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Adsorption mechanism and property of novel composite material PMAA/SiO_2 towards phenol

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ABSTRACT

In this paper, functional macromolecule poly(methacrylic acid) (PMAA) was grafted on the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as intermedia, and the grafted particle PMAA/SiO_2 with strong adsorption ability for phenol was prepared. The adsorption mechanism and properties of PMAA/SiO_2 for phenol were researched by static and dynamic methods. The experimental results showed that PMAA/SiO_2 possesses strong adsorption ability for phenol with interaction of three kinds of hydrogen bonds including peculiar O–H···π hydrogen bond (aromatic hydrogen bond) and O–H···O=C π hydrogen bond. The saturated adsorption amount could reach up to 162.88 mg g^{-1}. The empirical Freundlich isotherm was found to describe well the equilibrium adsorption data. pH and temperature were found to have great influence on the adsorption amount. Finally, PMAA/SiO_2 was observed to possess excellent reusability properties as well.

1. Introduction

Phenol, listed as top priority contaminants by the US EPA, is the common substructure of many potentially carcinogenic pollutants occurring in the industrial effluents of pharmaceutical, dyestuff, photographic, and agrochemical industries. Phenol-contained wastewater brings a series of serious environmental problem due to its high toxicity and accumulation in the environment [1–3]. For the treatment of phenol-contained wastewater, adsorption with various adsorption materials, such as activated carbon, bentonite, synthetic polymeric adsorbents and so on [2–11], and degradation with various microorganisms [12–18] have been studied extensively. However, some problems have been identified, such as lower adsorption capacity, high costs, lower regenerability and so on. In recent years, functional polymers have been increasingly used as adsorbents for the efficient removal of phenol from wastewater [19,20] because of the strong interaction between the functional groups of polymer and phenol.

Poly(methacrylic acid) (PMAA) has been extensively used for wastewater treatment [21,22]. On its macromolecular chains, there are a great number of carboxyl groups; so extremely strong hydrogen bond interaction can be produced between MAA and phenol. However, it is unstable under shearing. In addition, it contains toxic monomers, which could cause severe secondary environmental pollution problems. Thus, a more efficient and environmentally friendly adsorbent is desirable. In this study, PMAA was grafted on the surface of silica gel particles and a novel composite material PMAA/SiO_2 was prepared. The composite material combines well the strong interaction between PMAA and phenol with high specific area and fine mechanical stability of silica gel. PMAA/SiO_2 displayed excellent adsorption property for phenol in this study.

2. Experimental

2.1. Materials and instruments

Silica was purchased from the Ocean Chemical Company, Ltd. (120–160 mesh, about 125 μm in diameter, pore size: 6 nm, pore volume: 1.0 mL/g, surface area: 350 m^2/g, Qingdao, China). Methacrylic acid (MAA) was purchased from Ruijinte Chemical Ltd. (Tianjin, China, AR grade). MAA was purified by distillation under vacuum before use. γ-Methacryloylpropyl trimethoxysilane (MPS) was purchased from Nanking Chuangshi Chemical Aux Ltd. (Jiangsu, China, AR grade). Phenol was purchased from Beijing Chemical Plant (Beijing, China, AR grade). Ammonium persulfate was purchased from Shanghai Chemical Reagent Plant (Shanghai, China, AR grade).

The instruments used in this study were as follows: STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany), Unic-2602 UV-VIS spectrophotometer (Unic Company, American), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China).

2.2. Preparation and characterization of adsorbent PMAA/SiO_2

10 g of silica gel particles activated with methane sulfoacid and 15 mL of coupling agent MPS were added into 200 mL of a mixed

