Journal of Hazardous Materials 168 (2009) 352–357

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Adsorption mechanism and property of a novel adsorption material PAM/SiO_2 towards 2,4,6-trinitrotoluene

Fuqiang An, Xiaoqin Feng, Baojiao Gao*

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

ARTICLE INFO

Article history:
Received 26 November 2008
Received in revised form 7 February 2009
Accepted 9 February 2009
Available online 20 February 2009

Keywords:
2,4,6-Trinitrotoluene (TNT)
Adsorption
Polyacrylamide (PAM)
Silica gel
π Hydrogen bond

ABSTRACT

2,4,6-Trinitrotoluene (TNT) is toxic and mutagenic to many living organisms, so more and more rigorous limits on the letting amount of TNT have been established. In this paper, functional monomer acrylamide (AM) was grafted step by step on the surface of silica gel particles, and the grafted particle PAM/SiO_2 with strong adsorption ability for TNT was formed. The adsorption mechanism and properties of PAM/SiO_2 for TNT were researched through static and dynamic methods. The experimental results showed that PAM/SiO_2 possesses strong adsorption ability for TNT with interaction of three kinds of hydrogen bonds including peculiar N—H···π hydrogen bond (aromatic hydrogen bond) and C—H···O=C π hydrogen bond. The saturated adsorption amount could reach to 0.873 mg g^{-1}. The empirical Freundlich isotherm was found to describe well the equilibrium adsorption data. In addition, the pH and temperature were found to have great influence on the adsorption amount. Mixture solution of HCl and ethanol is used as eluent, and the adsorbed TNT is eluted easily from PAM/SiO_2. Finally, PAM/SiO_2 was found to have excellent reusability.

1. Introduction

2,4,6-Trinitrotoluene (TNT) is a nitroaromatic explosive that is released into soil and ground water mainly by military activities such as munitions manufacturing, packing and storage. TNT is a mutagen and a group C human carcinogen. Exposure to TNT is known to cause rashes, skin hemorrhages, mucus and blood disorders. Because of the toxic and mutagenic effects on many living organisms of TNT, more and more rigorous limits on the letting amount of TNT have been established. For treating wastewater containing TNT, adsorption with various adsorption materials, such as activated carbon and so on [1–5], degradation with various microorganisms [6–9], destruction with catalyst [10,11], and advanced oxidation employing UV and hydrogen peroxide [12–17] were studied extensively, but there are some problems, such as lower adsorption capacity, high costs and low reusability, to name a few.

Polyacrylamide (PAM) is a kind of water-soluble polymer, is an efficient flocculant, and has been extensively used for wastewater treatment and sludge dewatering [18–24]. On its macromolecular chains, there are a great number of acetylamine groups, so strong hydrogen bond interaction can be produced between AM and TNT. The adsorption mechanism could be explained satisfactorily with introducing peculiar N—H···π (benzene ring)hydrogen bond (aromatic hydrogen bond) and C—H···π (C=O double bond)hydrogen bond [25–29]. However, it is unstable under shearing. In addition, it contains toxic residual monomers, which could cause severe secondary environmental pollution problems. Thus, a more efficient and environment friendly adsorbent is desirable. In this study, PAM macromolecules were grafted on the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as coupling agent and a novel adsorption material PAM/SiO_2 was prepared. PAM/SiO_2 displayed excellent adsorption property towards TNT, and the adsorption amount can get up to 0.873 mg g^{-1} at 290 K and pH of 6 in 7 h.

