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# Removal of 2,4,6-trinitrotoluene from wastewater using a novel adsorbent polyvinyl alcohol/$SiO_2$

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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, monomer vinyl acetate (VAc) is grafted step by step on the surface of silica gel particles, and the grafted particle PVAc/$SiO_2$ is formed. Then, the novel adsorbent polyvinyl alcohol (PVA)/$SiO_2$ possessing strong adsorption ability for TNT is obtained through the alcoholysis reaction of PVAc. The grafted particles PVAc/$SiO_2$ and PVAc/$SiO_2$ are characterized by Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The adsorption performance of PVA/$SiO_2$ toward 2,4,6-trinitrotoluene (TNT) is investigated through static methods. The experimental results show that PVA/$SiO_2$ possesses strong adsorption ability for TNT with adsorption amount of $18.21\,mg\,g^{-1}$. The empirical Freundlich isotherm is also found to agree well with the equilibrium adsorption data. In addition, pH is found to have great influence on the adsorption amount. Finally, PVA/$SiO_2$ is found to have excellent reusability.

*Keywords:* Vinyl acetate; Polyvinyl alcohol; Adsorption; 2,4,6-trinitrotoluene (TNT)

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## 1. Introduction

The chemical compound 2,4,6-trinitrotoluene (TNT) is a nitroaromatic explosive, which is released into the soil and ground water mainly through military-related activities, such as munitions manufacturing, packing and storage, resulting in contamination of large tracts of soils and groundwater over almost all the world. TNT is a mutagen and a Group C human carcinogen. Exposure to TNT is known to cause rashes, skin hemorrhages, and mucus and blood disorders. Due to its toxic and mutagenic effects to many living organisms, increasingly rigorous limits on the amount of TNT that can be manufactured and released have been established worldwide. For the treatment of wastewater containing TNT, adsorption with various adsorption materials [1–6], degradation and destruction with various microorganisms or catalytic [7–13] have been studied extensively. However, some problems have been identified, such as lower adsorption capacity and high costs, etc. Among these treating methods, adsorption is commonly used. However, the reusability property of the adsorption material must be promoted.

Polyvinyl alcohol (PVA) is a widely used water-soluble polymer. It is frequently utilized in the general industrial applications [14–16]. As a topic of great interest, PVA was chosen as the protective polymer because it has the desired solution properties in water

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and contains many isolated hydroxyl functional groups, which can adsorb organic molecules with a high adsorption capacity based mainly on hydrogen bond interactions. Functional polymer PVA have important applications such as the design of a new drug slow/controlled release system, the extraction of pharmacological active substance, the clean of metabolites, the removal of heavy metal ions and organic pollutants [17–21]. These properties allow its broad use in various science and technology fields.

In order to realize the surface-initiated graft-polymerization of water-soluble monomer vinyl acetate (VAc) on silica gel particles, a facile and convenient surface-initiated free-radical polymerization method is designed and put forward. The coupling agent γ-aminopropyltrimethoxysilane is used for surface modification of micron-sized silica gel particles leading to the introduction of amino groups onto the modified silica gel particles, and then, a redox initiation system is constituted by the amino groups on the surfaces of the particles and persulfate molecules in the solution. As a result, primary free radicals are generated on the surfaces of the modified silica gel particles, and the surface-initiated free radical graft-polymerization of VAc is realized, obtaining the grafted particles PVAc/$SiO_2$ with a high grafting degree. And then, the functional grafted particles PVA/$SiO_2$ is obtained through the alcoholysis reaction of VAc. The adsorption performance of PVA/$SiO_2$ towards TNT is researched. The experimental results show that PVA/$SiO_2$ possesses strong adsorption ability toward TNT by hydrogen bond interaction.

