



Research Article

Adsorption of 2,4,6-trinitrotoluene on a novel adsorption material PEI/SiO₂

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ABSTRACT

In this paper, functional macromolecule polyethyleneimine (PEI) was grafted onto the surface of silica gel particles in order to produce the novel adsorption material, PEI/SiO₂. Then this novel material's adsorption properties for TNT were investigated through static methods, and the experimental results showed that PEI/SiO₂ possessed strong adsorption ability for TNT. In fact, the saturated adsorption amount could reach 14.47 mg g⁻¹. The empirical Freundlich isotherm was also found to describe well the equilibrium adsorption data. In addition, the pH and temperature were found to have great influence on the adsorption amount. Finally, PEI/SiO₂ was observed to possess excellent reusability properties as well.

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1. Introduction

The 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. Due to its toxic and mutagenic effects on 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, such as activated carbon [1–4], degradation with various microorganisms [5–7], destruction through catalytic, as well as advanced oxidation employing UV and hydrogen peroxide [8–12] have been studied extensively. However, some problems have been identified, such as lower adsorption capacity and high costs, to name a few.

Meanwhile, polyethyleneimine (PEI) is a kind of water-soluble polyamine possessing a great number of nitrogen atoms of amino groups on its macromolecular chains. As such, an extremely strong hydrogen bond interaction can be produced between PEI and TNT. In this study, PEI macromolecules were bound covalently onto the surface of silica gel particles by coupling grafting in order to produce PEI/SiO₂. This material displayed excellent adsorption property for TNT as its adsorption capacity reached up to 14.47 mg g⁻¹.

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 m² g⁻¹, Qingdao, China). Polyethyleneimine was purchased from the Qianglong Chemical Company, Ltd. (Wuhan, China, AR grade), while γ-chloropropyl trimethoxysilane was purchased from the Yongchang Chemical Company, Ltd. (Naking, China, AR grade). The TNT was obtained from the Chemical Engineering Department of the North University of China. All other chemicals were purchased from the Beijing Chemical Plant (AR grade).

The instruments used in this study included the following: 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, Shanghai, China). 438VP scanning electron microscope (LEO Company, England).

2.2. Absorption spectroscopy of the mixed PEI and TNT solutions

In this study, 100 mg of TNT was transferred into a 1000 mL measuring flask, and diluted with distilled water up to the index mark to obtain the TNT solution with a concentration of 100 mg L⁻¹. Next, another 100 mg of TNT was transferred into a 1000 mL measuring flask, and was diluted with PEI aqueous solution up to the index mark in order to obtain the TNT–PEI mixed solution. The adsorption spectra of these mixtures were determined in the wavelength range of 200–500 nm.

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2.3. Preparation of adsorbent PEI/SiO₂

The adsorption material, PEI/SiO₂, was prepared and characterized according to the process described in a previous study [13]. The typical procedures were as follows: First, silica gel particles were treated by activating the aqueous solution of methane sulfonic acid as activation reagent; Second, the activated silica gel was reacted with γ -chloropropyl trimethoxysilane (CP) at 80 °C, using xylene as solvent into which a little water was added in order to obtain chloropropylation silica (CP-SiO₂); This was then added into the PEI aqueous solution with a certain level of concentration and a reaction was observed at 90 °C for 6 h; Afterwards, PEI was grafted onto the silica gel surface through coupling. The novel adsorption particles of PEI/SiO₂ were finally produced.

2.4. Adsorption of TNT on PEI/SiO₂

2.4.1. Measurement of the kinetic adsorption curve

Approximately 0.25 g of PEI/SiO₂ was 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 was added. The conical flask was placed in a shaker at a presettled temperature and pH and was then shaken. At different times, the concentration (C_t) of the TNT solution was determined. The adsorption amount (Q) was calculated according to the following equation:

$$Q = V(C_0 - C_t)/m \quad (1)$$

where Q (mg g⁻¹) is the adsorption amount, V (L) is the volume of the phenol solution, and m (g) is the weight of the adsorbent PEI/SiO₂.

