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Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO_2

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ABSTRACT

In this paper, functional monomer acrylamide (AM) was grafted step by step onto the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as coupling agent and the grafted particle PAM/SiO_2 was prepared. The adsorption properties of PAM/SiO_2 towards aniline were researched using batch and column adsorption methods. The experimental results showed that PAM/SiO_2 possesses strong adsorption ability for aniline with interaction of hydrogen bond. The saturated adsorption amount could reach up to 52 mg g^{-1}. The empirical Langmuir isotherm was found to describe well the equilibrium adsorption data. pH and temperature were found to have great influence on the adsorption amount. Finally, PAM/SiO_2 was observed to possess excellent reusability properties as well.

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. Aniline has great harmful effect for public health and environmental quality, aniline-contained wastewater has brought a series of serious environmental problem due to its high toxicity and accumulation of aniline in the environment. Now, more and more rigorous limits on the letting amount of aniline have been established. Traditionally, aniline-contained wastewater is treated using photodecomposition [1–3], electrolysis [4], adsorption [5,6], oxidation [7,8], biodegradation [9] and some other processes. These processes can decompose or remove aniline in wastewater to some extent. 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 developed and used as adsorbents for efficient removal of aniline from wastewater [10,11] by way of the strong interaction between the functional groups of polymer and aniline or other aromatic compounds.

Polyacrylamide (PAM) is a kind of water-soluble polymer, and has been extensively used for wastewater treatment and sludge dewatering as an efficient flocculant [12–15]. On its macromolecular chains, there are a great number of acetylamine groups, so strong hydrogen bond interaction can be produced between AM and aniline [16]. However, it is instable under shearing. In addition, it contains toxic residual monomers, which could cause severe secondary environmental pollution problems. Thus, a more efficient and environmentally friendly adsorbent is desirable. In this study, functional monomer acrylamide (AM) was grafted step by step onto the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as coupling agent and a novel adsorbent PAM/SiO_2 was prepared. The composite adsorbent combined well the strong interaction between AM and aniline with high specific area and fine mechanical stability of silica gel. The influences of pH and temperature on the adsorption amount were researched using batch and column adsorption methods. PAM/SiO_2 displayed excellent adsorption and reusable property for aniline.

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^{-1}, surface area: 350 m^2 g^{-1}, Qingdao, China). Acrylamide was purchased from the Ruijinte Chemical Ltd. (Tianjin, China, AR grade). Acrylamide was recrystallized using acetone before use. 3-Methacryloylpropyl trimethoxysilane was purchased from Nanking Chuangshi Chemical Aux Ltd. (Jiangsu, China, AR grade). Aniline was purchased from Beijing Chemical Plant (Beijing, China, AR grade). Ammonium persulphate 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),

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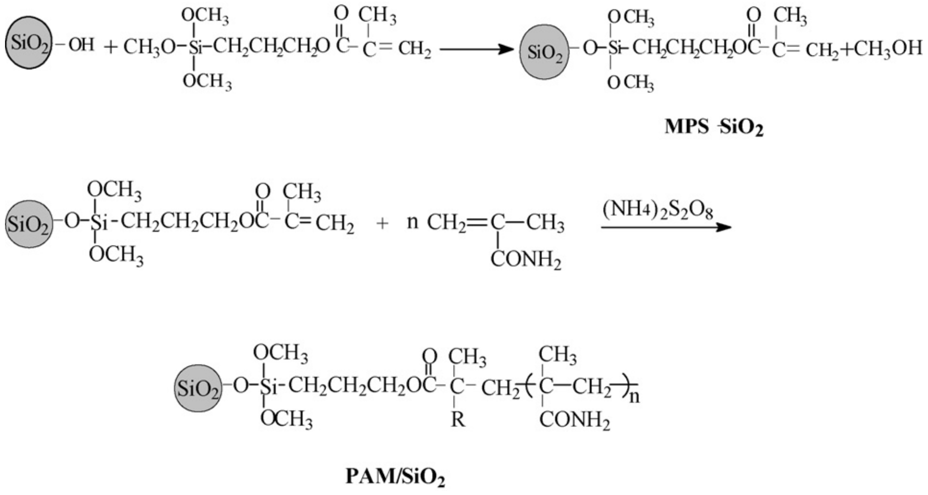

Scheme 1. Synthesis process of composite adsorption material PAM/SiO_2.