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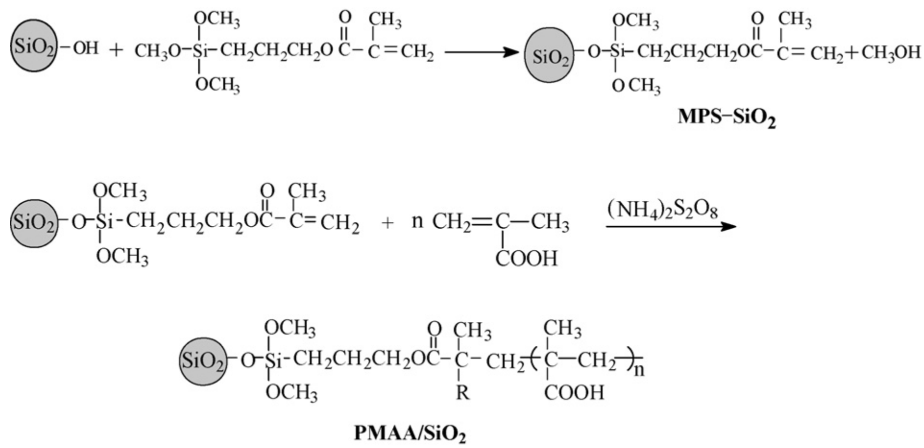


Scheme 1. Synthesis process of composite material PMAA/SiO_2.

solvent of ethanol and water (v/v = 1:1), and the contents were maintained at 50 °C and was reacted for 24 h, resulting in the formation of the surface-modified particles MPS–SiO_2, on which polymerisable double bonds were attached chemically. Afterwards, 6 g of particles MPS–SiO_2 and 20 g of methacrylic acid were added into 400 mL of water, and the graft polymerisation was performed by initiating of $(NH_4)_2S_2O_8$ (0.012 g, 0.6 wt.% of monomer) under N_2 atmosphere at 70 °C for 24 h. The product particles were extracted with ethanol in a soxhlet to remove the polymers attached physically to the particles, dried under vacuum, and finally the grafted particles PMAA/SiO_2 were gained. The total preparation processes of PMAA/SiO_2 are expressed in Scheme 1. The grafting degree of PMAA/SiO_2 was determined with TGA method. The particles PMAA/SiO_2 used in this study have a grafting degree of 0.1732 g g^{-1}.

2.3. Adsorption of phenol on PMAA/SiO_2

2.3.1. Measurement of kinetic adsorption curve

About 0.2 g of PMAA/SiO_2 were introduced into a conical flask directly. 50 mL of aqueous phenol solution with a initial concentration (C_0) of 8000 mg L^{-1} was then added into conical flasks. This conical flask was placed in a shaker at a presettled temperature and pH and was then shaken. At different times, the concentration (C_t) of phenol solution was determined by UV analysis performed on a UV-VIS spectrophotometer with the wavelength at 270 nm. The adsorption amount (Q) was calculated according to Eq. (1).

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

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

2.3.2. Measurement of adsorption isotherm with static method

About 0.2 g of PMAA/SiO_2 was introduced into a conical flask directly. 50 mL aqueous solution of phenol with concentration (C_0) of 1000, 2000, until 8000 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 were then 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).

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

2.4. Examination of influence of various factors on adsorption property of PMAA/SiO_2

By varying the pH of each sample solution by NaOH and HCl solutions, the influence of pH on the adsorption property of PMAA/SiO_2 was examined. By varying the temperature, the influence of temperature on the adsorption property of PMAA/SiO_2 was examined.

2.5. Dynamics adsorption and elution experiment

1.5324 g of PMAA/SiO_2 was filled in a glass column with 8 mm of diameter and 2 mL of the bed volume. The phenol solution with concentration of 1 g L^{-1} and pH of 6 was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV h^{-1}). The effluent with one bed volume was collected and the concentration of phenol was determined. Then the dynamics adsorption curve was plotted. 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^{-1} as eluting agent, and the flow rate of the eluting agent was controlled at 1 BV h^{-1}. The eluent with one bed volume was collected, the concentration of the phenol was determined, and the elution curve was plotted.

2.6. Repeated use experiment

Repeated usability (i.e., regenerability) is an important factor for an effective absorption material. Desorption of the adsorbed phenol from PMAA/SiO_2 also studied by static experiment using 0.01 mol L^{-1} of sodium hydroxide solution as eluent. PMAA/SiO_2 that have adsorbed phenol was placed in the eluent and stirred continuously at room temperature for 10 h. The final concentration of phenol in aqueous phase was determined. Desorption ratio was calculated from the amount of phenol adsorbed on the PMAA/SiO_2 and final phenol concentration in the eluent. In order to test the reusability of PMAA/SiO_2, phenol adsorption–desorption procedure was repeated ten times by using the same PMAA/SiO_2.

