

Removal of Nitro Aromatic Compounds and Sulfite Acid from Distillate of 2,4,6-Trinitrotoluene Red Water Using Modified Porous Polystyrene Microspheres

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ABSTRACT: To remove the nitro aromatic compounds (NACs) and SO_3^{2-} from distillate of 2,4,6-trinitrotoluene (TNT) red water, the carboxylated and aminated polystyrene (PSt) microspheres were used as adsorbents. GC-MS and HPLC analysis were used to determine the types and concentrations of NACs before and after adsorption. The carboxylated PSt, which was prepared by modifying PSt with phthaldione (PA), could remove the neutral NACs including 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), and 2,4,6-trinitrotoluene (2,4,6-TNT), with the acid 2,4-dinitrophenol (2,4-DNP) and SO_3^{2-} remained in the distillate. The aminated PSt that was synthesized by activating PSt with chloroacetyl chloride followed by reaction with 1,2-ethanediamine (EDA) could remove all the NACs and SO_3^{2-} . The results suggested that EDA-PSt adsorbed the NACs through multimode interactions, i.e., hydrogen bond and electrostatic attraction. After adsorption using EDA-PSt, chemical oxygen demand (COD) was reduced from 86.1 to 11.2 mg L^{-1} , and a colorless, transparent, and nontoxic solution with neutral pH value was obtained. Five grams of EDA-PSt could purify 1600 cm^3 of distillate of TNT red water, and the adsorbents could be recycled by elution with methanol to desorb the neutral NACs followed by elution with 0.1 mol L^{-1} NaOH to wash off 2,4-DNP and SO_3^{2-} . © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Wastewater generated in the purification of 2,4,6-trinitrotoluene (TNT) using sulfites is a dark red aqueous solution, thus was called TNT red water. TNT red water contains mainly dinitrotoluene sulfonates (DNSTs) with low concentration of other nitro aromatic compounds (NACs)¹ and sodium sulfite. Because of its high toxicity to human, animals, plants, and microorganisms, TNT red water is forbidden to be discharged to environment without proper treatment.

Methods used to eliminate the potential danger of TNT red water to the environment include incineration, wet air oxidation (WAO), adsorption, and vacuum distillation. Incineration, in which TNT red water and heavy oil are mixed and burned in an oven, is convenient and, hence, widely used in TNT red water treatment.² However, incineration causes secondary pollution to the atmosphere.³ In addition, this process becomes more expensive because of the rise of fuel cost, especially in China. WAO uses high-pressure air to oxidize pollutants under high tempera-

ture (125–350°C) to remove the chemical oxygen demand (COD). Although WAO is considered as an economical and environment-friendly way for treatment of wastewater,⁴ some S-containing organic compounds were difficult to remove using this method.⁵ Adsorption, which is suitable for treatment of low COD waste water, is not practical in treatment of TNT red water, because large amount of adsorbents is needed to lower the high COD to the discharging standard, and the regeneration of the adsorbent produces waste water again. In our previous studies, vacuum distillation was used to treat red water.^{1,6} The results showed that almost all of pollutants were contained in the distillate and the COD of the distillate was lower than 100 mg L^{-1} . However, the distillate still contained NACs and exhibited toxicity.¹ Obviously, TNT red water cannot be treated satisfactorily by a one-step process.

In this study, attention was paid to treatment of distillate of TNT red water. Because of the low concentration of NACs, it is not appropriate to treat distillate of TNT red water using

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biological and chemical^{7–9} methods, which were widely used in NACs removal. Adsorption method, on the contrary, is suitable to remove low-concentration substances,¹⁰ and hence, was chosen. Because nitro group can interact with amino¹¹ and carboxylic groups¹² through hydrogen bond, aminated and carboxylated polystyrene microspheres were used to adsorb the compounds from the distillate of TNT red water. COD, suspended substance (SS), chrominance, and acute toxicity were measured to evaluate the water quality before and after adsorption. Gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) analyses were carried to determine the types and concentrations of compounds in the solutions.