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 PAM/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 water, 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, 10 g of particles MPS–SiO_2 and 20 g of acrylamide were added into 400 mL of water, and the graft polymerization was performed by initiating of $(NH_4)_2S_2O_8$ (0.012 g, 0.6 wt% of monomer) under N_2 atmosphere at 90 °C for 24 h. The product particles were extracted with ethanol in a soxhlet to remove the polymers attaching physically to the particles and dried under vacuum. Finally, the grafted particles PAM/SiO_2 were gained. The total preparation processes of PAM/SiO_2 are expressed in Scheme 1. The grafting degree of PAM/SiO_2 was determined using thermogravimetric analyzer. The particles PAM/SiO_2 used in this study have a grafting degree of 104.5 mg g^{-1}.

2.3. Adsorption of aniline on PAM/SiO_2

2.3.1. Measurement of kinetic adsorption curve

About 0.2 g of PAM/SiO_2 was introduced into a conical flask into which 50 mL of aqueous aniline solution with an initial concentration (C_0, mg L^{-1}) of 500 mg L^{-1} and pH of 8. This conical flask was placed in a shaker at a presettled temperature (20 °C). At different times, the concentration (C_t, mg L^{-1}) of aniline solution was determined using UV–vis spectrophotometer. 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 aniline solution; m (g) is the weight of the absorbent PAM/SiO_2.

2.3.2. Measurement of adsorption isotherm

About 0.2 g of PAM/SiO_2 was introduced into a conical flask, into which 50 mL of the aqueous aniline solution with concentrations (C_0, mg L^{-1}) of 50, 100, 200, until 500 mg L^{-1} and pH of 8 were added respectively. These conical flasks were placed in a shaker at a presettled temperature (20 °C). After the adsorption reached equilibrium, the equilibrium concentration (C_e, mg L^{-1}) of aniline solution was determined using UV–vis spectrophotometer. The equilibrium adsorption amount (Q_e, mg g^{-1}) was calculated according to Eq. (2).

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

2.4. Examination of influences of various factors on adsorption amount of PAM/SiO_2

Varying the pH of each sample solution using NaOH and HCl solutions, the influence of pH on the adsorption amount of PAM/SiO_2 was examined. Varying the temperature, the influence of temperature on the adsorption amount of PAM/SiO_2 was examined.

2.5. Columns adsorption and elution experiment

1.4533 g of PAM/SiO_2 was filled in a glass column with 8 mm of diameter and 2 mL of the bed volume. The aniline solution with concentration of 500 mg L^{-1} and pH of 8 was allowed to flow upstream 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 the breakthrough 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, the concentration of the aniline was determined, and the elution curve was plotted.

2.6. Repeated use experiment

Reusability (i.e., regenerability) was an important factor for an effective absorbent. Desorption of the adsorbed aniline from PAM/SiO_2 was also studied by batch experiment using 0.01 mol L^{-1} of hydrochloric acid solution as eluent. PAM/SiO_2 that have adsorbed aniline was placed in the eluent and stirred continuously at 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 PAM/SiO_2 and final aniline concentration in the eluent. In order to test the reusability of PAM/SiO_2, aniline adsorption–desorption procedure was repeated ten times using the same PAM/SiO_2.

3. Results and discussion

3.1. Kinetic adsorption curve of PAM/SiO$_2$ for aniline

The kinetic adsorption curve is shown in Fig. 1. The composite adsorbent PAM/SiO$_2$ has very strong adsorption ability and high affinity for aniline. The adsorption reached to equilibrium at 5 h, and the saturated adsorption amount reached 52 mg g^{-1}. This could be attributed to the hydrogen bond interaction between them, and the interaction mechanism will be discussed below.