2.4.2. Measurement of the adsorption isotherm

Next, another 0.25 g of PEI/SiO₂ was directly introduced into a number of conical flasks, into which 50 ml of the aqueous TNT solution with concentrations (C_0) of 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 were then shaken. After reaching the adsorption equilibrium, the concentrations (C_e) of the TNT solutions were determined. The equilibrium adsorption amount (Q_e) was then calculated according to the equation:

$$Q_e = V(C_0 - C_e)/m. \quad (2)$$

2.4.3. Examination of the influences of various factors on the adsorption property of PEI/SiO₂

By varying the pH of each sample solution through buffer solutions (NH₄NO₃-NH₃·H₂O and NaAc-HAc), its influence on the adsorption property of PEI/SiO₂ was examined. Meanwhile, by varying the temperature of each sample solution, the influence of

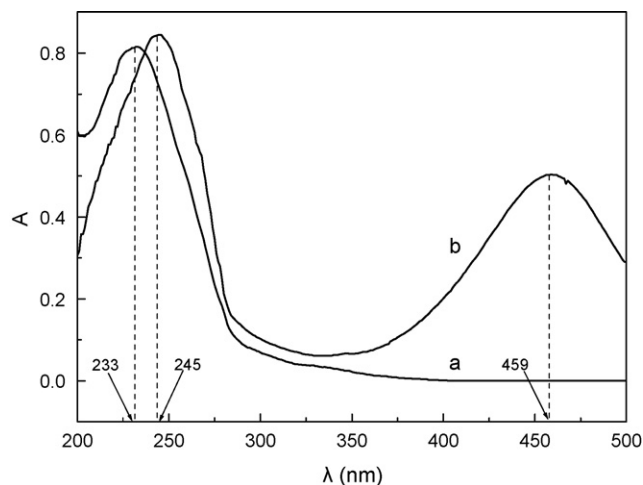


Fig. 1. Absorption spectroscopy. (a) TNT under distilled water as standard and (b) mixture of TNT and PEI under PEI solution as standard.

temperature on the adsorption property of PEI/SiO₂ was also examined.

2.5. Repeated use experiment

Repeated usability (i.e., regenerability) is an important factor for an effective absorption material. As such, the desorption of the adsorbed TNT from the PEI/SiO₂ was also studied by static experiment. As observed, the adsorbed TNT was desorbed using the mixture solution of HCl and ethanol with a pH of 2 as an eluting agent. The PEI/SiO₂ that adsorbed TNT was placed in the eluent and stirred continuously at room temperature for 10 h. The final concentration of TNT in the aqueous phase was determined. The desorption ratio was calculated from the amount of TNT adsorbed on the PEI/SiO₂ and from the final TNT concentration in the eluent. In order to test the reusability of PEI/SiO₂, the adsorption–desorption procedure was repeated 10 times using the same material.

3. Results and discussion

3.1. Interaction between PEI and TNT

Fig. 1 shows the absorption spectroscopy of TNT and its mixture with PEI: curve *a* represents the absorption spectroscopy of the aqueous TNT solution, while curve *b* represents the absorption spectroscopy of the mixed TNT and PEI solution. The characteristic adsorption peak of the mixture is 245 nm, while that of TNT is 233 nm. Moreover, there appears a new adsorption peak at 459 nm in the absorption spectroscopy of the mixture. This indicates that an

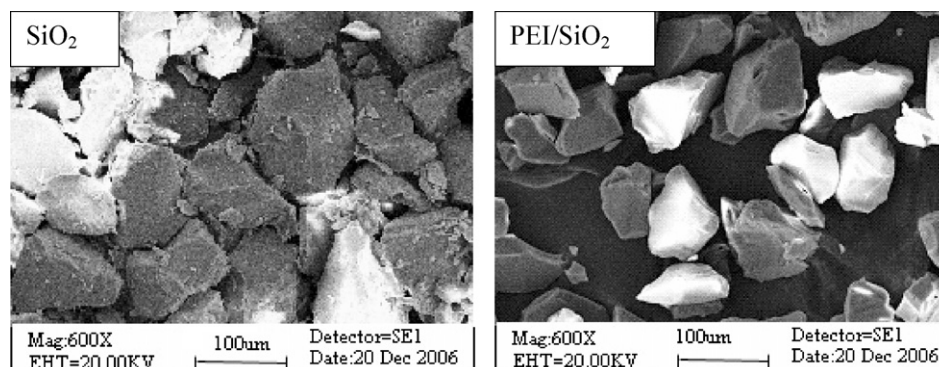


Fig. 2. The SEM of SiO₂ and PEI/SiO₂.