MATERIALS AND METHODS

Materials

Porous polystyrene (PSt) microspheres (average diameter: 60 μm , pore size: 200 nm, surface area: 150 $\text{m}^2 \text{g}^{-1}$) crosslinked with 45% divinylbenzene (DVB) were obtained from National Engineering Research Centre for Biotechnology (Beijing, China). TNT red water containing mainly $51 \times 10^3 \text{ mg L}^{-1}$ DNTS ($20 \times 10^3 \text{ mg L}^{-1}$ 2,4-DNT-3-S and $30 \times 10^3 \text{ mg L}^{-1}$ 2,4-DNT-5-S) was supplied by Dongfang Chemical Corporation (Hubei Province, China). The initial COD was 100,800 mg L^{-1} and pH value was 5.4. The luminescent bacterium *Vibrio qinghaiensis sp. Nov.* was provided by Beijing HAMAMATSU Photon Techniques (Beijing, China). Other chemicals (AR grade) were provided by Beijing Chemical Plant (Beijing, China).

The major instruments used in this study were: RE-52AA rotary evaporator (Shanghai Qingpu Huxi instrument Factory, China), Agilent 1100 liquid chromatograph (Agilent Corporation, USA), GC-MS system (GC6890/MSD5973 N, Agilent Corporation, USA), and BHP9511 water quality toxicity analyzer (Beijing Hamamatsu Photon Techniques, China).

Preparation of the Adsorbents and Determination of Density of Functional Groups

Preparation of Aminated PSt (EDA-PSt). EDA-PSt was first activated with chloroacetyl chloride and then allowed to react with 1,2-ethanediamine (EDA). Ten grams of PSt, 5 g of chloroacetyl chloride and 150 cm^3 of dichloromethane were added into a 500 cm^3 three-necked flask and agitated with a mechanical stirrer at 25°C for 10 min. Then, 5 g of AlCl_3 was slowly added. After reaction for 7 h at 25°C, the microspheres were transferred into a G3 sintered-glass funnel, and washed successively with 500 cm^3 of HCl (0.2 mol L^{-1}), deionized water and THF. The washed microspheres were suction-dried until no THF drops were observed from the sintered-glass funnel. The suction-dried microspheres together with 60 cm^3 of THF, 40 cm^3 of ethanol, 20 cm^3 of EDA, and 10 g of NaHCO_3 were added into a 250 cm^3 three-necked flask and agitated with a mechanical stirrer at 80°C. After reaction for 18 h, the microspheres were washed with ethanol and water in a G3 sintered-glass funnel, followed by suction-drying. The suction-dried adsorbent was dried at 105°C for 2 h and then stored in an airtight vial.

Preparation and Characterization of Carboxylated PSt (PA-PSt). PA-PSt was prepared by Friedel-Crafts acetylation of PSt with phthlandione (PA). Ten grams of PSt, 10 g of PA, 100 mL of dichloromethane, and 20 mL of nitrobenzene were added into a

500 mL three-necked flask equipped with a mechanical stirrer at 50°C. Then 30 g of AlCl_3 was slowly added. After reaction for 9 h, the microspheres were transferred into a G3 sintered-glass funnel, and washed successively with 500 mL of 0.2 mol L^{-1} HCl, deionized water, THF, and deionized water, followed by suction-drying. The suction-dried adsorbent was dried at 105°C for 2 h and then stored in an airtight vial.

Determination of the Density of Functional Groups. The total amino group density of the prepared adsorbent was determined by Kjeldahl method.¹³ The sample (0.1 g) was mixed with 0.8 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 6.0 g of K_2SO_4 , and 20 cm^3 of concentrated H_2SO_4 in a 100 cm^3 digestion flask. The flask was heated using an oven to about 400°C. After digestion for 6 h, the obtained solution was cooled to room temperature and then transferred to a 100 cm^3 measuring flask. The volume was set to the mark with deionized water. Ten milliliters of solution from the measuring flask was analyzed by Kjeldahl titration.

The density of the primary amino was determined using a titration method.¹⁴ One gram of EDA-PSt, 120 cm^3 of deionized water, 20 cm^3 of concentrated HCl, and 10 cm^3 of 100 g L^{-1} KBr were added into a 400 cm^3 beaker. The suspension was agitated with a magnetic stirrer and titrated with 0.5 mol L^{-1} NaNO_2 until the solution made the potassium iodide-starch test paper exhibit sky-blue. The density of primary amino was calculated according to the NaNO_2 consumed.