3.2. Adsorption isotherm of PAM/SiO$_2$ for aniline

The adsorption isotherm of PAM/SiO$_2$ for aniline is shown in Fig. 2. It can be seen that the equilibrium adsorption amount of aniline increases rapidly with the increase of equilibrium concentrations. The also implied that PAM/SiO$_2$ 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. The adsorption isotherm is typical monomolecular layer adsorption of Langmuir type.

Langmuir equation is as follows.

$$Q_e = Q_m \frac{kC_e}{1 + kC_e} \tag{3}$$

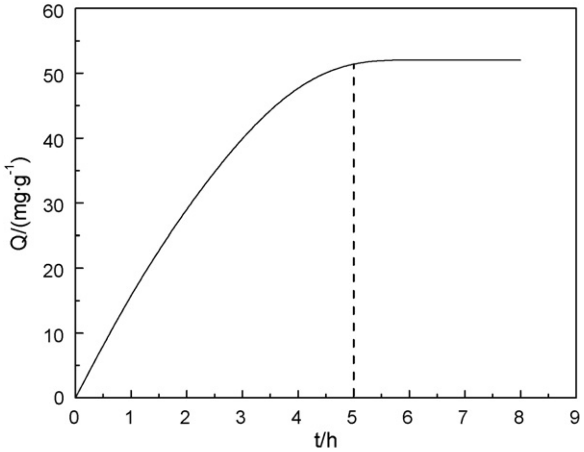

Fig. 1. Kinetic adsorption curve of PAM/SiO$_2$ for aniline. Temperature: 20 °C; pH 8.

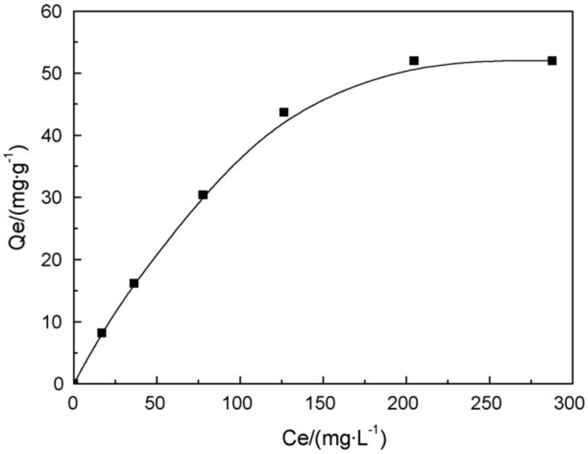

Fig. 2. Adsorption isotherm of PAM/SiO$_2$ for aniline. Temperature: 20 °C; adsorption time: 5 h; pH 8.

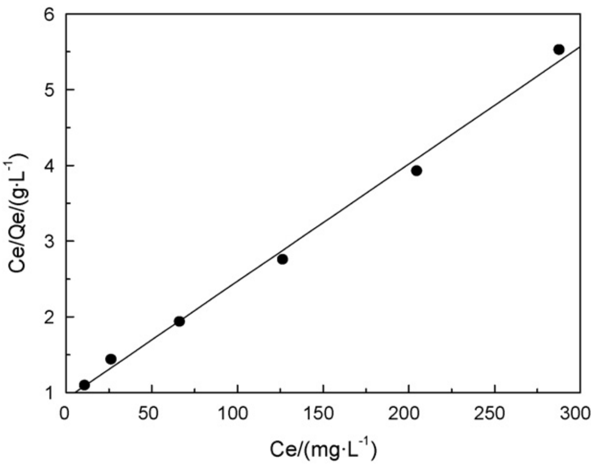

Fig. 3. Plot of C_e/Q_e vs. C_e.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m} \tag{4}$$

where, Q_m (mg g^{-1}) is the saturated adsorption amount; k is the combine constant. The data in Fig. 2 are treated using Langmuir adsorption equation, and the straight line is displayed in Fig. 3. The linear regression coefficient is 0.9973. This indicates fully that the adsorption of aniline onto the PAM/SiO$_2$ is typical monomolecular layer adsorption of Langmuir type.

