



Adsorption property and mechanism of composite adsorbent PMAA/SiO₂ for aniline

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ABSTRACT

In this paper, functional monomer methacrylic acid (MAA) was grafted onto the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as intermedia, and grafting particles PMAA/SiO₂ were prepared. The adsorption properties and mechanism of PMAA/SiO₂ towards aniline were researched through batch and column adsorption methods. The experimental results showed that PMAA/SiO₂ possesses strong adsorption ability for aniline with interaction of hydrogen bond. The saturated adsorption amount could reach up to 140 mg g⁻¹. The empirical Langmuir isotherm was found to agree well with the equilibrium adsorption data. pH and temperature were found to have great influence on the adsorption amount. Finally, PMAA/SiO₂ was observed to possess excellent reusability properties as well.

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1. Introduction

Aniline is frequently used by the chemical industry such as the raw material in the manufacture of dyes, rubbers, pharmaceutical preparation, plastic and paint. It is also a common by-product from paper and textile industries. The amount of aniline produced in US and China is over 457,000 and 80,000 t per year, respectively. There were more than 150 kinds of down-stream products of aniline. Aniline has great harmful effect for public health and environmental quality, so more and more rigorous limits on the letting amount of aniline have been established. Especially, aniline-contained wastewater has brought a series of serious environmental problem because of its high toxicity and accumulation in the environment. Traditionally, aniline-contained wastewater was treated using photodecomposition [1–3], electrolysis [4], adsorption with activated carbon, clay and other adsorbent [5–8], oxidation [9,10], biodegradation [11] and some other processes. These processes could decompose or remove aniline in wastewater to some extent. However, some problems have been identified, such as lower adsorption capacity and lower regenerability of adsorbent, high costs of biodegradation and electrolysis, and so on. In recent years, functional polymers have been increasingly used as adsorbents for efficient removal of aniline from wastewater [12,13] by way of the strong interaction between the functional groups of polymer and aniline or other aromatic com-

pounds. However, the reusability property of the adsorbent must be promoted.

Poly(methacrylic acid) (PMAA) has been extensively used for wastewater treatment [14,15]. On its macromolecular chains, there are a great number of carboxyl groups; so extremely strong hydrogen bond interaction can be produced between MAA and aniline [16]. However, it is instable under shearing. In addition, it contains toxic residual monomers, which could cause severe secondary environmental pollution problems [14]. Thus, a more efficient and environmentally friendly adsorbent is desirable. In this study, functional monomer methacrylic acid (MAA) was grafted step by step onto the surface of silica gel particles and a novel composite material PMAA/SiO₂ was prepared. The composite adsorbent combined well the strong interaction between PMAA and aniline with fine mechanical stability of silica gel. PMAA/SiO₂ displayed excellent adsorption property and reusability in this study.

2. Experimental

2.1. Materials and instruments

Silica gel 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⁻¹, surface area: 350 m² g⁻¹, Qingdao, China). Methacrylic acid (MAA) was purchased from Ruijinte Chemical Ltd. (Tianjin, China, AR grade). MAA was purified by distillation under vacuum before use. 3-Methacryloylpropyl trimethoxysilane (MPS) was purchased from Nanking Chuangshi Chemical Aux Ltd. (Jiangsu, China, AR grade). Aniline was purchased from Beijing

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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/SiO₂

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 solvent of ethanol and water (v/v = 1:1). Then, it was maintained at 50 °C and was reacted for 24 h, resulting in the formation of the surface-modified particles MPS-SiO₂, on which polymerizable double bonds were attached chemically. Afterwards, 6 g of particles MPS-SiO₂ and 20 g of methacrylic acid were added into 400 ml of water, and the graft polymerization was performed by initiating of (NH₄)₂S₂O₈ (0.012 g, 0.6 wt.% of monomer) under N₂ atmosphere at 70 °C for 24 h. The product particles were extracted with ethanol in a Soxhlet to remove the polymers attaching physically to the particles. After dried under vacuum, the grafted particles PMAA/SiO₂ were prepared. The total preparation processes of PMAA/SiO₂ are expressed in Scheme 1. The grafting degree of PMAA/SiO₂ was determined with TGA method. The particles PMAA/SiO₂ used in this study have a grafting degree of 0.1758 g g⁻¹.