The density of carboxyl group was determined based on the Ref. 15 with slight modifications. Fifty milliliters of 4 mol L^{-1} HCl and 1 g of PA-PSt were added to a 100 cm^3 conical flask. The suspension was sonicated for 10 min, stirred for 1 day, and filtered with a G3 sintered-glass funnel. The microspheres were washed with hot deionized water to wash out HCl and suction-dried. The residue in the funnel was dried at 105°C for overnight. This pretreated PA-PSt was suspended in 30 cm^3 of 0.1 mol L^{-1} NaCl solution and was stirred for 30 min. The suspension was titrated with NaOH. The density of carboxyl group was calculated according to the NaOH consumed.

Vacuum Distillation of TNT Red Water

Six hundred milliliters of TNT red water was transferred into a 1000 cm^3 distillation retort connected to the rotary evaporator and then vacuumized. The rotary speed was set at 80 rpm, and the pressure was adjusted so that the TNT red water fluidized at 80°C. The distillation process was stopped when there was no liquid dropped from the condenser tube.

Batch Adsorption of Distillate of TNT Red Water

Batch adsorption was performed to investigate the adsorption kinetics. The adsorbents were both washed successively by ethanol and deionized water in a G3 sintered glass funnel, and then suction-dried. Five grams of suction-dried adsorbent was added directly to 1600 cm^3 of distillate of TNT red water agitated with a mechanical stirrer in a 2000 cm^3 beaker at 25°C. The chemical oxygen demand (COD) of the solution at different time was measured.

Dynamic Adsorption and Desorption of Distillate of TNT Red Water

The adsorbents were both washed successively by ethanol and deionized water in a sintered glass funnel (G3), and then suction-dried. Five grams of the suction-dried adsorbent was slurry-

packed in a glass column (200 × 10 mm² I.D.). Two hundred milliliters of distillate of TNT red water was then allowed to flow through the column. Elution efficiency of acetone and 0.1 mol L⁻¹ NaOH was investigated. Flow rate of both the loading and elution was controlled at 2.0 cm³ min⁻¹. The effluents during adsorption and desorption were collected separately, and the water quality and component were analyzed.

Water Quality Detection

The water quality was detected according to Chinese standard GB 14470.1-2002 (Discharge standard for water pollutants from ordnance industry: Powder and explosive). The COD, suspended substance (SS), and chrominance were determined using the methods provided by Chinese standard GB 11914, GB 11901, and GB 11903, respectively.

Acute Toxicity Test

The acute toxicity before and after adsorption was determined by measuring the luminescence inhibition ratio of *V. qinghaiensis* sp. Nov., a freshwater luminescent bacterium separated from body surfaces of *Gymnocypris przewalskii* which lives in Qinghai Lake, China.^{16,17} Fifty microlitres of suspensions containing luminescent bacterium was exposed to 2 cm³ of water samples with different dilution ratios for 15 min at room temperature before measuring bioluminescence. Deionized water was used as reference. The luminescence inhibition ratio, LIR (%), was calculated according to the following equation.

$$\text{LIR (\%)} = \frac{[\text{RLI}_{\text{ref}} - \text{RLI}_s]}{\text{RLI}_{\text{ref}}} \times 100$$

where RLI is the relative light intensity of the luminescence emitted from luminescent bacteria. The indices “ref” and “s” represent the reference and sample, respectively.

Composition Analysis

HPLC Analysis. An Agilent 1100 liquid chromatograph with an Agilent SB-Aq column (250 × 4.6 mm I.D.) as the separation system was used with the detection wavelength of 246 nm. The mobile phase was methanol/water (45 : 55, V/V) and the operation temperature was 30°C. Twenty microlitres of the sample was injected, and the flow rate was 1.0 cm³ min⁻¹.

GC-MS Analysis. The samples for GC-MS analysis were prepared as follows. A 100 cm³ of water sample was extracted by 5 cm³ of dichloromethane for three times under acidic, neutral, and basic conditions. The three extract layers were collected and dried by nitrogen, and then, the residue was dissolved into 1.0 cm³ of dichloromethane for use.

One microlitre of sample was injected into the GC-MS system, operated from 40 to 280°C at a programming rate of 2.0°C min⁻¹. A DB-35MS capillary column with inner diameter of 0.25 mm and length of 60 m was adopted in the separation system. Pure helium gas was used as carrier gas at a flow rate of 1.0 cm³ min⁻¹. For MS, the emission current of the ionization filament was set 30 μA generating electrons with 70 eV energy and the used electron multiplier voltage was 2000 V.

