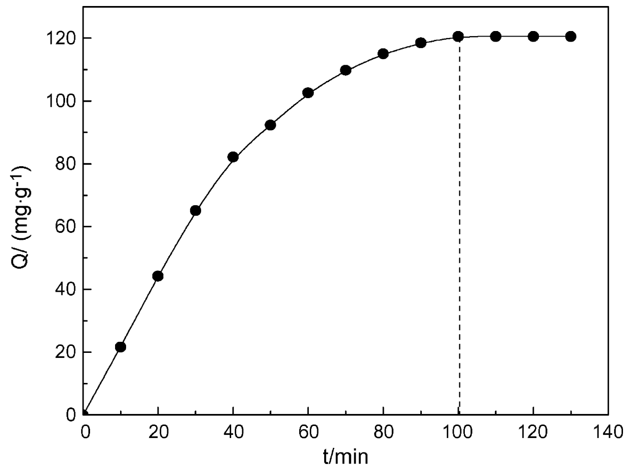


Fig. 2. Kinetic adsorption curve of PEI/SiO_2 for phenol. Temperature: 20 °C; pH 7; grafting degree of PEI of used PEI/SiO_2: 3.21 g/100 g; initial concentration of phenol: 200 mg L^{-1}.

increase also shows that there is a high affinity [14] between phenol and PEI/SiO_2 particles. The high affinity attributes to the hydrogen bond interaction (main) and electrostatic interaction between them, and the interaction mechanism will be discussed below.

Freundlich adsorption equation and its logarithms form are follows:

$$Q_e = kC_e{}^n \tag{3}$$

$$\ln Q_e = \ln k + n \ln C_e \tag{4}$$

The data in Fig. 3 are treated using Freundlich adsorption equation, and the straight line is displayed in Fig. 4. Linear regression is performed according to the logarithmic form, and the linear regression coefficient is 0.9994, the curve of the ln Q_e vs. ln C_e fit satisfactorily to Freundlich equation.

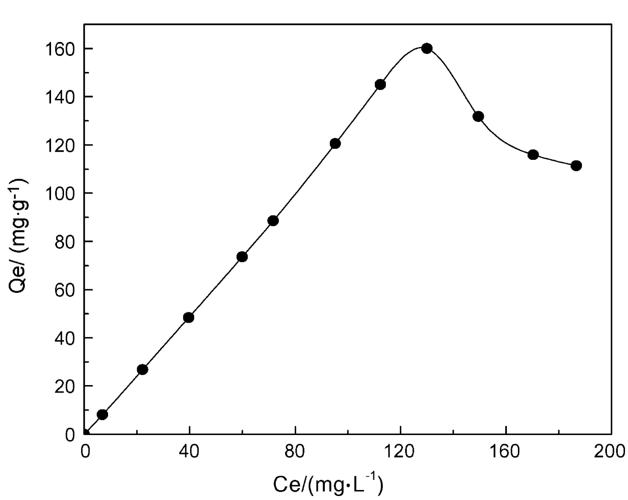


Fig. 3. Adsorption isotherms of PEI/SiO_2 for phenol. Grafting degree of PEI of PEI/SiO_2: 4.11 g/100 g; temperature: 20 °C; adsorption time: 100 min; pH 7.

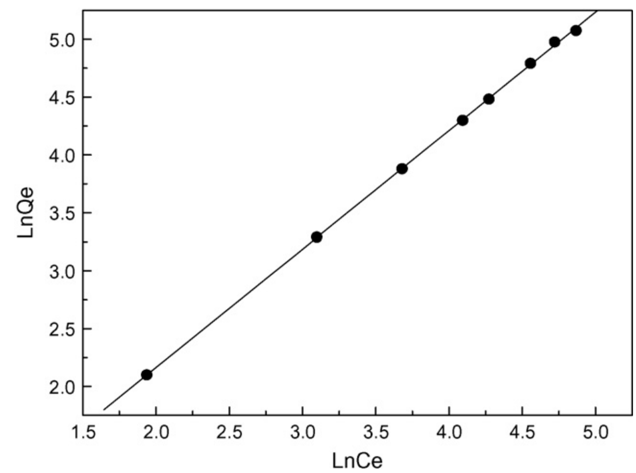


Fig. 4. Plot of ln Q_e vs. ln C_e.

3.4. Influences of different factors on adsorption property of PEI/SiO_2

3.4.1. Influence of pH

There are different adsorption capacities of PEI/SiO_2 for phenol as the phenol solutions have different pH values, and the adsorption isotherms at different pH values are shown in Fig. 5. The effect of pH value on the adsorption property of PEI/SiO_2 can be seen clearly from Fig. 6, which comes from the data of Fig. 5. Obviously, the value of pH has a great influence on the adsorption property of PEI/SiO_2 for phenol, in acidic and basic solutions, the adsorption capacities are all lower, and in neutral solution there is the greatest adsorption capacity. The reasons for this have been analyzed in detail in the previous study [7], and here it is again described briefly.