2.3. Batch adsorption of aniline on PMAA/SiO₂

2.3.1. Measurement of kinetic adsorption curve

About 0.1 g of PMAA/SiO₂ was directly introduced into a conical flask, into which 50 ml of aqueous aniline solution with an initial concentration (C₀) of 500 mg l⁻¹ and pH of 8 was added. This conical flask was placed into a shaker at a presettled temperature and then shaken. At different times, the concentration (C_t) of aniline solution was determined with UV-vis spectrophotometer at 280 nm. The adsorption amount (Q) was calculated according to the following equation:

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

where Q (mg g⁻¹) is the adsorption amount; V (l) is the volume of the aniline solution; m (g) is the weight of the adsorbent PMAA/SiO₂.

2.3.2. Measurement of adsorption isotherm

About 0.1 g of PMAA/SiO₂ was directly introduced into several conical flasks, into which 50 ml aqueous solution of aniline with concentration (C₀) of 100, 200, until 800 mg l⁻¹ and the same pH of 8 were added, respectively. These conical flasks were placed into a shaker at a presettled temperature and then shaken. After reaching the adsorption equilibrium (5 h), the equilibrium concentration (C_e) of aniline solution was determined with UV-vis spectrophotometer. The equilibrium adsorption amount (Q_e) was calculated according to the following equation:

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

2.4. Examination of influences of various factors on adsorption property of PMAA/SiO₂

Varying the pH of each sample solution using NaOH and HCl solutions, the influence of pH on the adsorption property of PMAA/SiO₂ was examined. Varying the temperature of the shaker, the influence of temperature on the adsorption property of PMAA/SiO₂ was examined.

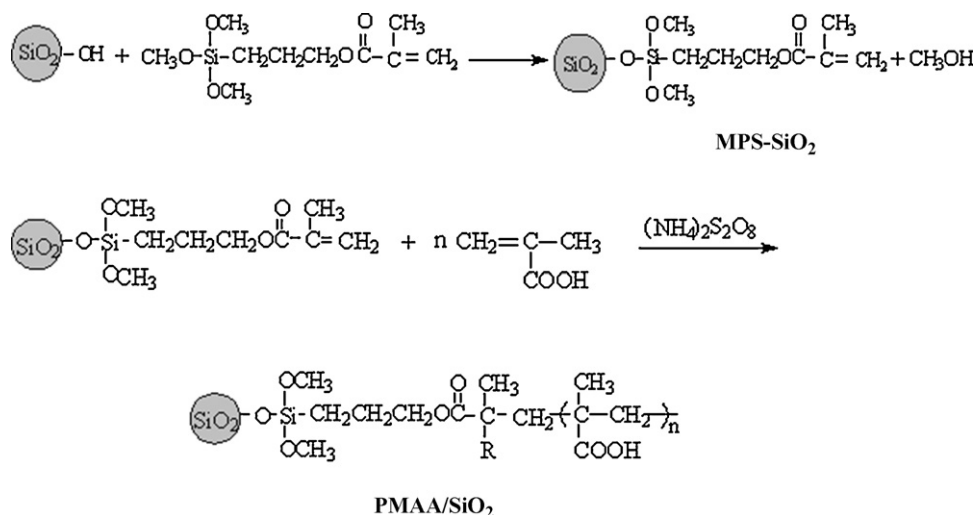
2.5. Column adsorption and elution experiment

1.4876 g of PMAA/SiO₂ was filled in a glass column with 8 mm of diameter and 2 ml of the bed volume. The aniline solution with concentration of 1 g l⁻¹ and pH of 8 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 aniline was determined. Then dynamics adsorption curve was plotted. The leaking adsorption amount and the saturated adsorption amount were also calculated.