3. Results and discussion

3.1. Kinetic adsorption curve of PMAA/SiO_2 for phenol

The kinetic adsorption curve is shown in Fig. 1. The adsorption reached to equilibrium at 10 h, and the saturated adsorption amount reached 162.88 mg g^{-1}. To our knowledge, the adsorption amount of 162.88 mg g^{-1} is very high compared with other values (3–40 mg g^{-1}) reported [2,10,11] and at least there is an enhance-

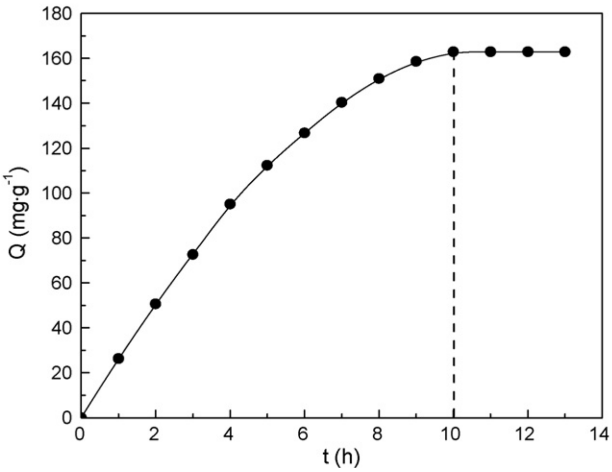


Fig. 1. Kinetic adsorption curve of PMAA/SiO_2 for phenol. Temperature: 20 °C; pH = 6.

ment of three times. Obviously, the composite material PMAA/SiO_2 has very strong adsorption ability and high affinity for phenol. This can be attributed to the hydrogen bond interaction between them, and the interaction mechanism will be discussed below.

3.2. Adsorption isotherm of PMAA/SiO_2 for phenol

The adsorption isotherms of PMAA/SiO_2 for phenol are shown in Fig. 2. It can be seen that the equilibrium adsorption amount of phenol increases rapidly with the increase of equilibrium concentrations. This also implied that PMAA/SiO_2 possesses very strong adsorption ability and high affinity for phenol.

Freundlich adsorption equation and its logarithms form are follows:

$$Q_e = kC_e^{1/n} \tag{3}$$

$$\text{Ln } Q_e = \text{Ln}\,k + \frac{1}{n\,\text{Ln}\,C_e} \tag{4}$$

The data in Fig. 2 are treated using Freundlich adsorption equation, and the straight line is displayed in Fig. 3. Linear regression is performed according to the logarithmic form, and the linear regression coefficient is 0.9996, the curve of the Ln Q_e vs. Ln C_e fit satisfactorily to Freundlich equation.

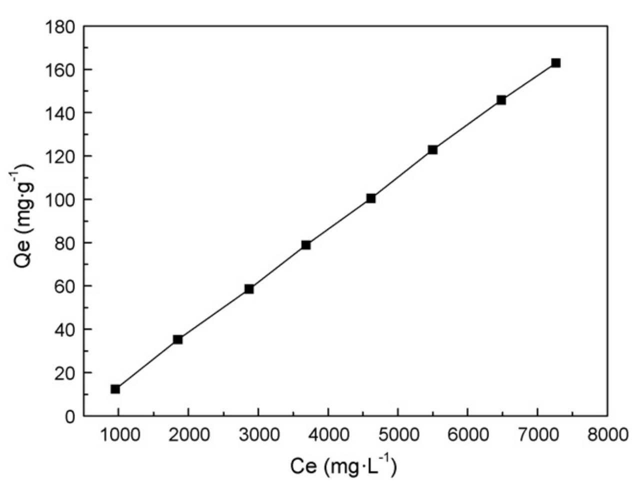


Fig. 2. Adsorption isotherm of PMAA/SiO_2 for phenol. Temperature: 20 °C; adsorption time: 10 h; pH = 6.