Determination of Concentrations of SO₃²⁻. Because sulfite was used in purification of TNT, it was possible that the distillate of TNT red water contained H₂SO₃. SO₃²⁻ was determined by titration using 0.01 mol L⁻¹ KI solution with the starch as the indica-

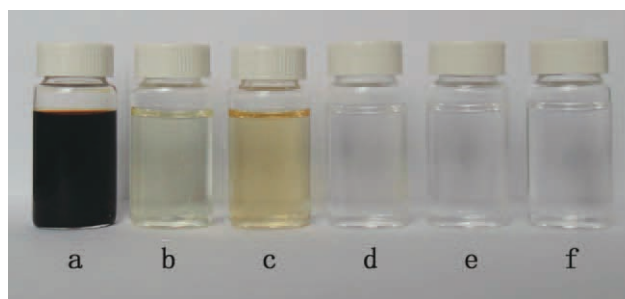


Figure 1. Photographs of TNT red water (a), fresh distillate of TNT red water (b), distillate of TNT red water after preserved for a week (c), distillate adsorbed by PA-PSt (d) and EDA-PSt (e), and deionized water (f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tor. The concentration of SO₃²⁻ was calculated according to the amount of KI consumed.

RESULTS AND DISCUSSION

Density of Functional Groups of the Adsorbents

After reaction, the density of functional groups was determined. For EDA-PSt, the results showed that the density of total amino group was 2.72 mmol g⁻¹. However, the density of primary amino was only 0.43 μmol g⁻¹, which means that almost all of the 1,2-ethanediamine molecules were immobilized to PSt through both of the terminal —NH₂. Therefore, the functional group of the synthesized EDA-PSt was imino group and the density was 2.72 mmol g⁻¹. For PA-PSt, the density of carboxyl group was 2.54 mmol g⁻¹. By weighing the suction-dried adsorbents before and after heating at 105°C for 2 h, it was found both the suction-dried adsorbents contained 55% of water.

Water Quality and Acute Toxicity

After 600 cm³ of TNT red water was distilled, 515 cm³ of faint yellow distillate was obtained [Figure 1(b)]. Then, 200 cm³ of distillate was allowed to flow through the column packed with 5.0 g of suction-dried PA-PSt or EDA-PSt. Water quality and acute toxicity of four solutions, namely TNT red water, distillate of TNT red water, and distillate after adsorbed by PA-PSt and EDA-PSt, were listed in Table I. The dilution ratio at which the water samples exhibited no LIR was chosen to evaluate acute toxicity.

The COD, SS, pH value, and chrominance specified by Chinese discharging standard of TNT wastewater were <100 mg L⁻¹, <200 mg L⁻¹, 6–9, and <150°, respectively. With most of compounds remained in the distillation retort, the COD of the distillate was only 86.1 mg L⁻¹ and lower than the specified maxim value. When compared with the nearly neutral pH value of TNT red water, the pH value of the distillate decreased to 2.7, indicating that some acid compounds with low boiling point transferred from TNT red water to the distillate during the distillation. The color of the distillate was due to the nitro aromatic compounds. Although the fresh distillate was faint yellow, it became dark [Figure 1(c)] after preserved for a week at room temperature and the chrominance rose from 17° to 260°,

Table I. Water Quality of TNT Red Water, Its Distillate, and Distillate Adsorbed by PA-PSt and EDA-PSt

Sample name	COD (mg L ⁻¹)	SS (mg L ⁻¹)	Chrominance	pH	DR _{T0} ^a
TNT red water	100,800	35,000	100,000°	5.4	10,000
Distillate of TNT red water	86.1	0	17–260°	2.7	1000
Distillate adsorbed by PA-PSt	35.7	0	1°	4.0	64
Distillate adsorbed by EDA-PSt	11.2	0	1°	6.5	1

^aDilute ratio where solution exhibited no toxicity.

which might be caused by the reaction between NACs and SO₃²⁻ that existed in the distillate. More important, the distillate exhibited toxicity and it should be diluted 1000 times to be harmless. The low pH value, high chrominance, and acute toxicity made the distillate cannot be discharged to the environment. Hence, the distillate needs to be treated further.

PA-PSt, which contains —COOH as functional group, was expected to remove the nitro aromatic compounds from the distillate though the hydrogen bond interaction between —COOH and —NO₂. Although the water sample became colorless after adsorption [Figure 1(d)] and the COD was decreased by 50.3 mg L⁻¹, the pH value was 4.5 and the effluent still exhibited toxicity. The results indicated that the some acid compounds in the distillate could not be adsorbed by PA-PSt.