Elution experiment was performed using hydrochloric acid 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 and the concentration of the aniline was determined. Then 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 aniline from PMAA/SiO₂ was also studied by batch experiment using 0.01 mol l⁻¹ of hydrochloric acid solution as eluting agent.



Scheme 1. Synthesis process of composite adsorption material PMAA/SiO₂.

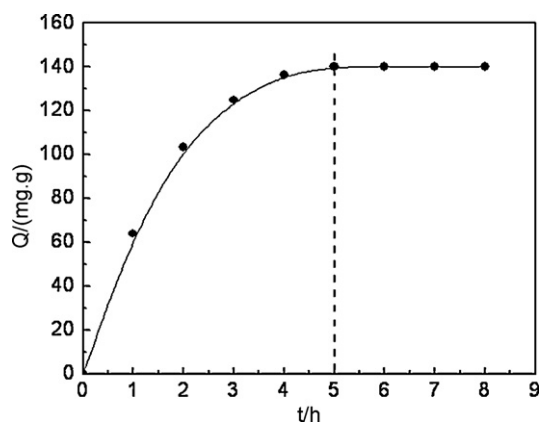


Fig. 1. Kinetic adsorption curve of PMAA/SiO₂ for aniline. Temperature: 20 °C and pH = 8.

PMAA/SiO₂ that adsorbed aniline was placed in the hydrochloric acid solution and stirred continuously at room temperature (20 °C) for 10 h. The final concentration of aniline in aqueous phase was determined. Desorption ratio was calculated from the amount of aniline adsorbed on the PMAA/SiO₂ and final aniline concentration in the eluent. In order to test the reusability of PMAA/SiO₂, adsorption–desorption procedure was repeated 10 times using the same PMAA/SiO₂.

3. Results and discussion

3.1. Kinetic adsorption curve of PMAA/SiO₂ for aniline

The kinetic adsorption curve is shown in Fig. 1. The adsorption reached to equilibrium in 5 h, and the saturated adsorption amount reached 140 mg g⁻¹. This is more higher than that of some adsorbents (2–20 mg g⁻¹) [5,6]. Obviously, the composite adsorption material PMAA/SiO₂ possesses very strong adsorption ability and high affinity for aniline. This can be attributed to the hydrogen bond interaction between them, and the interaction mechanism will be discussed below.

3.2. Influences of different factors on adsorption property of PMAA/SiO₂

3.2.1. Adsorption isotherms at different solvent

The adsorption isotherms at different solvent (H₂O and CCl₄) are shown in Fig. 2. It can be seen that the adsorption amount of

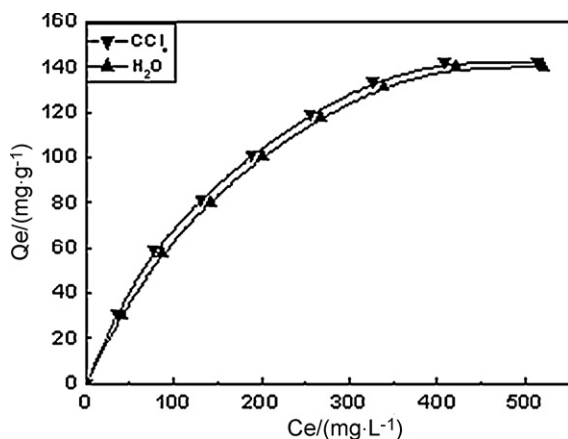


Fig. 2. Adsorption isotherms of PMAA/SiO₂ for aniline at different solvent. Temperature: 20 °C and adsorption time: 5 h.

