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

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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).

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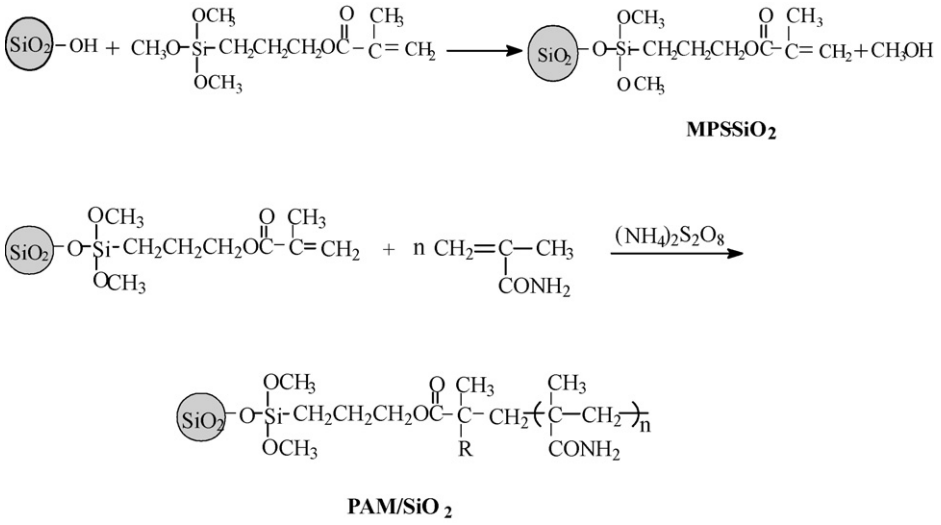

Scheme 1. Schematic expression of preparing process of PAM/SiO_2.

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).

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

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).

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

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