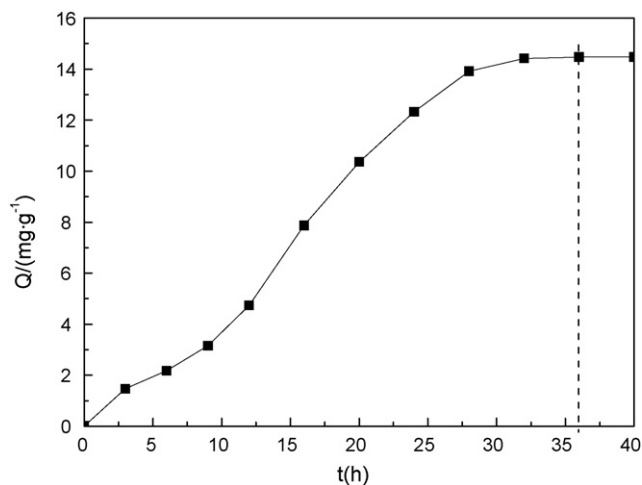


Fig. 3. Kinetic adsorption curve of PEI/SiO₂ for TNT. Temperature: 40 °C; pH 6; initial concentration of TNT: 100 mg L⁻¹.

interaction between the TNT and PEI occurred, and that this reaction had taken place under the base condition of PEI, in which a new colored medial production had been produced.

Generally, 2,4,6-trinitrotoluene and other nitro compounds, such as 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, picric acid, and tetryl, are known to form CT (charge-transfer) complexes with amines, hydrocarbons, drugs, and alkaloids [14,15]. The charge density of the donor and the acceptors are responsible for the formation of CT complexes. Due to the strong electron affinity of -NO₂ groups, the 2, 4, and 6 positions of TNT should be electron deficient, and the N atoms with a lone pair of electrons in amines are expected to donate electrons to form $n \rightarrow \pi$ charge transfer complexes, resulting in its absorption in the long wavelength region.

3.2. Kinetic adsorption curve of TNT on PEI/SiO₂

Fig. 2 is the SEM of SiO₂ and PEI/SiO₂. It can be seen that the surface of PEI/SiO₂ is smoother than that of SiO₂. This implied that PEI was grafted onto the silica gel surface.

The kinetic adsorption curve is shown in Fig. 3. The adsorption of TNT by PEI/SiO₂ reached equilibrium at 36 h, and the saturated adsorption amount reached 14.47 mg g⁻¹. This suggests that PEI/SiO₂ possesses strong adsorption ability for TNT.

3.3. Adsorption isotherm of PEI/SiO₂ for TNT

The adsorption isotherm of PEI/SiO₂ for TNT is shown in Fig. 4. It can be seen that the equilibrium adsorption amount of TNT increases rapidly along with the increase of equilibrium concentration. This high affinity can be attributed to the hydrogen bond interaction between PEI and TNT. It can be also seen that the adsorption isotherm contains two stages. This indicates that the adsorption is either a double-molecular layer or a combination of two monomolecular layers.

The Freundlich adsorption equation and its logarithm forms are

$$Q_e = kC_e^n \quad (3)$$

$$\ln Q_e = \ln k + n \ln C_e \quad (4)$$

The data in Fig. 4 are treated using the Freundlich adsorption equation, and the straight lines at two different stages are displayed in Fig. 5. Linear regression was performed according to the logarithmic form, and the linear regression coefficients for each were 0.9993 and 0.9901, respectively. From the figure, we can see that the curve of the $\ln Q_e$ vs. $\ln C_e$ satisfactorily fits the Freundlich equation.