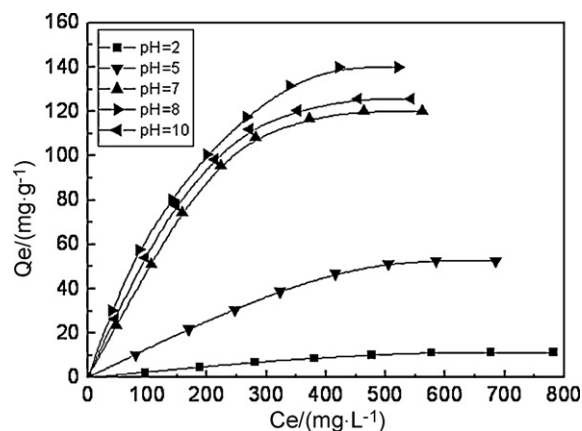


Fig. 3. Adsorption isotherms of PMAA/SiO₂ for aniline at different pH. Temperature: 20 °C and adsorption time: 5 h.

aniline on PMAA/SiO₂ in different solvent (H₂O and CCl₄) was same nearly. In solvent of CCl₄, the interaction between PMAA and aniline is only the hydrogen bond interaction. Under this interaction, the PMAA/SiO₂ possesses strong adsorption amount for aniline. In solvent of H₂O, there is also hydrogen bond interaction between PMAA/SiO₂ and H₂O, which can decrease the hydrogen bond interaction between PMAA/SiO₂ and aniline. However, the adsorption does not decrease on the whole. This implied that the hydrogen bond interaction between PMAA/SiO₂ and H₂O has very small influence on the adsorption ability of PMAA/SiO₂ for aniline.

3.2.2. Influence of pH

The adsorption isotherms at different pH values are shown in Fig. 3. It can be seen that the equilibrium adsorption amount of aniline increases rapidly with the increase of equilibrium concentrations. This also implied that PMAA/SiO₂ possesses very strong adsorption ability and high affinity for aniline. When the equilibrium concentration of the aniline reaches to a certain value, the equilibrium adsorption amount change nearly no longer, namely the adsorptions become saturated. Langmuir equation is as follows:

$$Q_e = Q_m \frac{kC_e}{1 + kC_e} \quad (3)$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m} \quad (4)$$

where Q_m (mg g⁻¹) is the saturated adsorption amount and k is the combine constant.

Freundlich equation and its logarithms form are as follows:

$$Q_e = kC_e^n \quad (5)$$

$$\ln Q_e = \ln k + n \ln C_e \quad (6)$$

where k and n are the empirical constant.

The data at pH of 8 in Fig. 3 are treated using Langmuir adsorption equation, and the straight line is displayed in Fig. 4. The linear regression coefficient is 0.9936. The data at pH of 8 in Fig. 3 are also treated using Freundlich adsorption equation, and the straight line is displayed in Fig. 5. Linear regression is performed according to the logarithmic form, and the linear regression coefficient is 0.9828.

These indicated fully that the adsorption of aniline onto the PMAA/SiO₂ is typical monomolecular layer adsorption of Langmuir type.

Additional, the effect of pH value on the adsorption property of PMAA/SiO₂ can be seen clearly from Fig. 3. Obviously, the value of pH has a great influence on the adsorption property of PMAA/SiO₂ for aniline. In acidic and basic solutions, the adsorption capacities are all lower, and in neutral solution (pH = 8) there is the greatest

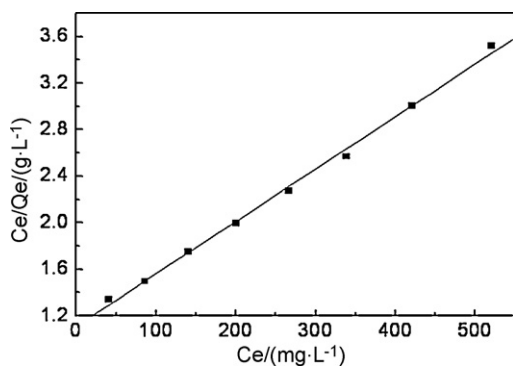


Fig. 4. Plot of C_e/Q_e vs. C_e .

adsorption capacity. The change of the adsorption capacity with pH value reflects the special adsorption mechanism. There are two kinds of forms of hydrogen bond occurring possibly between MAA and aniline. First, the $-OH$ of carboxyl groups could form hydrogen bond ($O-H \dots N$ hydrogen bond) with N atom of aniline that act as the acceptor. Second, the $-NH_2$ of aniline could also form hydrogen bond ($N-H \dots O$ hydrogen bond) with O atom of carboxyl groups in MAA molecules.