## 2. Experimental

### *2.1. Material and equipment*

Silica (120–160 mesh, about 125 μm of diameter, Ocean Chemical Limited Company, Qingdao City, China) is of reagent grade. γ-Aminopropyltrimethoxysilane (AMPS, Qufu Wanda Chemical Co., Ltd., Province Shandong, China) is of analytical grade. Vinyl acetate (VAc, Guangfu Chemical Reagent, Tianjin City, China) is of analytical grade and is purified by vacuum distillation before use. Ammonium persulfate (APS, Fushu Chemical Engineering Inc., Shanghai) is of analytical grade. Other reagents are all commercial chemicals with analytical grade and purchased from Beijing Chemical Plant.

The instruments used in this study are as follows: Perkin-Elmer 1700 infrared spectrometer (Fourier transform infrared (FTIR), Perkin-Elmer Company, USA), STA449 thermogravimetric analyzer (thermogravimetric analysis (TGA), Netzsch Company, Germany), PHS-3C pH meter (Shanghai Precision scientific Apparatus Inc., Shanghai, China).

### *2.2. Preparation and characterization of grafted particles PVAc/$SiO_2$*

#### *2.2.1. Surface modification of silica gel particle with AMPS*

The modified particle AMPS–$SiO_2$ is prepared according to the procedures described in Ref. [22]. The typical procedure is as follows. Firstly, silica gel particles are treated for activation by using aqueous solution of methane sulfonic acid with the concentration of 5% (wt.%) as activation reagent. The activation reaction is carried out at 90℃ for 8 h. The activated silica gel particles are washed repeatedly with distilled water to neutral and dried under vacuum. Secondly, activated silica gel particles are surface-modified with coupling agent AMPS, where a primary amine group is contained. The modification reaction is carried out at 50℃ with stirring for 24 h. The resultant particles are washed with water and ethanol and dried under vacuum, resulting in the surface-modified particles AMPS–$SiO_2$.

#### *2.2.2. Preparation and characterization of grafted particles PVAc/$SiO_2$*

The graft-polymerization of VAc on the surfaces of the modified particles AMPS–$SiO_2$ is carried out in a solution polymerization system. The modified particles AMPS–$SiO_2$ (1 g) are added into a four-necked flask equipped with a mechanical agitator, reflux condenser, thermometer and a $N_2$ inlet, followed by adding 36 mL of DMSO, 44 mL of distilled water and 8.4 mL of monomer VAc. The content is stirred and the modified particles AMPS–$SiO_2$ are dispersed fully. $N_2$ is bubbled for 30 min to exclude air. The content is heated to 30℃, and 20 mL of aqueous solution containing 0.0599 g of initiator is added. The graft polymerization is performed under $N_2$ atmosphere at 30℃ for 12 h. The resultant particles are extracted with methanol in a soxhlet extractor for 24 h to remove the polymer attaching physically to the particles, dried under vacuum, and finally, the grafted particles PVAc/$SiO_2$ are obtained.

The FTIR spectrum of the grafted particles PVAc/$SiO_2$ is determined with KBr pellet method to confirm their structures, and their morphology is observed with SEM. The grafting degree (GD, g/100 g) of PVAc on the grafted particles PVAc/$SiO_2$ is determined by TGA under air atmosphere.

#### 2.2.3. Preparation and characterization of functional grafted particles PVA/SiO$_2$

The grafted particles PVAc/SiO$_2$ (1 g) are added into a four-necked flask, followed by adding 100 g of methanol in which 4 g of NaOH is dissolved. The alcoholysis reaction is carried out at a constant temperature of 35℃ with stirring for 12 h. The resultant particles are washed repeatedly with distilled water to neutral and dried under vacuum, resulting in the functional grafted particles PVA/SiO$_2$.

The FTIR spectrum of the functional grafted particles PVA/SiO$_2$ is determined with a KBr pellet method to confirm their structures. On the basis of grafting degrees data of PVAc/SiO$_2$, the alcoholysis degree (AD, g/100 g) of PVAc/SiO$_2$ is determined by acid/base titration. The AD of PVAc/SiO$_2$ is 90%.

The entire chemical process to prepare PVA/SiO$_2$ is expressed schematically in Fig. 1.