Table I shows that after adsorption with EDA-PSt that contains —NH— as functional groups, the COD was decreased to 11.0 mg L⁻¹ and the pH value rose to 6.5. The effluent is colorless [Figure 1(e)] and exhibited no acute toxicity. EDA-PSt presented adsorption ability for both the colored and acid compounds.

Compounds Analysis

The organic compounds in distillate and the two effluents were determined by GC-MS and HPLC. Because sulfite was used in purification of TNT and TNT red water contained the residual SO₃²⁻, it was possible that SO₃²⁻ was transformed to SO₂ and dissolved in the distillate to form H₂SO₃. SO₃²⁻ was determined by titration using KI solution.

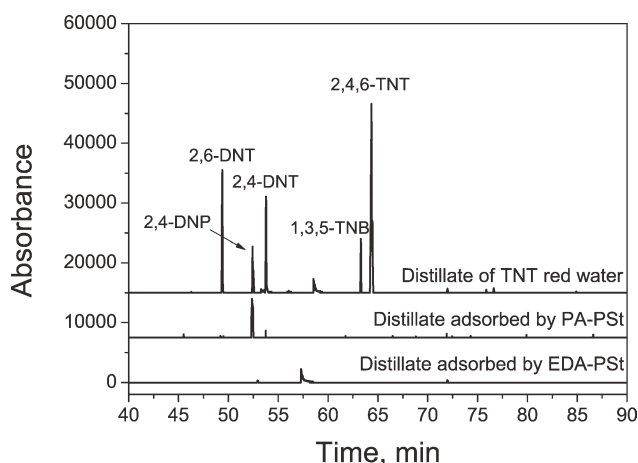


Figure 2. GC-MS measurement of distillate of TNT red water and distillate adsorbed by PA-PSt and EDA-PSt.

GC-MS Analysis. The compounds detected by GC-MS in the distillate of TNT red water and distillate adsorbed by PA-PSt and EDA-PSt are shown in Figure 2. There were five NACs detected in distillate of TNT red water, including acid 2,4-dinitrophenol (2,4-DNP) and neutral 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), and 2,4,6-trinitrotoluene (2,4,6-TNT). With the neutral nitro aromatic compounds adsorbed by PA-PSt, only the acid 2,4-DNP was detected in the effluent of PA-PSt column. After adsorbed by EDA-PSt, no compound was detected in the effluent.

HPLC Analysis. Figure 3 presents the HPLC analysis profiles. Based on the results of GC-MS, pure 2,4-DNP, 2,6-DNT, 2,4-DNT, 1,3,5-TNB, and 2,4,6-TNT were used as standard substances to assign the peaks and measure the concentration. For distillate of TNT red water, P1–P5 were determined to be 1,3,5-TNB, 2,4-DNP, 2,4,6-TNT, 2,6-DNT, and 2,4-DNT, respectively. For the HPLC profile of distillate after adsorption using PA-PSt, peak of 2,4-DNP remained nearly unchanged. Meanwhile, peaks of 2,4,6-TNT, 2,6-DNT, and 2,4-DNT disappeared, and peak of 1,3,5-TNB became very little. For that using EDA-PSt, only a little peak of 1,3,5-TNB appeared.