3.3. Influences of different factors on adsorption amount of PAM/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 amount of PAM/SiO$_2$ can be seen clearly from Fig. 5. Obviously, the value of pH has a great influence on the adsorption amount of PAM/SiO$_2$ for aniline. In neutral and basic solution, the adsorption capacities are almost same, and higher than that in acidic solutions. This is caused by different interacting forces (hydrogen bond) between AM and aniline. There are two kinds of hydrogen bond occurring possibly between AM and aniline. First, the –NH$_2$ of acetylamine groups could form hydrogen bond (N–H. . .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. . .N hydrogen bond) with N atom of acetylamine groups in AM molecules.

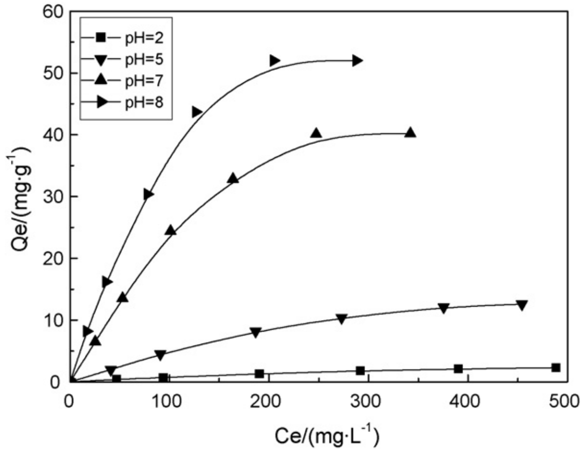

Fig. 4. Adsorption isotherms of PAM/SiO$_2$ for aniline at different pH. Temperature: 20 °C; adsorption time: 5 h.

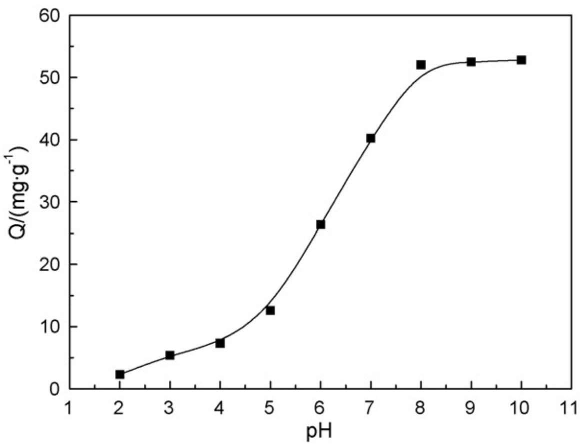

Fig. 5. Adsorption capacity of PAM/SiO_2 at different pH. Temperature: 20 °C; adsorption time: 5 h.

As pH value is lower, there are lots of HCl in solution. The aniline could form easily $C_6H_5NH_2·HCl$ with HCl in solution, which could dissolve 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 quantity of HCl decreases with the increases of pH value, and this resulted in strengthening and increase of the two kinds of hydrogen bond. So the adsorption capacity increases with the increase of pH value. When pH is of 8, there is not HCl in solution. So two kinds of hydrogen bond could be formed easily and adsorption ability is very strong and the adsorption amount is very high. When pH > 8, the hydroxyl could impact hardly the formation of hydrogen bond. So the adsorption amount did not change.

3.3.2. *Influences of temperature*

The adsorption isotherms of PAM/SiO_2 towards aniline at different temperatures are shown in Fig. 6. It can be found that the adsorption amount of PAM/SiO_2 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 52 mg g^{-1}, which is far greater than 13.4 mg g^{-1} of the saturated adsorption amount at 315 K. The fact that the adsorption amount of aniline decreases with the increase of temperature implies that the adsorption of PAM/SiO_2 towards aniline is an exothermic process.