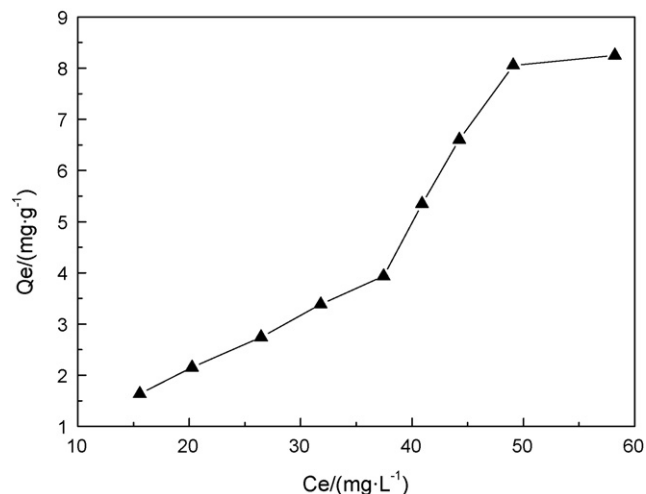


Fig. 4. Adsorption isotherms of PEI/SiO₂ for TNT. Temperature: 40 °C; pH 6; adsorption time: 36 h.

3.4. Influences of different factors on the adsorption property of PEI/SiO₂

3.4.1. Influence of pH

The adsorption isotherms at different pH values are shown in Fig. 6. The effect of pH value on the adsorption property of PEI/SiO₂ can be seen clearly from Fig. 7, which comes from the data shown in Fig. 6. Obviously, the pH value has a great influence on the adsorption ability of PEI/SiO₂ 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.

Meanwhile, the adsorption property is different at different pH values. This is caused by different molecular forms of PEI and TNT, as well as by the different acting forces between them. In an acidic solution, the N atoms in the PEI chains interact with TNT at a molecular state via hydrogen bond interaction. However, in an acidic solution, 70% of the N atoms in PEI chains are protonated. Hence, the hydrogen bond interaction between PEI on the PEI/SiO₂ surface and TNT is weaker, resulting to a smaller adsorption capacity. In a basic solution, only 32% the N atoms in the PEI chains are protonated, but the electronegative property of O atoms on TNT is lower; thus the hydrogen bond interaction is also very weak, again resulting in lower adsorption capacity. Finally, in a neutral solution, the protonation degree of the N atoms in the PEI chains is about 64%.

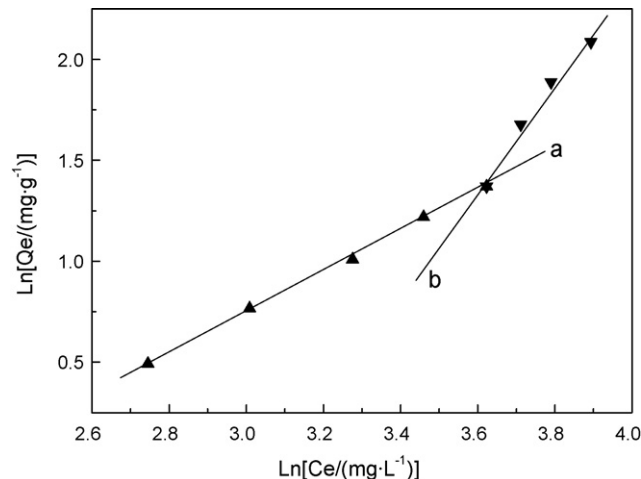


Fig. 5. Plot of $\ln Q_e$ vs. $\ln C_e$. (a) the first stage and (b) the second stage.