The adsorption capacity differences at different pH values are caused by different molecule forms of PEI and phenol and different acting forces between them. In acidic solution, the N atoms on PEI chains interact with phenol at molecular state via

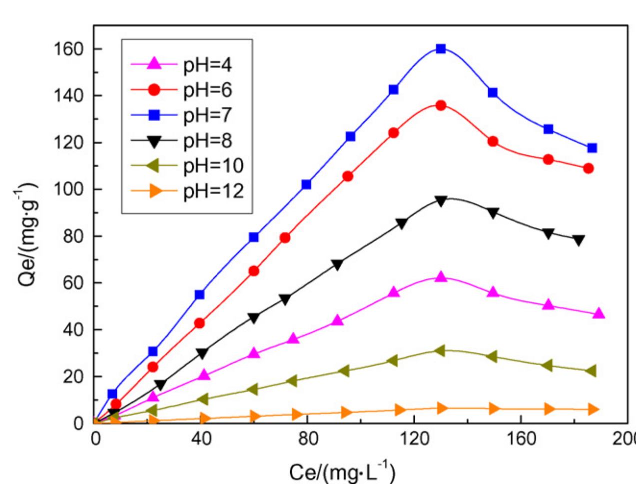


Fig. 5. Adsorption isotherms of PEI/SiO_2 for phenol at different pH. Grafting degree of PEI of PEI/SiO_2: 4.11 g/100 g; temperature: 20 °C; adsorption time: 100 min.

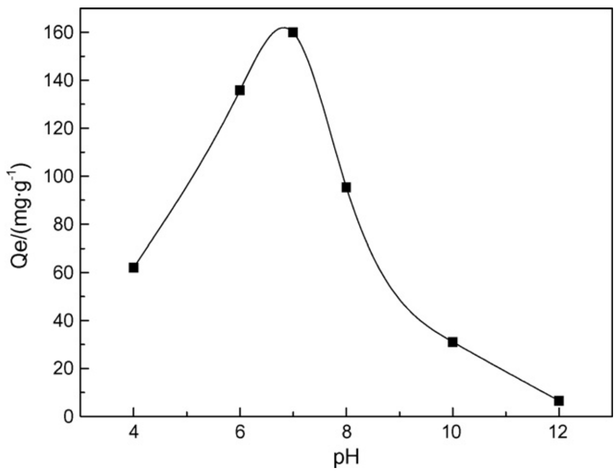


Fig. 6. Varying of adsorption capacity of PEI/SiO_2 with pH values. Grafting degree of PEI of PEI/SiO_2: 4.11 g/100 g.

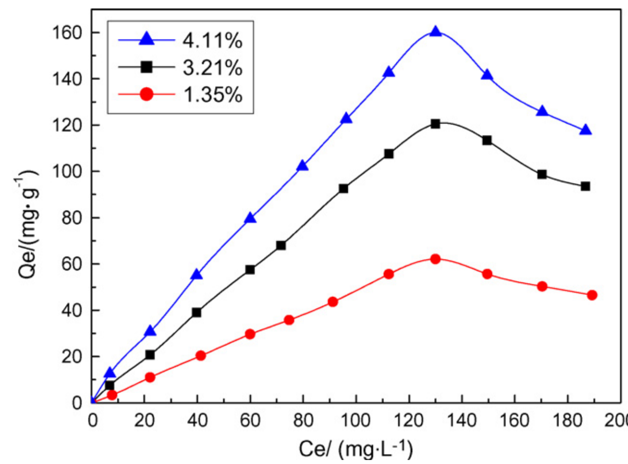


Fig. 7. Adsorption isotherms of PEI/SiO_2 with different grafting degree of PEI. temperature: 20 °C; time: 100 min; pH 7.

hydrogen bond interaction. However, in acidic solution, 70% of the N atoms on PEI chains are protonated [4], so the hydrogen bond interaction between PEI on PEI/SiO_2 surface and phenol is weaker, resulting in smaller adsorption capacity. In basic solution, the N atoms on PEI chains interact with phenol at negative ion state of benzene–oxygen via electrostatic interaction. However, in basic solution, only 32% the N atoms on PEI chains are protonated [4], so the electrostatic interaction PEI on PEI/SiO_2 surface and phenol is very weak, resulting in much lower adsorption capacity. It can be estimated according to the dissociation equilibrium of phenol that in neutral solution, phenol exists mainly as molecular state and at the same time, the negative ion of benzene–oxygen with a certain concentration also exists. In neutral solution, the protonation degree of the N atoms on PEI chains is about 60%. So in neutral solution, there is stronger hydrogen bond interaction between PEI on PEI/SiO_2 surface and phenol, and in the meantime, there is also electrostatic interaction with a certain degree between PEI on PEI/SiO_2 surface and phenol with negative benzene–oxygen ion state. With the cooperation of the two actions, very strong adsorption ability of PEI/SiO_2 for phenol is displayed in neutral solution.