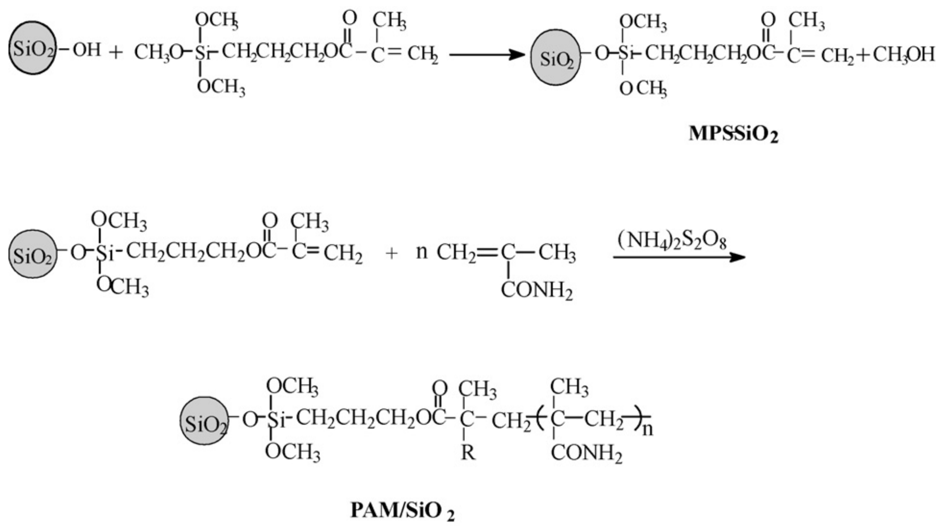
2. Experimental

2.1. Materials and instruments

Silica was purchased from Ocean Chemical Limited Company (120–160 mesh, about 125 μm in diameter, pore size: 6 nm, pore volume: 1.0 ml g^{-1}, surface area: 350 $m^2\,g^{-1}$. Qingdao, China). Acrylamide (AM) was purchased from Ruijinte Chemical Ltd. (Tianjin, China, AR grade). AM was recrystallized using acetone before use. Ammonium persulphate was purchased from Shanghai Chemical reagent plant (Shanghai, China, AR grade). γ-MPS was purchased from Nanking Chuangshi Chemical Aux Ltd. (Jiangsu, China, AR grade). TNT was obtained from Chemical Engineering Department of North University of China. Other chemicals were purchased from Beijing Chemical Plant (AR grade).

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

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.02.042



Scheme 1. Schematic expression of preparing process of PAM/SiO_2.

Used instruments in this study were as follows: 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), STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany).

2.2. Preparation and characterization of adsorbent PAM/SiO$_2$

Ten grams 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 were 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 $(NH_4)_2S_2O_8$ (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, dried under vacuum, and 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 with TGA method. The particles PAM/SiO_2 used in this study have a grafting degree of 0.1082 g g^{-1}.

2.3. Adsorption of TNT on PAM/SiO$_2$

2.3.1. Measurement of kinetic adsorption curve

Approximately 2 g of PAM/SiO_2 was introduced into a conical flask directly, into which 200 ml of the aqueous TNT solution with an initial concentration (C_0) of 100 mg L^{-1} was added. The conical flask was placed in a shaker at a presettled temperature and pH and shaken. At different times, the concentration (C_t) of TNT solution was determined. The adsorption amount (Q) was calculated according to equation (1).

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

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

2.3.2. Measurement of adsorption isotherm

Next, another 0.5 g of PAM/SiO_2 was introduced into a number of conical flasks directly, into which 50 ml of the aqueous TNT solution with concentrations (C_0) of 10, 20, 30, 40, 50, until 100 mg L^{-1} were respectively added. The conical flasks were placed in a shaker at a presettled temperature and pH and shaken. After adsorption reaching equilibrium, the concentration (C_e) of TNT solution was determined. The equilibrium adsorption amount (Q_e) was calculated according to equation (2).

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

2.3.3. Examination of influences of various factors on adsorption property of PAM/SiO$_2$

Varying the pH of each sample solution through NaOH and HCl solutions, the influence of pH on the adsorption property of PAM/SiO_2 was examined. Meanwhile, varying the temperature, the influence of temperature on the adsorption property of PAM/SiO_2 was examined.

2.4. Dynamics adsorption and elution experiment

1.5046 g of PAM/SiO_2 was filled in a glass column with 8 mm of diameter and 2 mL of bed volume. The TNT solution with concentration of 100 mg L^{-1} and pH 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 TNT was determined. Then the dynamics adsorption curve was plotted. The leaking adsorption amount and the saturated adsorption amount were also calculated.

Elution experiment was performed using mixture solution of HCl and ethanol with pH of 2 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 TNT was determined, and the elution curve was plotted.