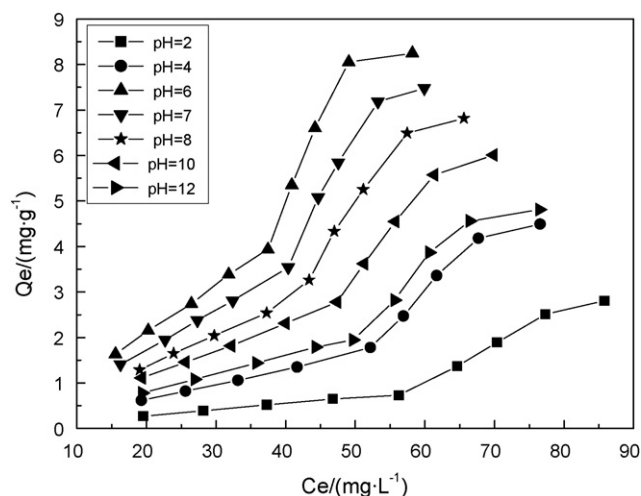


Fig. 6. Adsorption isotherms of PEI/SiO₂ for TNT at different pH. Temperature: 40 °C; adsorption time: 36 h.

This leads to a stronger hydrogen bond interaction between PEI and TNT and a larger adsorption capacity.

3.4.2. Influences of temperature

The adsorption isotherms at different temperatures are shown in Fig. 8. It can be observed that the adsorption capacity of PEI/SiO₂ for TNT increases along with a corresponding increase in temperature. This suggests the great influence of temperature on the adsorption property. The saturated adsorption amount at 333 K is 9.0 mg g⁻¹, which is considered far greater than the 7.1 mg g⁻¹ of the saturated adsorption amount at 293 K. In addition, the fact that the adsorption amount of TNT increases with the increase in temperature implies that the adsorption of PEI/SiO₂ for TNT is an endothermic process.

3.5. Reusability

When the mixture solution of HCl and ethanol with a pH value of 2 was used as an eluent, the hydrogen bond interaction between TNT and PEI was disrupted and subsequently, TNT was released into the eluent. In order to show the reusability of the PEI/SiO₂, the adsorption–desorption cycle was repeated 10 times using the same material.

The adsorption–desorption cycle of PEI/SiO₂ is shown in Fig. 9. The results clearly show that the PEI/SiO₂ could be used repeatedly without significantly losing its adsorption capacity.

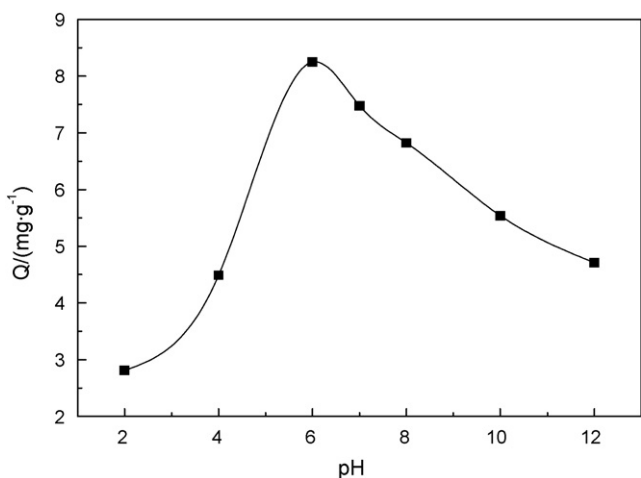


Fig. 7. Varying of adsorption capacity of PEI/SiO₂ with pH values.

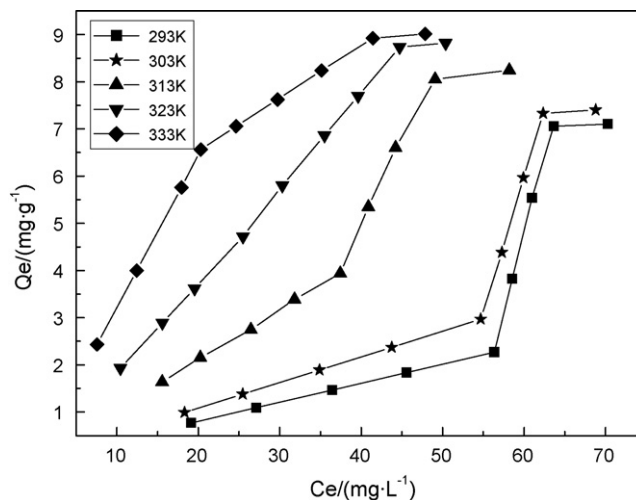


Fig. 8. Adsorption isotherms of PEI/SiO₂ for TNT at different temperatures. Adsorption time: 36 h; pH 6.