3.4.2. Influences of PEI grafting amount

The adsorption isotherms of PEI/SiO_2 with different grafting degrees of PEI for phenol are shown in Fig. 7. It can be found that the adsorption capacity of PEI/SiO_2 enhances remarkably with the increase of the grafting degrees of PEI due to the increase of amino groups, and the saturated adsorption amount of phenol on PEI/SiO_2 with a PEI grafting degree of 4.11 g/100 g is as high as 160 mg g^{-1}.

3.5. Dynamic adsorption curve

Fig. 8 shows the dynamic adsorption curve of PEI/SiO_2 for phenol. It can found that when phenol solution passes through the column packed with PEI/SiO_2 at a flow rate of five bed volumes per hour (5 BV/h) upstream, the leaking appears only at 68 BV, the leaking adsorption amount to be calculated is 95.35 mg/g, and the saturated adsorption amount is 112.74 mg/g. Obviously, analogous to the static adsorption result, the dynamic adsorption capacity is also very high.

3.6. Elution curve

Fig. 9 gives the elution curve of phenol from PEI/SiO_2. Sodium hydroxide solution with a concentration of 0.01 mol/L is used as the eluant, and the eluant at a rate of 1 BV/h flows upstream through the column of PEI/SiO_2 particles on which the adsorption of phenol has reached to saturation. It can be seen that the shape of desorption curve is cuspate and without tailing, and it shows the fine elution result. The calculation results show that within 10 bed volumes, phenol is eluted from PEI/SiO_2 column with a desorption ratio of 98.53%. The fact reveals fully that PEI/SiO_2 on which phenol is adsorbed in saturation has outstanding elution property, and this novel composite material PEI/SiO_2 has excellent reusing property.

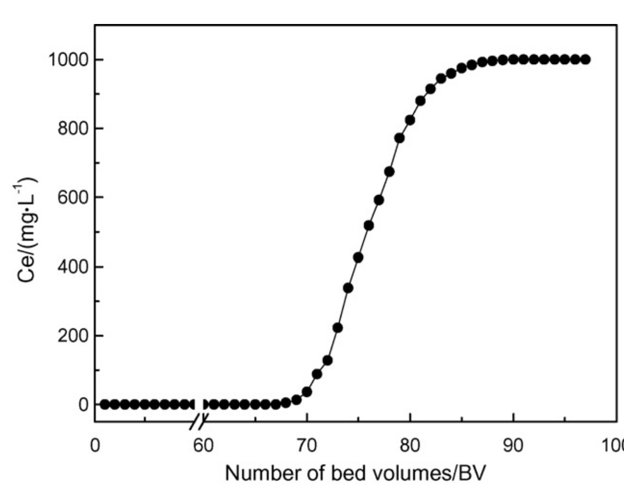


Fig. 8. Breakthrough curve of phenol on PEI/SiO_2 column. Temperature: 20 °C; initial phenol concentration: 1 g/L; grafting degree of PEI of used PEI/SiO_2: 3.21 g/100 g.

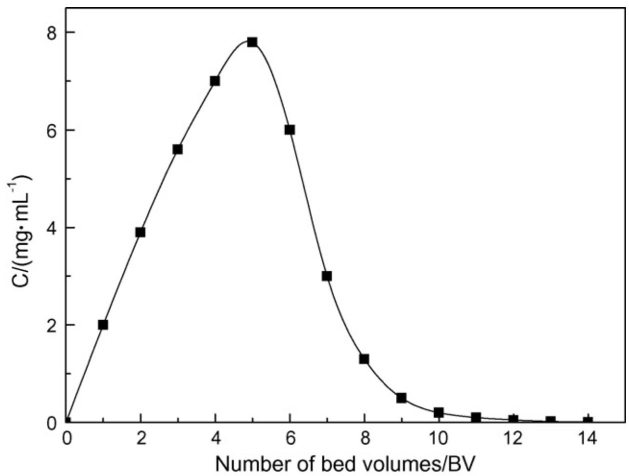


Fig. 9. Elution curve of phenol from PEI/SiO_2; temperature: 20 °C.

4. Conclusions

In this study, functional macromolecule polyethyleneimine was grafted onto micron-sized silica gel by coupling grafting manner, and the novel adsorption material PEI/SiO_2 was successfully prepared. PEI/SiO_2 has very strong adsorption ability for phenol by way of hydrogen bond interaction (main action force) and electrostatic interaction. The adsorption ability of PEI/SiO_2 for phenol is dependent on pH value of solution greatly, and in neutral solution there is the strongest adsorption capacity in neutral solution as compared with acidic and basic solutions. The adsorption capacity enhances still with the grafting degree of PEI on silica gel, and the greater the grafting degree of PEI is, the higher the adsorption capacity is, and it can get up to 160 mg/g as PEI/SiO_2 with a grafting degree of 4.11 g/100 g was used at pH 7 and room temperature. This study shows that it is a promising route for preparing effective adsorption materials used in water treatment to graft functional polymer onto inorganic particles.

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