2.5. Repeated use experiment

The repeated usability, i.e. regenerability, is an important factor for an effective absorbent. As such, the desorption of the adsorbed TNT from the PAM/SiO_2 was also studied by static experiment. As observed, the adsorbed TNT was desorbed using mixture solution of HCl and ethanol with pH of 2 as eluting agent. PAM/SiO_2

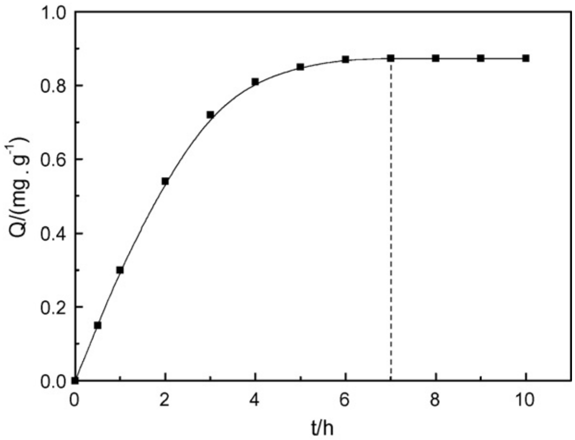


Fig. 1. Kinetic adsorption curve of PAM/SiO_2 for TNT.
Temperature: 290 K; pH 6; initial concentration of TNT: 100 mg L^{-1}.

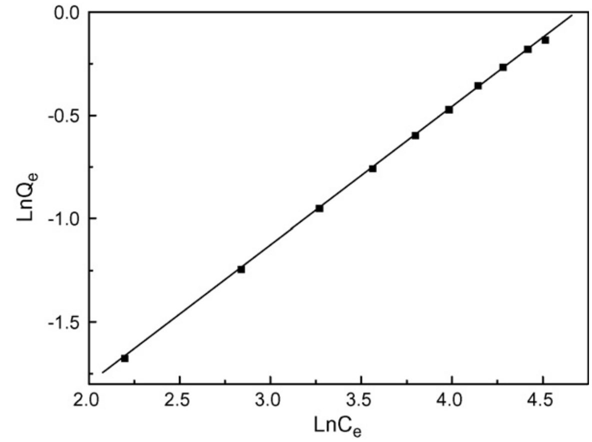


Fig. 3. Plot of Ln Q_e vs. Ln C_e.

adsorbed TNT was placed in the eluent and stirred continuously at room temperature for 7 h. The final concentration of TNT in aqueous phase was determined. Desorption ratio was calculated from the amount of TNT adsorbed on the PAM/SiO_2 and final TNT concentration in the eluent. In order to test the reusability of PAM/SiO_2, adsorption–desorption procedure was repeated ten times using the same material.

3. Results and discussion

3.1. Kinetic adsorption curve of TNT on PAM/SiO_2

The kinetic adsorption curve is shown in Fig. 1. The adsorption of PAM/SiO_2 towards TNT reaches to equilibrium in 7 h, the adsorption rate is quick. The saturated adsorption amount could reach to 0.873 mg g^{-1}. It was implied that PAM/SiO_2 possesses strong adsorption ability and affinity towards TNT.

3.2. Adsorption isotherm of PAM/SiO_2 for TNT

The adsorption isotherm of PAM/SiO_2 towards TNT is shown in Fig. 2. It can be seen that the equilibrium adsorption amount increases rapidly with the increase in equilibrium concentrations. The high affinity attributes to the hydrogen bond interaction between AM and TNT.

Freundlich adsorption equation and its logarithms form are follows:

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

$$\mathrm{Ln}Q_e = \mathrm{Ln}k + n\,\mathrm{Ln}C_e \tag{4}$$

The data in Fig. 2 are treated using Freundlich adsorption equation, and the straight lines at two different stages are displayed in Fig. 3. Linear regression is performed according to the logarithmic form, and the linear regression coefficient is 0.9999. The curve of the Ln Q_e vs. Ln C_e fit satisfactorily to Freundlich equation. This indicated that the adsorption of PAM/SiO_2 towards TNT belongs to Freundlich-type adsorptions, and is a kind of typical monomolecular layer adsorptions.