As pH value is lower, there are lots of HCl in solution. The aniline could form $C_6H_5NH_2 \cdot HCl$ with HCl in solution, which is diffuent in water. So two kinds of hydrogen bond could not be formed and adsorption ability is the weakest and the adsorption amount is the lowest. The easy of forming hydrogen bond is enhanced with the increases of pH value, resulting in two kinds of hydrogen bond could be easily formed gradually. When $pH=8$, adsorption ability is the strongest and the adsorption amount is the highest. As $pH > 8$, carboxyl groups of PMAA were neutralized fully, $O-H \dots N$ hydrogen bond could not be formed, but $N-H \dots O$ hydrogen bond could be formed. The adsorption amount did not nearly decrease when $pH > 8$. It was implied that the $N-H \dots O$ hydrogen bond is the main acting force.

In order to confirm that the $N-H \dots O$ hydrogen bond is the main acting force, the adsorption of N,N-dimethylaniline onto PMAA/SiO₂ was also carried out. The adsorption isotherms of PMAA/SiO₂ for aniline and N,N-dimethylaniline are shown in Fig. 6.

The adsorption force of PMAA/SiO₂ towards N,N-dimethylaniline is only the $O-H \dots N$ hydrogen bond while the adsorption force of PMAA/SiO₂ towards aniline are the $O-H \dots N$ hydrogen bond and $N-H \dots O$ hydrogen bond. It can be seen that the adsorption amount of PMAA/SiO₂ towards aniline is very higher than that of PMAA/SiO₂ towards N,N-dimethylaniline. So the $N-H \dots O$ hydrogen bond is the main acting force and this is very accordant to the theoretic computation [16].

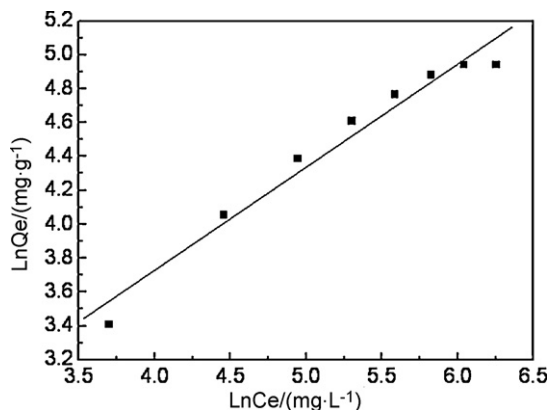


Fig. 5. Plot of $\ln Q_e$ vs. $\ln C_e$.

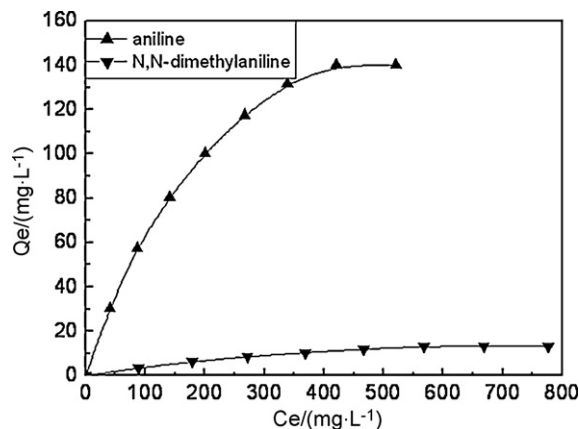


Fig. 6. Adsorption isotherms of PMAA/SiO₂ for aniline and N,N-dimethylaniline. Temperature: 20 °C; adsorption time: 5 h; pH = 8.