### 2.3. Adsorption property of PVA/SiO$_2$ towards TNT

#### 2.3.1. Measurement of the kinetic adsorption curve

One gram of PVA/SiO$_2$ is directly introduced into a conical flask, into which 500 mL of the aqueous TNT solution with an initial concentration ($C_0$) of 100 mg L$^{-1}$ and pH of 6 is added. This conical flask is placed in a shaker at a preset temperature and then shaken. At different times, the concentration ($C_t$) of the TNT solution is determined. The adsorption amount ($Q$) is calculated according to the following 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 TNT solution; and $m$ (g) is the weight of the adsorbent PVA/SiO$_2$.

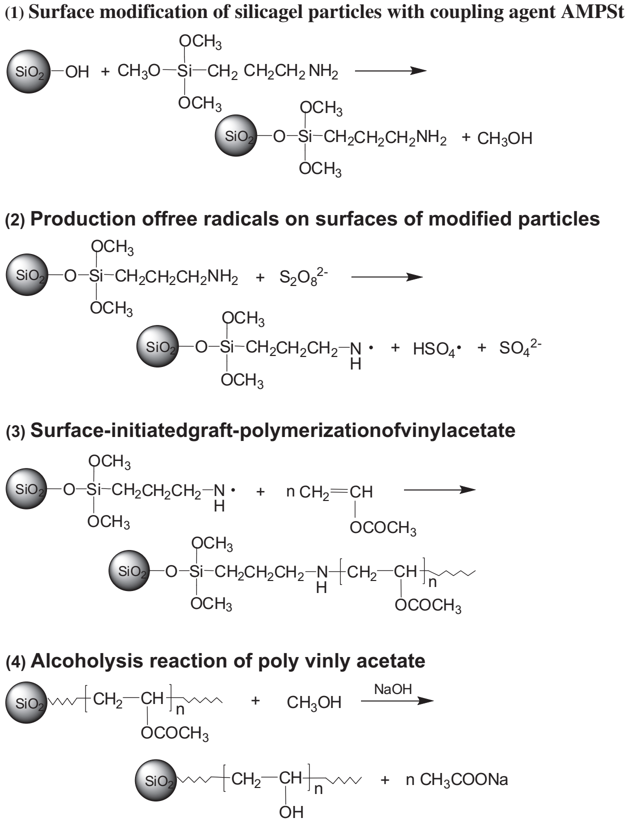

Fig. 1. Schematic expression of preparing process of PVA/SiO$_2$.

#### 2.3.2. Measurement of the adsorption isotherm

About 0.1 g of PVA/SiO$_2$ is directly introduced into a number of conical flasks, into which 50 mL of the aqueous TNT solution with concentrations ($C_0$) of 20, 40, 60, 80, 100 mg L$^{-1}$ and pH of 6 are added, respectively. These conical flasks are placed in a shaker at a presettled temperature and then shaken. After reaching the adsorption equilibrium, the concentrations ($C_e$) of the TNT solutions are determined. The equilibrium adsorption amount ($Q_e$) is then calculated according to Eq. (2):

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

### 2.4. Repeated usability experiment

Repeated usability (i.e. regenerability) is an important factor for an effective absorption material. Desorption of the adsorbed TNT from the PVA/SiO$_2$ is also studied by static experiment. As observed, the adsorbed TNT is desorbed using the HCl solution with a pH of 2 as eluting agent. The PVA/SiO$_2$ that adsorbed TNT is placed in the eluent and stirred continuously at room temperature for 10 h. The final concentration of TNT in the aqueous phase is detected. In order to test the reusability of PVA/SiO$_2$, the adsorption/desorption procedure is repeated 10 times using the same material.