3.3. Influences of different factors on adsorption property 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 property of PAM/SiO_2 can be seen clearly from Fig. 5, which comes from the data of Fig. 4. Obviously, the value of pH has great influence on the adsorption property of PAM/SiO_2 towards TNT. The higher is the pH value, the higher is the adsorption amount. The adsorption amount of PAM/SiO_2 towards TNT increases with the increase in pH value. This is caused by different molecule interactions (hydrogen bond) between AM and TNT at different pH values. The forms

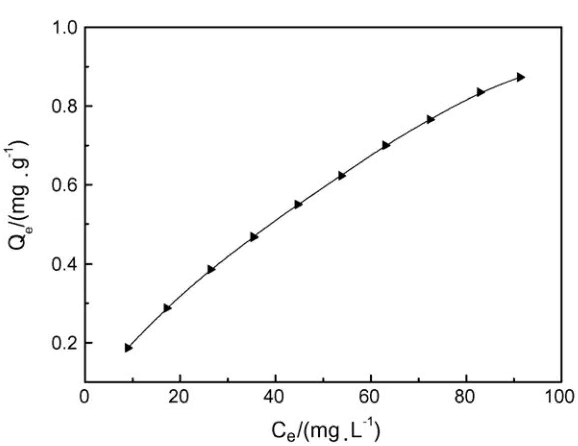


Fig. 2. Adsorption isotherms of PAM/SiO_2 for TNT.
Temperature: 290 K; pH 6; adsorption time: 7 h.

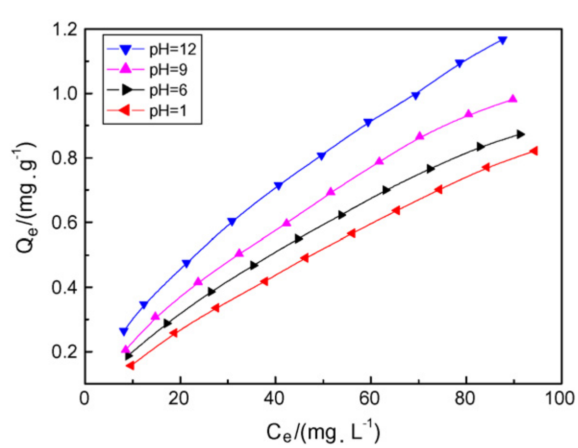


Fig. 4. Adsorption isotherms of PAM/SiO_2 for TNT at different pH.
Temperature: 290 K; adsorption time: 7 h

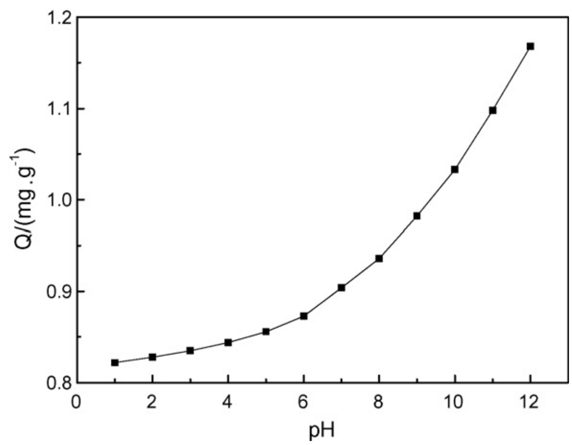


Fig. 5. Adsorption amount of PAM/SiO_2 at different pH.