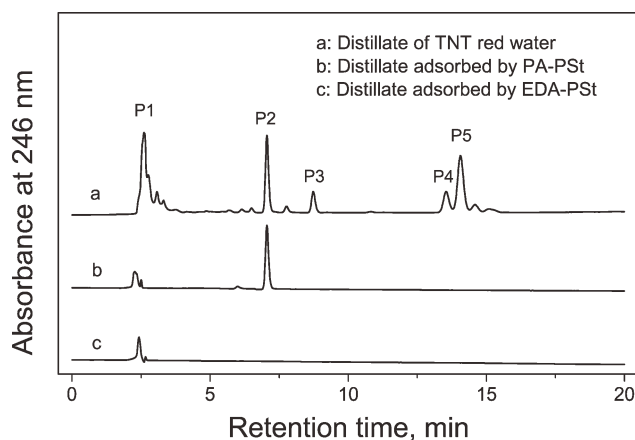


Figure 3. HPLC profiles of distillate of TNT red water and distillate adsorbed by PA-PSt and EDA-PSt. For distillate of TNT red water, P1 to P5 were determined to be 1,3,5-TNB (15.55 mg L⁻¹), 2,4-DNP (6.24 mg L⁻¹), 2,4,6-TNT (2.23 mg L⁻¹), 2,6-DNT (2.18 mg L⁻¹), and 2,4-DNT (3.75 mg L⁻¹), respectively. Distillate adsorbed by PA-PSt contained 1,3,5-TNB (2.32 mg L⁻¹) and 2,4-DNP (6.13 mg L⁻¹). Distillate adsorbed by EDA-PSt contained only 1,3,5-TNB (2.05 mg L⁻¹).

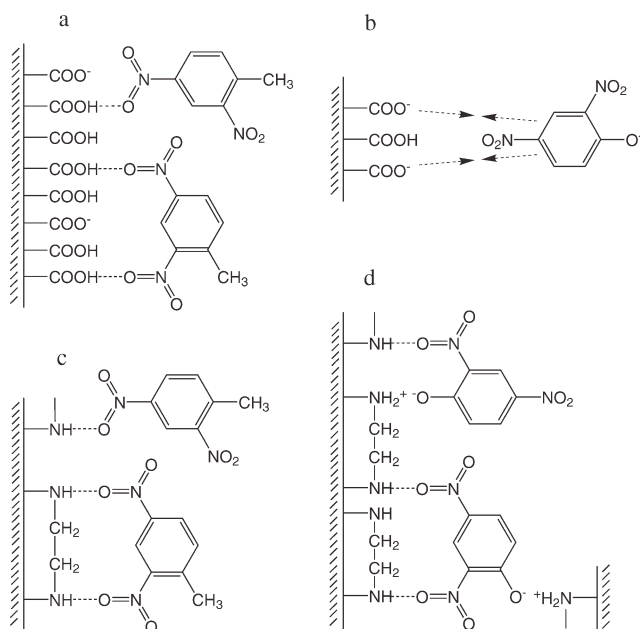
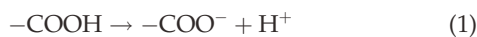


Figure 4. Interaction involved in adsorption of PA-PSt and EDA-PSt for the NACs.

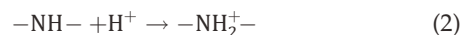
Determination of SO_3^{2-} . The concentration of SO_3^{2-} in distillate of TNT red water was 3.5 mg L^{-1} . It can be seen that H_2SO_3 together with 2,4-DNP lowered pH value of the distillate to 2.7. After adsorbed by PA-PSt, the concentration of SO_3^{2-} remained unchanged, suggesting that PA-PSt could not adsorb SO_3^{2-} . On the contrary, when EDA-PSt was used as adsorbent, SO_3^{2-} was completely removed and no sulfite was detected in the effluent.

Interactions Involved in Adsorption. According to the reported research, carboxyl and amido can interact with nitril through hydrogen bond. Hence, both PA-PSt and EDA-PSt were expected to remove all the NACs from distillate of TNT red water. The results indicated that the neutral NACs were adsorbed by PA-PSt, leaving the acid 2,4-DNP, which gave out H^+ and charged negative, remained in the effluent. The interaction between PA-PSt and neutral nitro aromatic compounds is schematically shown in Figure 4(a), taking 2,4-DNT as an example. The carboxyl on PA-PSt can dissociate into $-\text{COO}^-$ and H^+ in aqueous environment, which can be written as:



Therefore, although the nitril of 2,4-DNP can form hydrogen bond with the carboxyl of PA-PSt, the electrostatic repulsion between $-\text{COO}^-$ and 2,4-DNP prevented the adsorption [Figure 4(b)]. With more and more $-\text{COO}^-$ occupied by NACs during the adsorption, $-\text{COO}^-$ will associate more H^+ to keep the equilibrium of eq. (1), which can explain the raise of pH value. When EDA-PSt was used in adsorption, the neutral NACs were adsorbed through hydrogen bond between the nitril of NACs and imino group of EDA-PSt [Figure 4(c)]. For 2,4-DNP, besides hydrogen bond interaction, electrostatic attraction played an important role

in adsorption. Imino group can associate with H^+ and charged positive, which is presented as follow.