3.2.3. Influences of temperature

The adsorption isotherms of PMAA/SiO₂ towards aniline at different temperatures are shown in Fig. 7. It can be found that the adsorption amount of PMAA/SiO₂ towards aniline 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 140 mg g⁻¹, which is far greater than 44.7 mg g⁻¹ of the saturated adsorption amount at 350 K. The fact that the adsorption amount of aniline decreases with the increase of temperature implied that the adsorption of PMAA/SiO₂ towards aniline is an exothermic process.

According to the Van't Hoff equation:

$$\ln \frac{Q_e}{C_e} = -\frac{\Delta H}{RT} + C \quad (7)$$

When adsorption amount is 30 mg g⁻¹, the curve of the $\ln(Q_e/C_e)$ vs. $1/T$ is shown in Fig. 8. It gives the numerical values of ΔH from slope. The numerical value of ΔH is $-27.7 \text{ kJ mol}^{-1}$ and this is also very accordant to the theoretic computation [16]. This also indicated that the adsorption of PMAA/SiO₂ towards aniline is an exothermic process.

3.3. Dynamic adsorption curve

Fig. 9 shows the dynamic adsorption curve of PMAA/SiO₂ towards aniline. It can be found that when aniline solution passes through the column packed with PMAA/SiO₂ at a flow rate of 5 BV h⁻¹ upstream, the leaking appears at 92 BV. The leaking

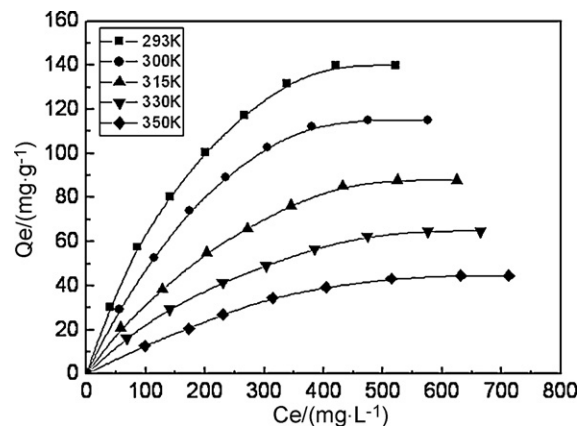


Fig. 7. Adsorption isotherms of PMAA/SiO₂ for aniline at different temperature. Adsorption time: 5 h and pH = 8.

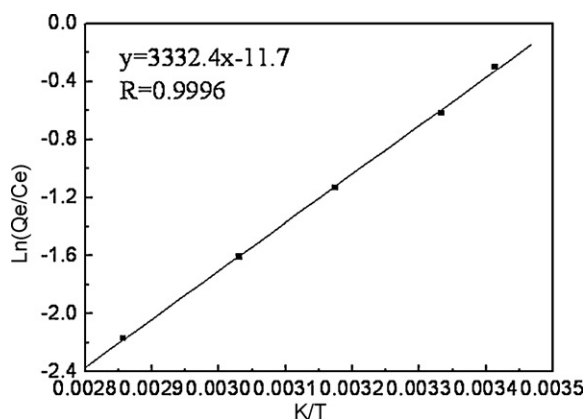


Fig. 8. Plot of $\ln(Q_e/C_e)$ vs. $1/T$.

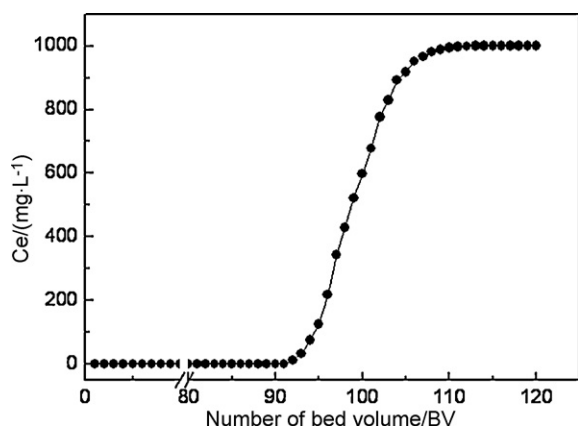


Fig. 9. Breakthrough curve of aniline on PMAA/SiO₂ column. Temperature: 20 °C; initial aniline concentration: 1 g l⁻¹; pH = 8.

adsorption amount is 122.3 mg g⁻¹, and the saturated adsorption amount is 132.7 mg g⁻¹. Obviously, the dynamic adsorption amount is analogous to the static adsorption amount.