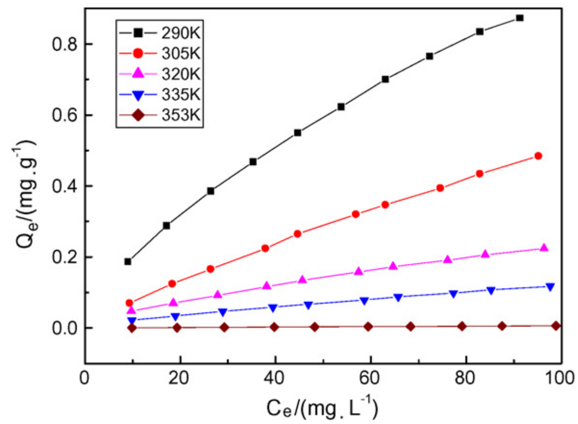
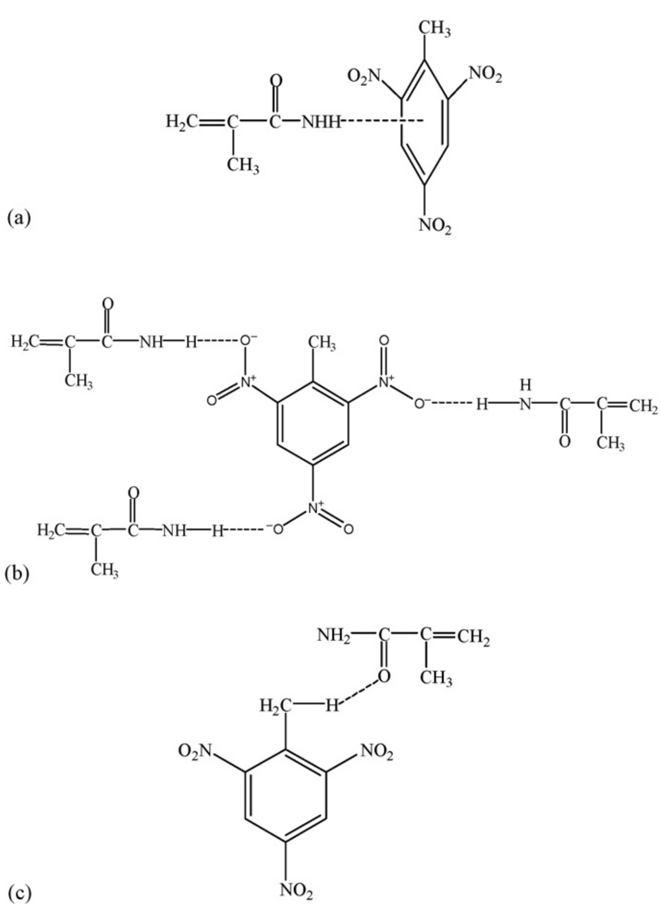


Fig. 6. Adsorption isotherms of PAM/SiO_2 for TNT at different temperatures. Adsorption time: 7 h; pH 6

of hydrogen bond occurring possibly between AM and TNT are expressed in Scheme 2. First, the—NH_2 of acetylamine groups could form aromatic hydrogen bond (N—H···π hydrogen bond) with π-electron cloud of TNT aromatic groups that act as the acceptor (a in Scheme 2) [25–27]. Second, the—NH_2 of acetylamine groups could also form hydrogen bond (N—H···O hydrogen bond) with oxygen atom of nitryl in TNT molecules (b in Scheme 2). Additionally, the methyl of TNT could form π hydrogen bond (CH···O=C hydrogen bond) with carbonyl π bond of carboxyl groups [28] ('c' in Scheme 2). This hydrogen bond interaction 'c' is weaker than that of 'a' and 'b'.



Scheme 2. Hydrogen bond between AM and TNT.

As pH value is lower, lots of H^+ in solution could form electrostatic interaction with π-electron cloud of benzene ring and oxygen atom of nitryl in TNT molecules, so the 'a' and 'b' kinds of hydrogen bonds are difficult to form. The adsorption amount is lower. The concentration of hydrogen ions H^+ is decreased with the increases in pH value, resulting in strengthening of hydrogen bond interaction of 'a' and 'b' forms. So the adsorption capacity increases with the increase in pH value.

3.3.2. *Influences of temperature*

The adsorption isotherms of PAM/SiO_2 towards TNT at different temperatures are shown in Fig. 6. It can be found that the adsorption amount of PAM/SiO_2 towards TNT decreases with the increase in temperature, and the influence of temperature on the adsorption amount is greater. The saturated adsorption amount at 290 K is 0.873 mg g^{-1}, which is far greater than 0.006 mg g^{-1} of the saturated adsorption amount at 350 K. The fact that the adsorption amount of TNT decreases with the increase in temperature implies that the adsorption of PAM/SiO_2 towards TNT is an exothermic process.

When equilibrium concentration is 80 mg L^{-1}, the curve of the $\mathrm{Ln}(Q_e/C_e)$ vs. $1/T$ is shown in Fig. 7. It gives the numerical value of ΔH from slope. The numerical value of ΔH is−38.06 kJ mol^{-1}. This also indicated that the adsorption of PAM/SiO_2 towards TNT is an exothermic process.