## 3. Results and discussion

### 3.1. Characterization of grafted particles

#### 3.1.1. Infrared spectrum

Fig. 2 presents the infrared spectra of four kinds of particles, silica gel particles, modified particles

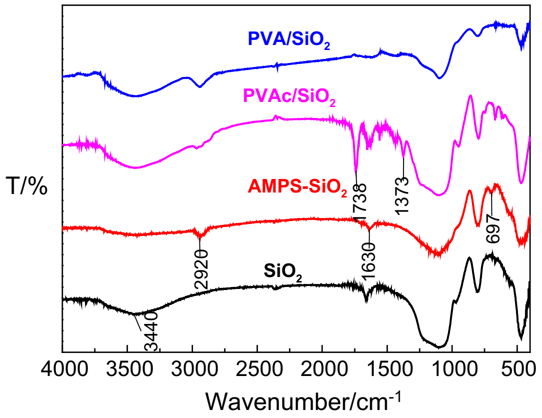

Fig. 2. TGA curves (a) AMPS–SiO$_2$; (b) PVAc/SiO$_2$.

AMPS–SiO$_2$, grafted particles PVAc/SiO$_2$ and functional grafted particles PVA/SiO$_2$.

In the spectrum of silica gel particles, the wide band at about 3,440 cm$^{-1}$ is an absorption peak associated with silanol group and adsorbed water. After the surface modification with the coupling agent AMPS, this band becomes obviously weak, and at the same time, two new bands at 2,920 and 697 cm$^{-1}$ appear. The former is the asymmetrical stretching vibration absorption of C–H bond and the latter is attributed to the bending vibration absorption of N–H bond of the primary amine group, showing that the coupling agent AMPS is bound on the surfaces of silica gel particles via the reaction between AMPS molecules and silanol groups of silica gel particles.

In the spectrum of PVAc/SiO$_2$ particles, all of the above various characteristic absorption of the primary amine group becomes obviously weak, and at the same time, the stretching vibration absorption of the carbonyl group C=O of ester group appears at 1,738 cm$^{-1}$, and the new bands at 1,373 cm$^{-1}$ is ascribed to the in-plane bending vibration absorption of -$CH_3$ groups. The above spectrum changes sufficiently show that the grafted particles PVAc/SiO$_2$ are formed.

In the spectrum of PVA/SiO$_2$ particles, the absorption peak at 1,738 cm$^{-1}$ which is stretching vibration absorption of the carbonyl group C=O of ester group almost completely disappeared. This indicates that the alcoholysis reaction of PVAc is realized and PVA/SiO$_2$ is formed.

### 3.1.2. *TGA curves of the grafted particles PVAc/SiO$_2$*

The weight loss curves of modified particles AMPS–SiO$_2$ and grafted particles PVAc/SiO$_2$ are shown in Fig. 3.

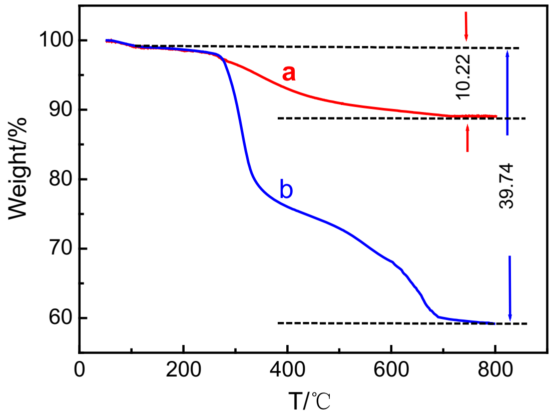

Fig. 3. Kinetic adsorption curve temperature: 25℃; pH=6; initial concentration of TNT: 100 mg L$^{-1}$.

It can be found that modified particles AMPS–SiO$_2$ and grafted particles PVAc/SiO$_2$ begin to decompose at around 150℃. (Below 150℃, the weight loss of particles AMPS–SiO$_2$ and particles PVAc/SiO$_2$ is less than 1%, which is mostly due to the evaporation of absorbed water). The weight loss curves (a) values of about 10.22% corresponds to modified particles AMPS–SiO$_2$, which is decomposed completely up to 700℃. The weight loss curves (b) values of particles PVAc/SiO$_2$ are about 39.74%. Thus, it is concluded that 29.52% of PVAc are grafted on the silica particle surface.