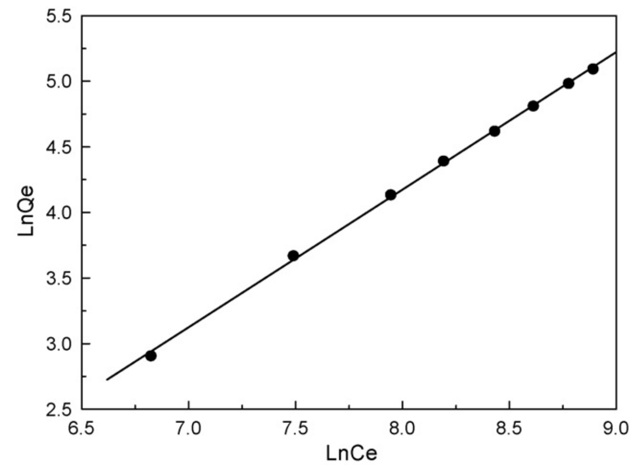


Fig. 3. Plot of Ln Q_e vs. Ln C_e.

3.3. Influence of different factors on adsorption property of PMAA/SiO_2

3.3.1. Influence of pH

The adsorption isotherms at different pH values are shown in Fig. 4. The effect of pH value on the adsorption property of PMAA/SiO_2 can be seen clearly from Fig. 5, which comes from the data of Fig. 4. Obviously, the value of pH has a great influence on the adsorption property of PMAA/SiO_2 for phenol. The lower the pH value, the higher the adsorption amount.

The adsorption amount of PMAA/SiO_2 towards phenol decreases with the increase of pH value. This is caused by different molecule forms of MAA and phenol and acting forces (hydrogen bond) between MAA and phenol. The forms of hydrogen bond occurring possibly between MAA and phenol are expressed in Scheme 2. First, the –OH of carboxyl groups could form aromatic hydrogen bond (O–H···π hydrogen bond) with π–electron cloud of aromatic groups that act as the acceptor (a in Scheme 2) [23–25]. Second, the –OH of carboxyl groups could also form hydrogen bond (O–H···O hydrogen bond) with –OH in phenol molecules (b in Scheme 2). Additional, the –OH of phenol could form π hydrogen bond (O–H···O=C hydrogen bond) with carbonyl π bond of carboxyl groups [26] (c in Scheme 2).

As pH value is lower, there are lots of hydrogen ions H^+ in solution, and the carboxyl groups of PMAA on PMAA/SiO_2 nearly do not dissociate. Three kinds of hydrogen bond could be formed at the

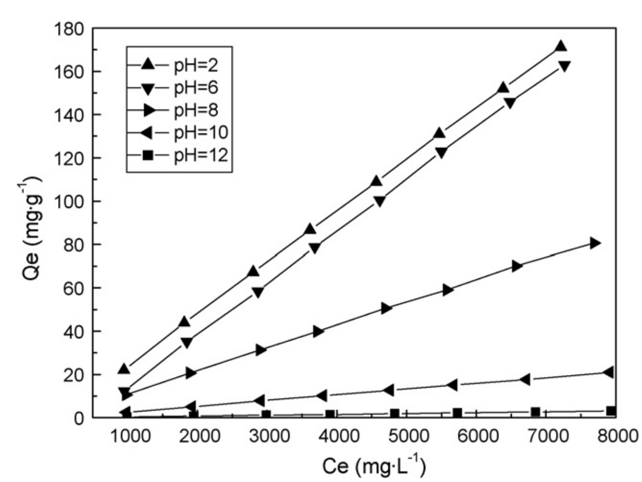


Fig. 4. Adsorption isotherms of PMAA/SiO_2 for phenol at different pH. Temperature: 20 °C; adsorption time: 10 h.