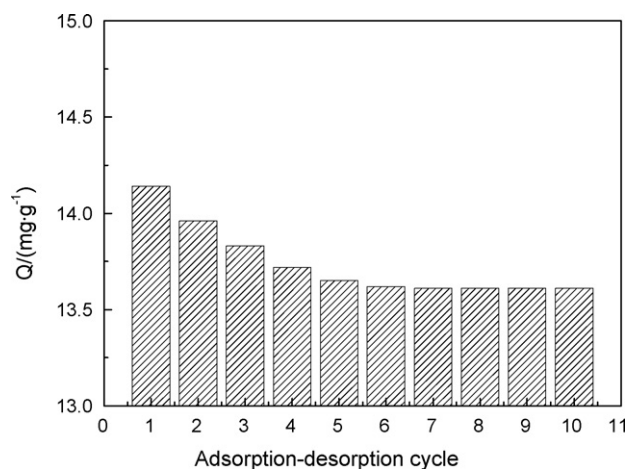


Fig. 9. Adsorption–desorption cycle of PEI/SiO₂.

4. Conclusions

In this study, functional macromolecule polyethyleneimine was grafted onto a micron-sized silica gel by coupling grafting in order to successfully prepare the novel adsorption material, PEI/SiO₂, which was found to have very strong adsorption ability for TNT by way of hydrogen bond interaction. However, the adsorption ability of PEI/SiO₂ for TNT is largely dependent on the pH value of the solution. Based on the results, the strongest adsorption capacity was found in the solution with pH of 6 as compared with the acidic and basic solutions. Moreover, it was found that the adsorption capacity of TNT increases with the temperature, such that the higher the temperature, the higher the adsorption capacity. Finally, PEI/SiO₂ was also found to possess excellent reusability properties. Indeed, this study shows that the processes described above signify a clear potential for future preparation of grafting functional polymer onto inorganic particles, toward the production of effective adsorption materials to be used in water treatment.

References

- [1] R. Lebeda, 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.

- [2] 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.
- [3] V. Marinović, M. Ristić, M. Dostanić, Dynamic adsorption of trinitrotoluene on granular activated carbon, *J. Hazard. Mater.* B117 (2005) 121–128.
- [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] 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.
- [6] S.G. Pavlostathis, G.H. Jackson, Biotransformation of 2,4,6-trinitrotoluene in a continuous-flow anaerobic system, *Water Res.* 36 (2002) 1699–1706.
- [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] R. Alnaizy, A. Akgerman, Oxidative treatment of high explosives contaminated wastewater, *Water Res.* 33 (1999) 2021–2030.
- [9] 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.
- [10] S. Hyun-Seok, L. So-Jin, C. Il-Hyoung, Z. Kyung-Duk, Kinetics and mechanism of TNT degradation in TiO₂ photocatalysis, *Chemosphere* 57 (2004) 309–317.
- [11] D.R. Felt, S.L. Larson, E.J. Valente, UV–VIS spectroscopy of 2,4,6-trinitrotoluene-hydroxide reaction, *Chemosphere* 49 (2002) 287–295.
- [12] C.K. Scheck, F.H. Frimmel, Degradation of phenol and salicylic acid by ultraviolet radiation/hydrogen peroxide/oxygen, *Water Res.* 29 (1995) 2346–2352.
- [13] F.Q. An, B.J. Gao, Q. Liu, Studies on adsorption properties of composite and chelating adsorption material of PEI/SiO₂ for Zn²⁺ and Cd²⁺ ions, *Chem. Bull.* 69 (2006) 201–205.
- [14] M. Gouterman, P.E. Steverson, Porphyrin charge–transfer complexes with sym-trinitrobenzene, *J. Chem. Phys.* 37 (1962) 2266–2273.
- [15] P.K.C. Pillai, R.C. Ahuja, Persistent internal polarization studies in poly(*N*-vinylcarbazole)/trinitrofluorenone charge transfer complex, *Polymer* 17 (1976) 192–194.