Hence, EDA-PSt can act as an anion exchange resin. The interaction between 2,4-DNP and EDA-PSt is shown in Figure 4(d).

Similar to 2,4-DNP, the anion SO_3^{2-} was repulsed by PA-PSt and adsorbed by EDA-PSt through electrostatic attraction.

Adsorption Kinetics and Equilibrium

COD removal ratio was calculated to investigate the adsorption kinetics of EDA-PSt and PA-PSt toward the compounds in the distillate of TNT red water (Figure 5). It can be seen that the adsorbents exhibited high adsorption rate, especially in the initial 10 min, which might be attributed to the large pore size of the adsorbents. The pore size of PSt was 150 nm, which improved the diffusion of the compounds into the pores of adsorbents. The adsorption equilibrium was reached in 150 min.

Breakthrough Curves

Distillate of TNT red water was continuously pumped into the glass column containing 5.0 g of suction-dried adsorbents. COD versus volume was adopted to describe the breakthrough curves of the two adsorbents for distillate of TNT red water. The results are shown in Figure 6. PA-PSt has a stepwise breakthrough curve for distillate of TNT red water. Because of the breakthrough of 2,4-DNP and SO_3^{2-} , COD of the effluent rose fast in the first 40 cm^3 to 37.8 mg L^{-1} , and then remained stable and the effluent kept colorless until the volume reached to 1400 cm^3 . The breakthrough curve of EDA-PSt is also stepwise and COD remained even at about 14.7 mg L^{-1} within the volume range from 200 to 1600 cm^3 . It seemed that there were some uncertain substances that could not be adsorbed by EDA-PSt in the distillate of TNT red water. However, these low-concentration substances were and exhibited no toxicity to the microorganism tested.

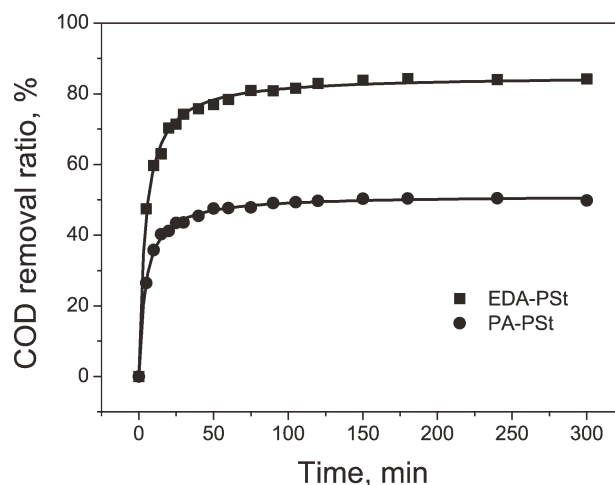


Figure 5. Adsorption kinetics curves of the adsorbents toward compounds in distillate of TNT red water. Temperature: 25°C ; amount of suction-dried adsorbents: 5 g; volume of distillate of TNT red water: 1600 mL.

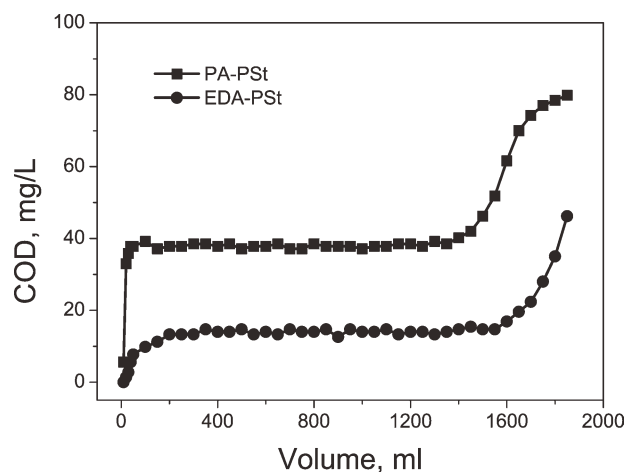


Figure 6. Breakthrough curves of PA-PSt and EDA-PSt for distillate of TNT red water.