### 3.2. *Kinetic adsorption curve*

The kinetic adsorption curve is shown in Fig. 4. The adsorption of TNT by PVA/SiO$_2$ reaches equilibrium at 8 h, and the saturated adsorption amount reached 18.21 mg g$^{-1}$. This suggests that PVA/SiO$_2$ possesses strong adsorption ability for TNT.

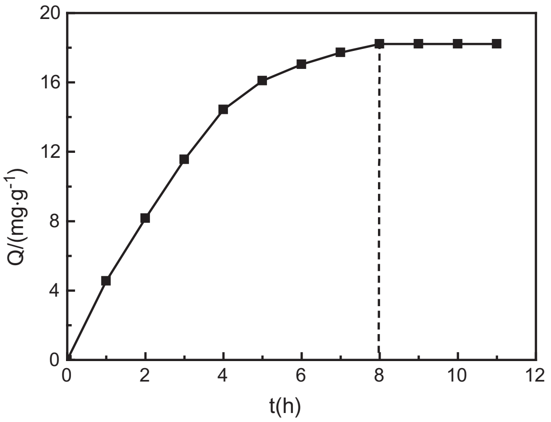

Fig. 4. Adsorption isotherms at different pH temperature: 25℃; adsorption time: 8 h.

### *3.3. Adsorption isotherm*

The adsorption isotherms of AMPS–$SiO_2$, PVAc/$SiO_2$, and PVA/$SiO_2$ at different pH values are shown in Fig. 5. It can be seen that the equilibrium adsorption amount of PVA/$SiO_2$ towards TNT increases rapidly along with the increase in equilibrium concentration. This high affinity can be attributed to the hydrogen bond interaction between PVA and TNT. Additionally, the amount of AMPS–$SiO_2$ and PVAc/$SiO_2$ toward TNT is very low. This indicates that the main force is the interaction between TNT and –OH of PVA, although the imino and the propilidene group can also interact with TNT.

The effect of pH value on the adsorption property of PVA/$SiO_2$ can be seen clearly from Fig. 6. Obviously, the pH value has a great influence on the adsorption ability of PVA/$SiO_2$ for TNT. Moreover, the adsorption capacity is lower in acidic and basic solutions but is at its greatest adsorption within a solution with pH of 6.

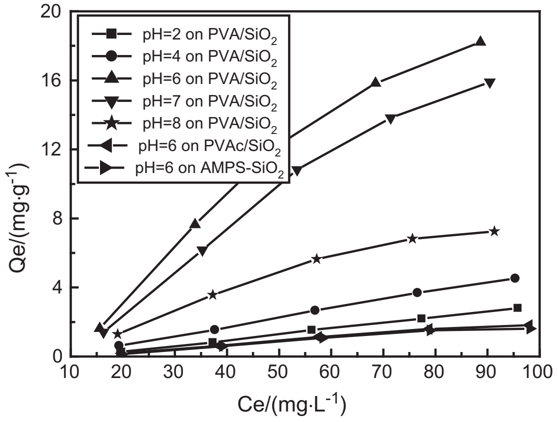

Fig. 5. Varying of adsorption capacity of PVA/$SiO_2$ with pH values.

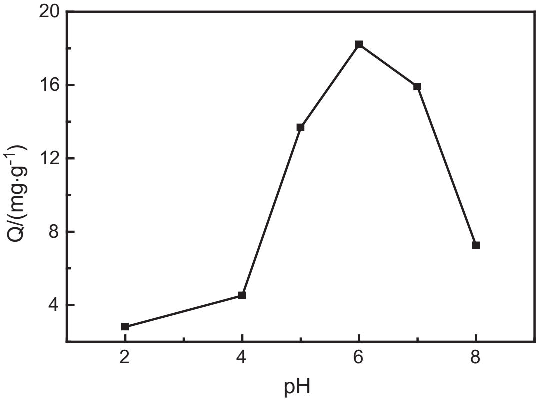

Fig. 6. IR spectra.