3.4. *Dynamic adsorption curve*

Fig. 8 shows the dynamic adsorption curve of PAM/SiO_2 for TNT. It can be observed that when TNT solution passes through the col-

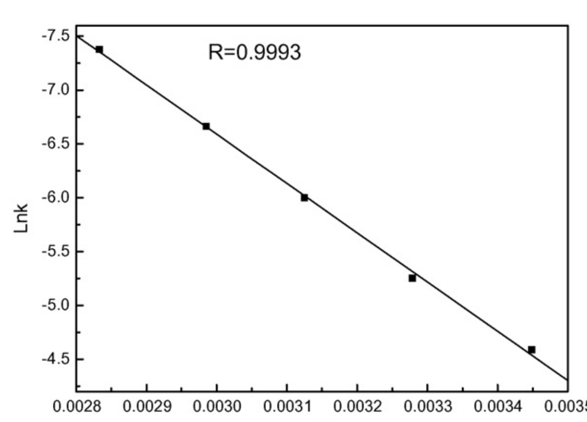


Fig. 7. Plot of $\mathrm{Ln}(Q_e/C_e)$ vs. $1/T$.

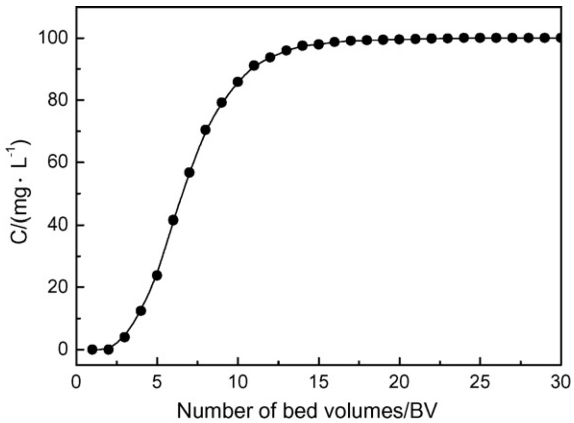


Fig. 8. Breakthrough curve.
Temperature: 290 K; initial TNT concentration: 100 mg/L; pH 6

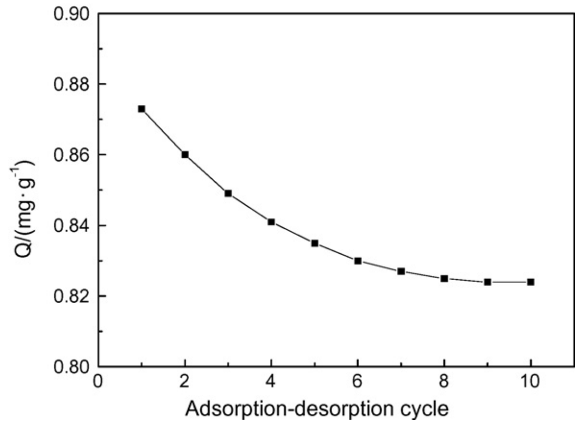


Fig. 10. Adsorption–desorption cycle of PAM/SiO_2.

umn packed with PAM/SiO_2 at a flow rate of 5 bed volumes per hour (5 BV h^{-1}) upstream, the leaking appears at 2 BV, the leaking adsorption amount to be calculated is 0.266 mg g^{-1}, and the saturated adsorption amount is 0.871 mg g^{-1}. Obviously, this is analogous to the static adsorption result.

3.5. Elution curve

Fig. 9 gives the elution curve of TNT from PAM/SiO_2. Mixture solution of HCl and ethanol with pH of 2 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 adsorption of TNT 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 14 BVs, TNT is eluted from PAM/SiO_2 column with a desorption ratio of 99.66%. The fact reveals fully that PAM/SiO_2 on which TNT is adsorbed in saturation has outstanding elution property, and this novel adsorption material PAM/SiO_2 has excellent reusability.

3.6. Reusability

Desorption ratios are very high (99.66%). When mixture solution of HCl and ethanol with pH of 2 is used as an eluent, the hydrogen bond interaction between TNT and AM is disrupted and subsequently TNT is released into eluent. In order to show the reusability of the PAM/SiO_2, adsorption–desorption cycle was repeated 10 times using the same material.