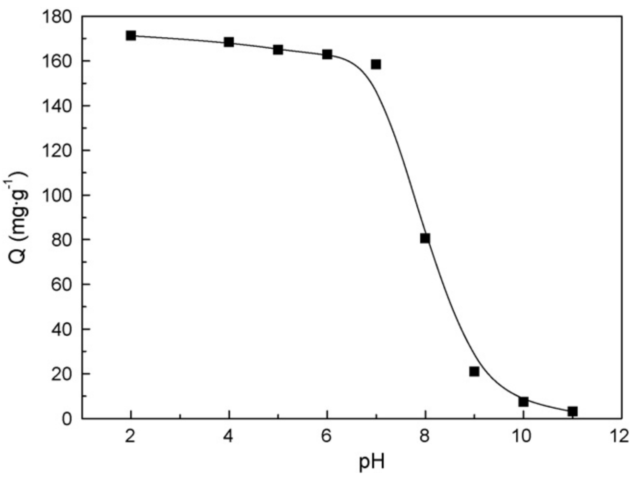


Fig. 5. Adsorption capacity of PMAA/SiO_2 at different pH.

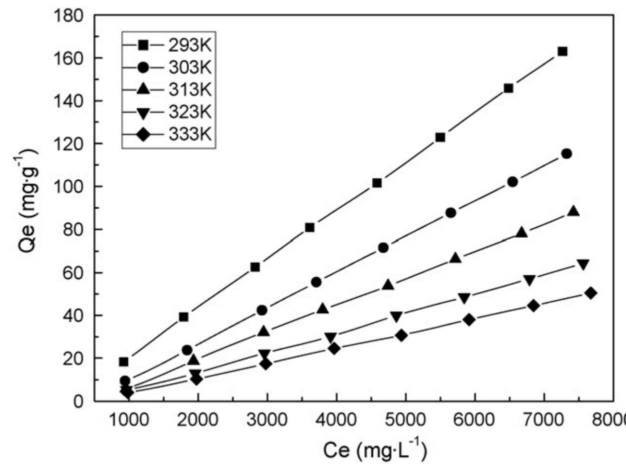
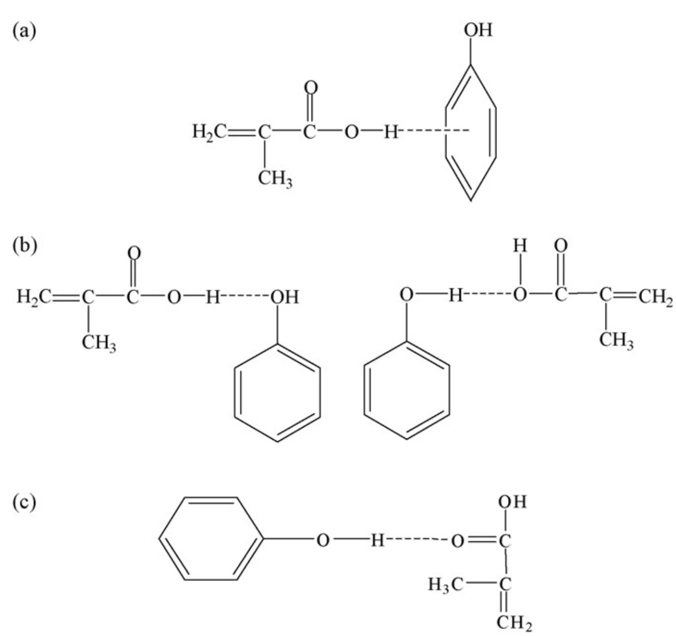


Fig. 6. Adsorption isotherms of PMAA/SiO_2 for phenol at different temperatures. Adsorption time: 10 h; pH = 6.

same time. So the adsorption ability is the strongest and the adsorption amount is the highest. The dissociation degree of the carboxyl groups of PMAA and hydroxy groups of phenol is enhanced with the increases of pH value, resulting in weakening and decrease of the three kinds of hydrogen bond. So the adsorption capacity decline with the increase of pH value. As pH > 7, carboxyl groups of PMAA and hydroxy groups of phenol were neutralized, all three kinds of hydrogen bond could not be formed. So adsorption amount is very low when pH > 7.