Recycle and Repeated Use of the Adsorbents

The adsorbed compounds were eluted by 20 cm³ of methanol and 0.1 mol L⁻¹ NaOH, and the recoveries were calculated according to the concentrations determined by HPLC (for NACs) and titration (for SO₃²⁻). The results were shown in Table II. For PA-PSt, all the adsorbed NACs could be desorbed by methanol, and the recovery was higher than 90%. By using 0.1 mol L⁻¹ NaOH, only 55–71% of NACs were recovered. For EDA-PSt, the neutral NACs could be desorbed by methanol whereas could not be desorbed by 0.1 mol L⁻¹ NaOH. The situation was exactly opposite for elution of 2,4-DNP and SO₃²⁻ which could desorbed by 0.1 mol L⁻¹ NaOH.

The repeated use of adsorbents is a key factor in industry application. Therefore, the dynamic adsorption–desorption circle was repeated for five times to study the reusability of the adsorbents toward distillate of TNT red water. As shown in Figure 7, when the fresh adsorbent was used in adsorption, the COD removal ratio was 85.8% and 55.4% for EDA-PSt and PA-PSt, respectively. In the following adsorption–desorption cycles, the COD removal ratio declined, and finally became stable after used for four times. The results indicate that the irreversible adsorption exist between the compounds and the adsorbents. However,

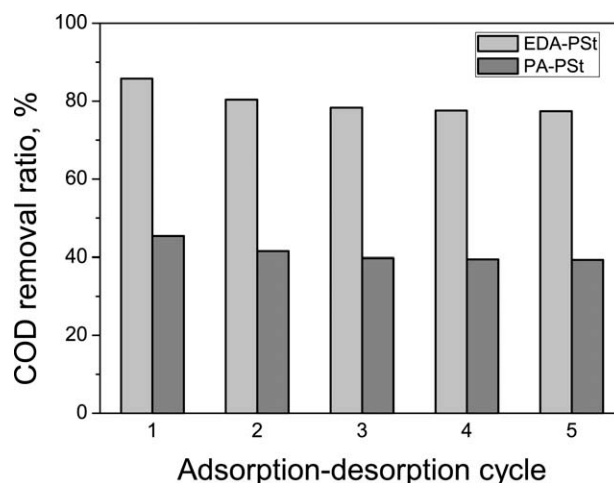


Figure 7. Repeated use of the adsorbents for treatment of distillate of TNT red water.

when the adsorption sites on the adsorbents related to irreversible adsorption were occupied, the adsorption–desorption is reversible.

CONCLUSIONS

Two PSt-based adsorbents were used in deep treatment of acid, toxic, and dark yellow distillate of TNT red water. The results suggested that the carboxylated PSt, namely, PA-PSt could remove the neutral NACs, but not the acid 2,4-DNP and SO₃²⁻ from the distillate of TNT red water. EDA-PSt could adsorb all the NACs and SO₃²⁻ through hydrogen bond and electrostatic attraction. After adsorption using EDA-PSt, COD was reduced from 86.1 to 11.2 mg L⁻¹, and a colorless, transparent, and nontoxic solution with neutral pH value was obtained. Five grams of EDA-PSt could purify 1600 cm³ of distillate of TNT red water, and the adsorbents could be recycled by elution with 20 cm³ of methanol to desorb the neutral NACs followed by elution with 20 cm³ 0.1 mol L⁻¹ NaOH to wash off 2,4-DNP and SO₃²⁻. The treatment process with EDA-PSt concentrated the pollutants for at least 40 times. Both the synthesis and application of the adsorbents are convenient to scale up. Because the adsorbents can be repeatedly used, the cost in industry application will be greatly lowered.

Although PA-PSt could not remove all the NACs form distillate of TNT red water, it exhibit a potential application in adsorption of neutral NACs, which can be applied to separate acid NACs like 2,4-DNP from neutral NACs.

Table II. Recovery of the Compounds from PA-PSt and EDA-PSt

Compounds	$R_{\text{PA-PSt}}^{\text{a}}$ (%)		$R_{\text{EDA-PSt}}^{\text{b}}$ (%)	
	Methanol	NaOH (0.1 mol L ⁻¹)	Methanol	NaOH (0.1 mol L ⁻¹)
1,3,5-TNB	92.3	55.4	94.7	0
2,4,6-TNT	91.5	59.5	95.3	0
2,4-DNT	93.6	67.2	96.5	0
2,6-DNT	90.5	70.7	92.8	0
2,4-DNP	-	-	4.6	85.2
SO ₃ ²⁻	-	-	0	89.3

^aRecovery of compounds eluted from PA-PSt column.

^bRecovery of compounds eluted from EDA-PSt column.

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