The adsorption property is different at different pH values. This is caused by different molecule interaction (hydrogen bond) between PVA and TNT at different pH value. The forms of hydrogen bond occurring possibly between PVA and TNT are expressed in Fig. 7. First, the –OH of PVA could form aromatic hydrogen bond (O–H…π hydrogen bond) with π–electron cloud of TNT aromatic groups that act as the acceptor (a in Fig. 7) [23–25]. Second, the –OH groups could also form hydrogen bond (O–H…O hydrogen bond) with oxygen atom of nitryl in TNT molecules (b in Fig. 7).

In an acidic solution, there are lots of hydrogen ions $H^+$ in solution. Lots of $H^+$ could form electrostatic interaction with oxygen atom of nitryl in TNT molecules, so the hydrogen bond is difficult to form. The concentration of hydrogen ions $H^+$ is decreased with the increases in pH value, resulting in strengthening and increase of hydrogen bond. So the adsorption capacity increases with the increase in pH value. In a basic solution, the electronegative property of oxygen atom of nitryl in TNT molecules is declined; thus the hydrogen bond interaction is also very weak, again resulting in lower adsorption capacity.

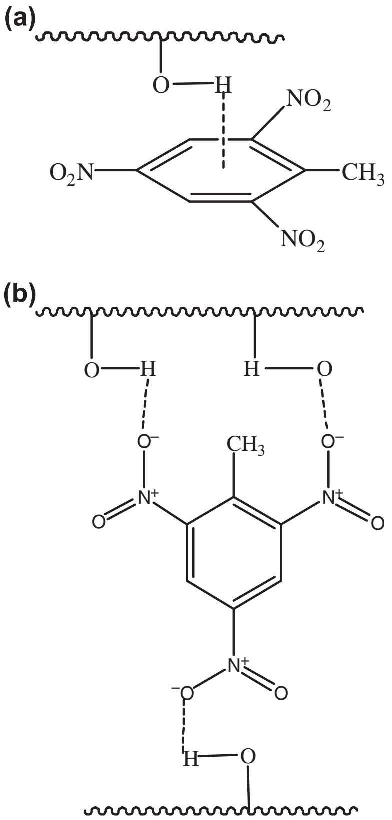

Fig. 7. Hydrogen bond between PVA and TNT.

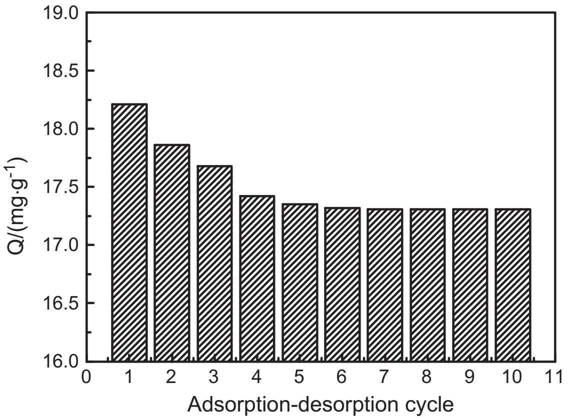

Fig. 8. Adsorption–desorption cycle.

### 3.4. Reusability

When the HCl with pH of 2 is used as eluent, the hydrogen bond interaction between TNT and PVA is disrupted and subsequently, TNT is released into the eluent. In order to show the reusability of the PVA/$SiO_2$, the adsorption/desorption cycle is repeated 10 times using the same material.

The adsorption/desorption cycle of PVA/$SiO_2$ is shown in Fig. 8. The results clearly show that the PVA/$SiO_2$ can be used repeatedly without significantly losing its adsorption capacity.

## 4. Conclusions

In this study, monomer VAc is grafted on the surface of silica gel particles step by step, and the novel adsorption material PVA/$SiO_2$ is obtained through the alcoholysis reaction of PVAc. PVA/$SiO_2$ has very strong adsorption ability for TNT by way of hydrogen bond interaction. However, the adsorption ability of PVA/$SiO_2$ for TNT is largely dependent on the pH value of the solution. Based on the results, the strongest adsorption capacity is found in the solution with pH of 6 as compared with the acidic and basic solutions. Finally, PVA/$SiO_2$ is also found to possess excellent reusability properties.

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