3.3.2. *Influence of temperature*

The adsorption isotherms of PMAA/SiO_2 towards phenol at different temperatures are shown in Fig. 6. It can be found that the adsorption amount of PMAA/SiO_2 towards phenol decreases with the increase of temperature, and the influence of temperature on the adsorption amount is great. The saturated adsorption amount at 293 K is 162.88 mg g^{-1}, which is far greater than 50.47 mg g^{-1} of the saturated adsorption amount at 333 K. The fact that the adsorption amount of phenol decreases with the increase of temperature implies that the adsorption of PMAA/SiO_2 towards phenol is an exothermic process.



Scheme 2. Hydrogen bond between MAA and phenol.

According to the Van't Hoff equation:

$$\mathrm{Ln}\ \frac{Q_e}{C_e} = -\frac{\Delta H}{RT} + C \qquad (5)$$

When adsorption amount is 30 mg g^{-1}, the curve of the $\mathrm{Ln}(Q_e/C_e)$ vs. $1/T$ is shown in Fig. 7. It gives the numerical values of ΔH from slope. The numerical values of ΔH is −22.5 kJ mol^{-1}. This also indicated that the adsorption of PMAA/SiO_2 towards phenol is an exothermic process.

3.4. *Dynamic adsorption curve*

Fig. 8 shows the dynamic adsorption curve of PMAA/SiO_2 for phenol. It can found that when phenol solution passes through the column packed with PMAA/SiO_2 at a flow rate of 5 bed volumes per hour (5 BV h^{-1}) upstream, the leaking appears only at 109 BV, the leaking adsorption amount to be calculated is 142.26 mg g^{-1}, and the saturated adsorption amount is 152.34 mg g^{-1}. Obviously, analogous to the static adsorption result, the dynamic adsorption capacity is also very high.

3.5. *Elution curve*

Fig. 9 gives the elution curve of phenol from PMAA/SiO_2. Sodium hydroxide solution with a concentration of 0.01 mol L^{-1} is used as

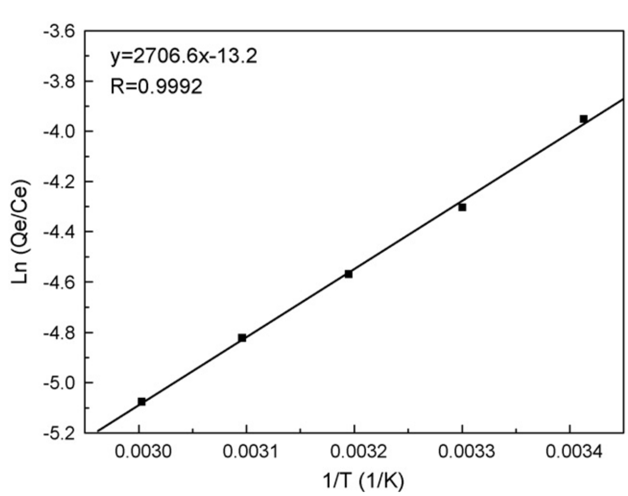


Fig. 7. Plot of $\mathrm{Ln}(Q_e/C_e)$ vs. $1/T$.

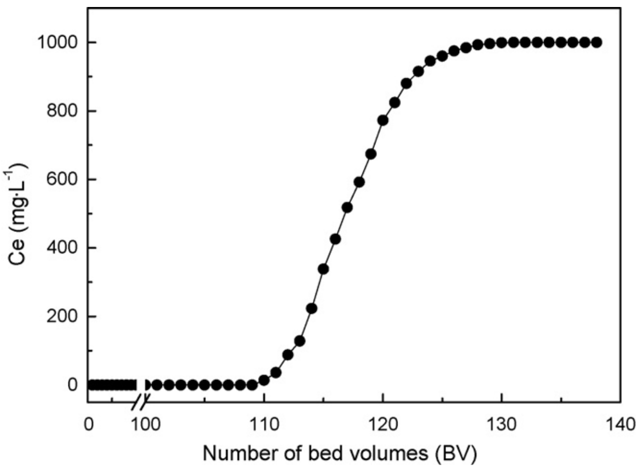


Fig. 8. Breakthrough curve of phenol on PMAA/SiO_2 column. Temperature: 20 °C; initial phenol concentration: 1 g L^{-1}; pH = 6.

the eluent, and the eluent at a rate of 1 BV h^{-1} flows upstream through the column of PMAA/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 21 bed volumes, phenol is eluted from PMAA/SiO_2 column with a desorption ratio of 99.64%. The fact reveals fully that PMAA/SiO_2 on which phenol is adsorbed in saturation has outstanding elution property, and this novel composite material PMAA/SiO_2 has excellent reusing property.