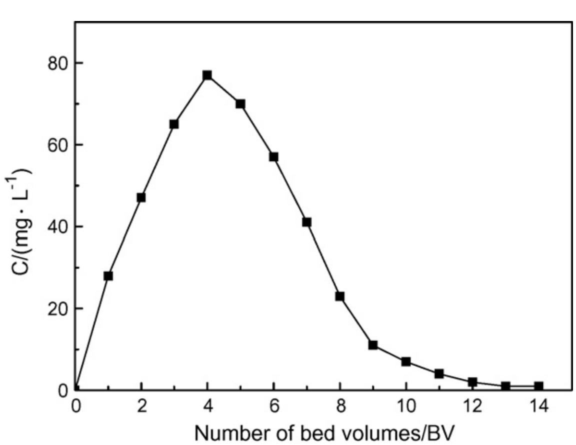


Fig. 9. Elution curve. Temperature: 333 K

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 losing adsorption capacities significantly.

4. Conclusions

In this paper, functional macromolecule PAM was grafted on the surface of silica gel particles using 3-MPS as coupling agent and the novel adsorption material PAM/SiO_2 was successfully prepared. PAM/SiO_2 has very strong adsorption ability for TNT by way of hydrogen bond interaction, and the adsorption mechanism was explained satisfactorily with introducing the π hydrogen bond. The adsorption ability of PAM/SiO_2 towards TNT is dependent on pH value and temperature of solution greatly. The higher is the pH value, the higher is the adsorption amount. The adsorption amount of TNT decreases with the increase in temperature. The lower is the temperature, the higher is the adsorption amount in range from 290 K to 350 K. The adsorption amount can get up to 0.873 mg g^{-1} at 290 K and pH of 6. This study shows that PAM/SiO_2 could dispose basic wastewater containing TNT. Additionally, PAM/SiO_2 has excellent reusability.

References

[1] J.W. Lee, T.H. Yang, W.G. Shim, T.O. Kwon, I.S. Moon, Equilibria and dynamics of liquid-phase trinitrotoluene adsorption on granular activated carbon: effect of temperature and pH, J. Hazard. Mater. 141 (2007) 185–192.
[2] V. Marinović, M. Ristić, M. Dostanić, Dynamic adsorption of trinitrotoluene on granular activated carbon, J. Hazard. Mater. B117 (2005) 121–128.
[3] S.W. Maloney, N.R. Adrian, R.F. Hickey, R.L. Heine, Anaerobic treatment of pinkwater in a fluidized bed reactor containing GAC, J. Hazard. Mater. 92 (2002) 77–88.
[4] C. Rajagopal, J.C. Kapoor, Development of adsorptive removal process for treatment of explosives contaminated wastewater using activated carbon, J. Hazard. Mater. B87 (2001) 73–98.
[5] R. Leboda, V.V. Turov, W. Tomaszewski, V.M. Gun'ko, J. Skubiszewska-Zie, Effect of adsorption of nitroaromatic compounds on the characteristics of bound water layers in aqueous suspensions of activated carbons, Carbon 40 (2002) 389–396.
[6] I. Soojhawon, P.D. Lokhande, K.M. Kodam, K.R. Gawai, Biotransformation of nitroaromatics and their effects on mixed function oxidase system, Enzyme Microb. Tech. 37 (2005) 527–533.
[7] B.L. Ki, B.G. Man, M. Seung-Hyeon, Degradation of 2,4,6-trinitrotoluene by immobilized horseradish peroxidase and electrogenerated peroxide, Water Res. 37 (2003) 983–992.
[8] S.G. Pavlostathis, G.H. Jackson, Biotransformation of 2,4,6-trinitrotoluene in a continuous-flow anabaena sp. system, Water Res. 36 (2002) 1699–1706.
[9] P. Hwang, T. Chow, N.R. Adrian, Transformation of trinitrotoluene to triaminotoluene by mixed cultures incubated under methanogenic conditions, Environ. Toxicol. Chem. 19 (2000) 836–841.
[10] M.J. Liou, M.C. Lu, Catalytic degradation of nitroaromatic explosives with Fenton's reagent, J. Mol. Catal. A: Chem. 277 (2007) 155–163.
[11] K.C. Makris, K.M. Shakya, R. Datta, D. Sarkar, D. Pachanoor, Chemically catalyzed uptake of 2,4,6-trinitrotoluene by vetiveria zizanioides, Environ. Pollut. 148 (2007) 101–106.