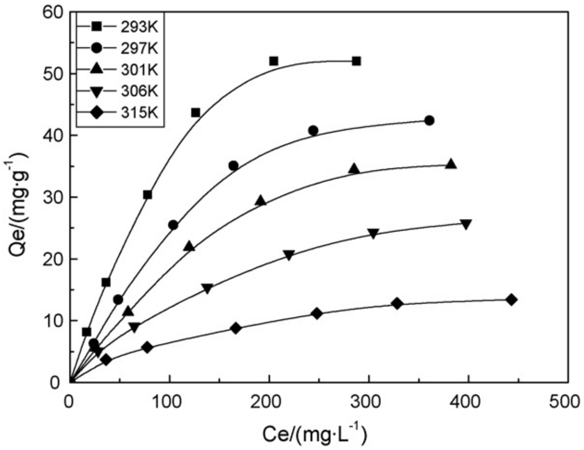

Fig. 6. Adsorption isotherms of PAM/SiO_2 for aniline at different temperature. Adsorption time: 5 h; pH 8.

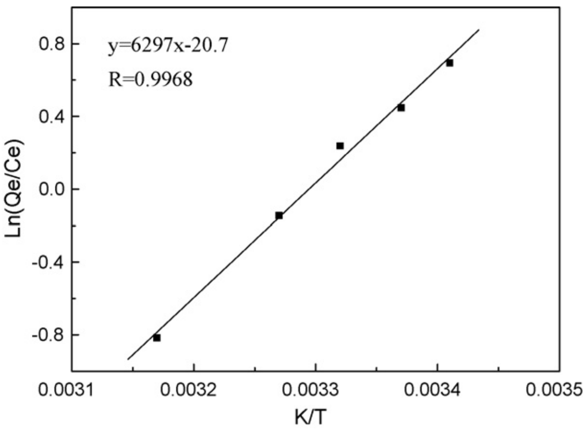

Fig. 7. Plot of Ln (Q_e/C_e) vs. $1/T$.

According to the Van't Hoff equation

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

When adsorption concentration is 26 mg L^{-1}, the curve of the 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 −52.4 kJ mol^{-1}, and this is relative accordant to the theoretic computation [16]. This also indicated that the adsorption of PAM/SiO_2 towards aniline is an exothermic process.

3.4. *Breakthrough adsorption curve*

Fig. 8 shows the breakthrough adsorption curve of PAM/SiO_2 for aniline. It can found that when aniline solution (500 mg L^{-1}) passes through the column packed with PAM/SiO_2 at a flow rate of 5 BV h^{-1} upstream, the leaking of aniline appears at 66 BV. The leaking adsorption amount to be calculated is 45.4 mg g^{-1}, and the saturated adsorption amount is 50.7 mg g^{-1}. Obviously, analogous to the batch adsorption result, the column adsorption amount is also very high.

3.5. *Elution curve*

Fig. 9 gives the elution curve of aniline from PAM/SiO_2. Hydrochloric acid solution with a concentration of 0.01 mol L^{-1} is used as the eluent, and the eluent at a rate of 1 BV h^{-1} flows upstream through the column of PAM/SiO_2 particles on which the

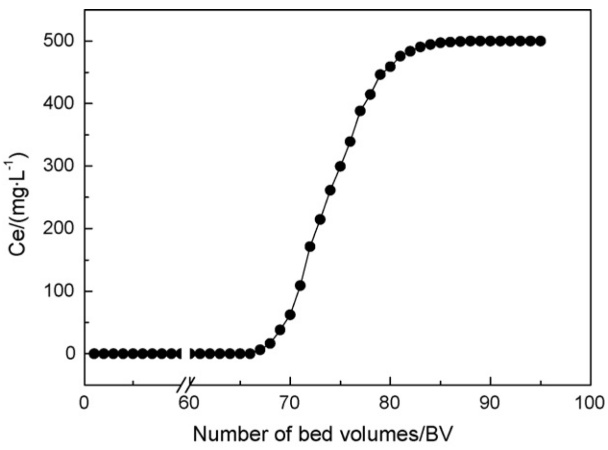

Fig. 8. Breakthrough curve of aniline on PAM/SiO_2 column. Temperature: 20 °C; initial aniline concentration: 1 g/L; pH 8.