3.6. Reusability

Desorption ratios are very high (97.9%). When sodium hydroxide solution with a concentration of 0.01 mol L^{-1} is used as an eluent, the hydrogen bond interaction between phenol and MAA is disrupted and subsequently phenol is released into eluent. In order to show the reusability of the PMAA/SiO_2, adsorption–desorption cycle was repeated 10 times by using the same material.

Adsorption–desorption cycle of PMAA/SiO_2 was shown in Fig. 10. The results clearly showed that the PMAA/SiO_2 could be used repeatedly without significantly loosing its adsorption amount.

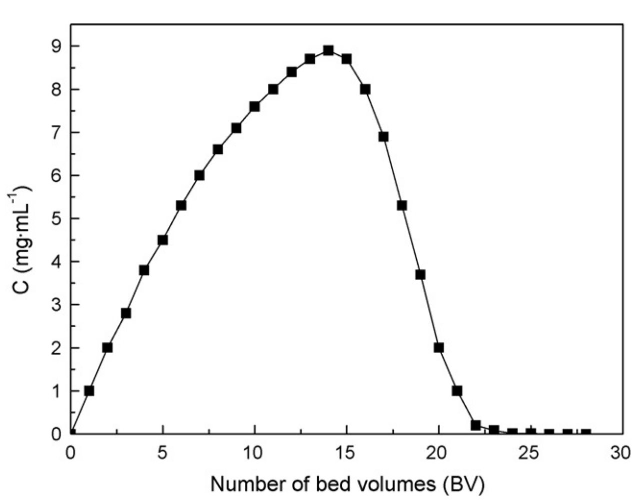


Fig. 9. Elution curve of phenol from PMAA/SiO_2. Temperature: 20 °C.

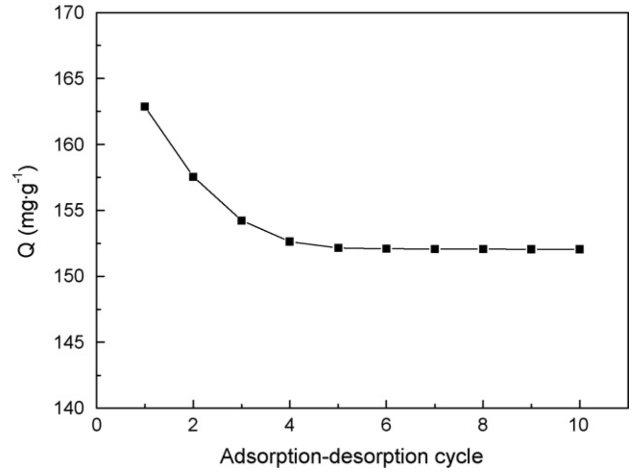


Fig. 10. Adsorption–desorption cycle of PMAA/SiO_2.

4. Conclusions

In this study, functional macromolecule poly(methacrylic acid) was grafted onto micron-sized silica gel using 3-methacryloxypropyl trimethoxysilane (MPS) as intermedia, and the novel adsorption material PMAA/SiO_2 was successfully prepared. PMAA/SiO_2 has very strong adsorption ability for phenol by way of hydrogen bond interaction, and the adsorption mechanism was explained satisfactorily with introducing the π hydrogen bond. The adsorption ability of PMAA/SiO_2 for phenol is largely dependent on pH value and temperature of solution. The lower the pH value, the higher the adsorption amount. The adsorption amount of phenol decreases with the increase of temperature. The lower the temperature, the higher the adsorption amount, and it can raise up to 162.88 mg g^{-1} at 293 K and pH of 6. This study shows that PMAA/SiO_2 could dispose acidic wastewater containing phenol. Additionally, PMAA/SiO_2 has excellent reusability.

Acknowledgement

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