3.4. Elution curve

Fig. 10 gives the elution curve of aniline from PMAA/SiO₂. It can be seen that the shape of desorption curve is cusped and without tailing. This indicated that the elution result is fine. The calculation results showed that aniline is eluted from PMAA/SiO₂ column with a desorption ratio of 96.99% within 21 bed volumes. This revealed fully that PMAA/SiO₂ possesses outstanding elution property, and

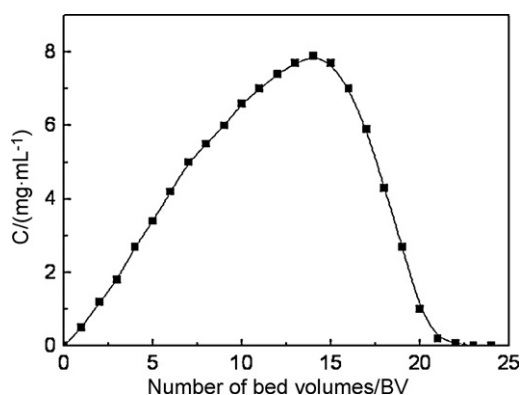


Fig. 10. Elution curve of aniline from PMAA/SiO₂. Temperature: 20 °C.

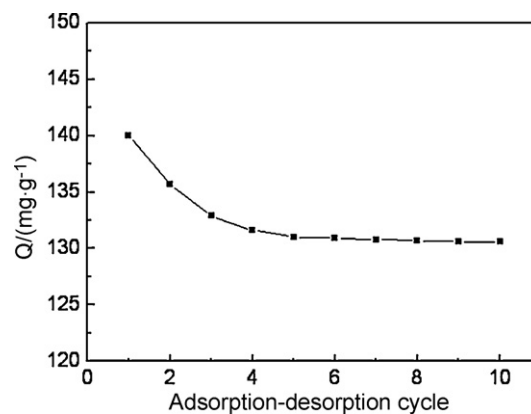


Fig. 11. Adsorption-desorption cycle of PMAA/SiO₂. Adsorption time: 5 h and desorption time: 10 h.

this novel composite adsorption material PMAA/SiO₂ has excellent reusing property.

3.5. Reusability

When hydrochloric acid solution with a concentration of 0.01 mol l⁻¹ was used as eluting agent, the hydrogen bond interaction between aniline and MAA is disrupted and subsequently, aniline was released into the eluent. In order to show the reusability of the PMAA/SiO₂, adsorption-desorption cycle was repeated 10 times using the same material.

Adsorption-desorption cycle of PMAA/SiO₂ is shown in Fig. 11. The results clearly showed that the PMAA/SiO₂ could be used repeatedly without significantly losing its adsorption amount.

4. Conclusions

In this study, functional monomer methacrylic acid was grafted onto the surface of micron-sized silica gel using 3-methacryloxypropyl trimethoxysilane as intermedia, and the novel adsorbent PMAA/SiO₂ was successfully prepared. PMAA/SiO₂ has very strong adsorption ability for aniline by way of hydrogen bond interaction, and the adsorption amount could reach up to 140 mg g⁻¹. The adsorption ability of PMAA/SiO₂ for aniline is largely dependent on pH value and temperature of solution. The strongest adsorption capacity was found in the solution with pH of 8 as compared with the acidic and basic solutions. The lower the temperature is, the higher the adsorption amount is. Additional, PMAA/SiO₂ has excellent reusability. It could be used repeatedly over 10 times without significantly losing adsorption capacity.

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