[12] S.J. Chang, Y.C. Liu, Degradation mechanism of 2,4,6-trinitrotoluene in supercritical water oxidation, J. Environ. Sci. 19 (2007) 1430–1435.
[13] Y.G. Wu, C.H. Zhao, H.Q. Wang, K. Ding, Integrated effects of selected ions on 2,4,6-trinitrotoluene-removal by O_3/H_2O_2, J. Hazard. Mater. B132 (2006) 232–236.
[14] R. Bajpai, D. Parekh, S. Herrmann, M. Popović, J. Paca, M. Qasim, A kinetic model of aqueous-phase alkali hydrolysis of 2,4,6-trinitrotoluene, J. Hazard. Mater. 106B (2004) 55–66.
[15] S. Hyun-Seok, L. So-Jin, C. II-Hyoung, Z. Kyung-Duk, Kinetics and mechanism of TNT degradation in TiO_2 photocatalysis, Chemosphere 57 (2004) 309–317.
[16] D.R. Felt, S.L. Larson, E.J. Valente, UV–vis spectroscopy of 2,4,6-trinitrotoluene-hydroxide reaction, Chemosphere 49 (2002) 287–295.
[17] R. Alnaizy, A. Akgerman, Oxidative treatment of high explosives contaminated wastewater, Water Res. 33 (1999) 2021–2030.
[18] A. McFarlane, K.Y. Yeap, K. Bremmell, J. Addai-Mensah, The influence of flocculant adsorption kinetics on the dewaterability of kaolinite and smectite clay mineral dispersions, Colloids Surfaces A: Physicochem. Eng. Aspects 317 (2008) 39–48.
[19] H. Ren, Y. Li, S. Zhang, J. Wang, Z. Luan, Flocculation of kaolin suspension with the adsorption of N,N-disubstituted hydrophobically modified polyacrylamide, Colloids Surfaces A: Physicochem. Eng. Aspects 317 (2008) 388–393.
[20] M.S. Nasser, A.E. James, Compressive and shear properties of flocculated kaolinite–polyacrylamide suspensions, Colloids Surfaces A: Physicochem. Eng. Aspects 317 (2008) 211–221.
[21] J.P. Wang, Y.Z. Chen, S.J. Zhang, H.Q. Yu, A chitosan-based flocculant prepared with gamma-irradiation-induced grafting, Bioresour. Technol. 99 (2008) 3397–3402.
[22] R.P. Singh, G.P. Karmakar, S.K. Rath, N.C. Karmakar, S.R. Pandey, T. Tripathy, Biodegradable drag reducing agents and flocculants based on polysaccharides: materials and applications, Polym. Eng. Sci. 40 (2000) 46–60.
[23] W.H. Hartley, S. Banerjee, Imaging c-PAM-induced flocculation of paper fibers, J. Colloid Interface Sci. 320 (2008) 159–162.
[24] Z. Nan, Z. Shi, B. Yan, R. Guo, W. Hou, A novel morphology of aragonite and an abnormal polymorph transformation from calcite to aragonite with PAM and CTAB as additives, J. Colloid Interface Sci. 317 (2008) 77–82.
[25] T. Steiner, A.M.M. Schreurs, J.A. Kanters, J. Kroon, Water molecules hydrogen bonding to aromatic acceptors of amino acids. The structure of Tyr–Tyr–Phe dihydrate and a crystallographic database study on peptides, Acta Crystallogr., Sect. D 54 (1998) 25–31.
[26] T. Steiner, Hydrogen bonds from water molecules to aromatic acceptors in very high-resolution protein crystal structures, Biophys. Chem. 95 (2002) 195–201.
[27] T. Steiner, G. Koellner, Hydrogen bonds with π–acceptors in proteins: Frequencies and role in stabilizing local 3D structures, J. Mol. Biol. 305 (2001) 535–557.
[28] Z.S. Derewenda, L. Lee, U. Derewenda, The occurrence of C—H···O hydrogen bonds in proteins, J. Mol. Biol. 252 (1995) 248–262.
[29] P. Cornago, R.M. Claramunt, L. Bouissane, J. Elguero, A molecular balance to measure the strength of N—H···π hydrogen bonds based on the tautomeric equilibria of C-benzylphenyl substituted NH-pyrazoles, Tetrahedron 64 (2008) 3667–3673.