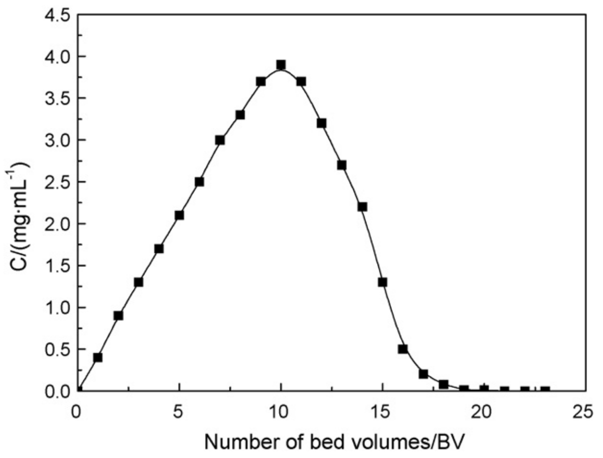

Fig. 9. Elution curve of aniline from PAM/SiO_2. Temperature: 20 °C.

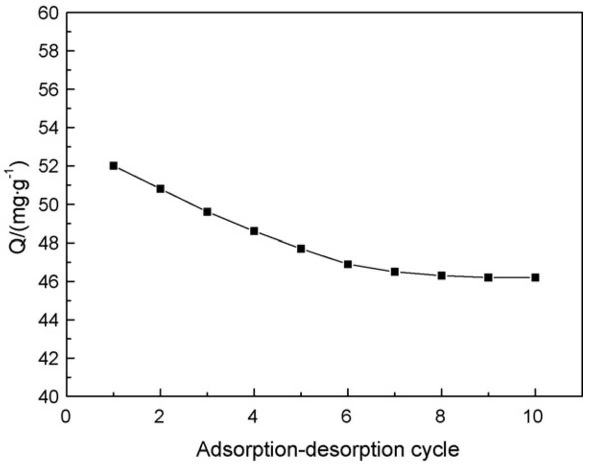

Fig. 10. Adsorption–desorption cycle of PAM/SiO_2. Adsorption time: 5 h; desorption time: 10 h; adsorption and desorption temperature: 20 °C.

adsorption of aniline 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 17 bed volumes, aniline is eluted from PAM/SiO_2 column with a desorption ratio of 99.4%. The fact reveals fully that PAM/SiO_2 on which aniline is adsorbed in saturation has outstanding elution property, and this novel composite adsorbent PAM/SiO_2 has excellent reusing property.

3.6. *Reusability*

Desorption ratios are very high (97.7%). When hydrochloric acid solution with a concentration of 0.01 mol L^{-1} is used as an eluent, the hydrogen bond interaction between aniline and AM is disrupted and subsequently aniline is released into eluent. In order to show the reusability of the PAM/SiO_2, adsorption–desorption cycle was repeated ten times using the same material.

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

4. Conclusions

In this study, functional monomer acrylamide was grafted step by step onto micron-sized silica gel using 3-methacryloxypropyl trimethoxysilane as coupling agent and the novel adsorbent PAM/SiO_2 was successfully prepared. The grafting degree of PAM/SiO_2 particles was 104.5 mg g^{-1}. PAM/SiO_2 has very strong adsorption ability for aniline by way of hydrogen bond interaction, and the adsorption amount could reach up to 26.84 mg g^{-1}. The adsorption mechanism was explained satisfactorily using hydrogen bond interaction. The adsorption ability of PAM/SiO_2 for aniline is largely dependent on pH value and temperature of solution. There is the greatest adsorption capacity in neutral and basic solution. The lower the temperature is, the higher the adsorption amount is. Additional, PAM/SiO_2 possesses excellent reusability. It could be used repeatedly over ten times without significantly losing adsorption amount.

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