Vacuum 95 (2013) 71–75

Contents lists available at SciVerse ScienceDirect

Vacuum

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

Reduction of COD in TNT red water through adsorption on macroporous polystyrene resin RS 50B

Quanlin Zhao [a], Yuchen Gao [a,b], Zhengfang Ye [a,*]

[a] Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China
[b] China Astronaut Research and Training Center, Beijing 100094, China

ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form
25 February 2013
Accepted 28 February 2013

Keywords:
Macroporous resin
TNT red water
COD
Adsorption

ABSTRACT

2,4,6-trinitrotoluene (TNT) is an important single compound explosive. During the purification stage of TNT production, a great amount of wastewater called red water is generated, which has an intense red color with high amount of chemical oxygen demand (COD). In this paper, macroporous polystyrene resin RS 50B was used to reduce COD in TNT red water. The effect of resin dosage, initial COD and temperature on COD removal was studied. The results showed that COD removal increased with increasing resin dosage and temperature. When the resin dosage was 120 g L^{-1}, 92.49% COD can be removed after 8 h of adsorption at 30 °C. The adsorption of COD on resin was coincident with Langmuir isotherm. The change in Gibbs free energy ΔG was −4.843, −5.468 and −5.833 kJ mol^{-1}, respectively, when the temperature was 30, 40 and 50 °C, indicating that the adsorption was spontaneous. The intraparticle diffusion of COD onto resin was identified to be the rate limiting step. Macroporous polystyrene resin RS 50B could be a potential adsorbent for treatment of TNT red water.

1. Introduction

2,4,6-trinitrotoluene (TNT) is an important single compound explosive widely used in many fields [1–5]. During its production, load, assemble and pack operations, large amount of wastewater with high chemical oxygen demand (COD) is produced, which can cause severe environmental pollution and do harm to peoples' health if it is discharged without effective treatment. So it is important to dispose TNT wastewater effectively before its discharge to environment.

According to its characteristic color, TNT wastewater can be classified as yellow water, red water and pink water. Barreto-Rodrigues et al. [6,7] evaluated a continual system treatment reactor (CSTR) consisting of column zero-valent iron and a system to promote a Fenton reaction for treating TNT yellow water. They optimized the treatment process and found that the most efficient condition for reducing the concentration of TNT generated sufficient amounts of iron (II) for the subsequent oxidative treatment through the Fenton reaction. It can remove 100% of TNT, 100% of the organic nitrogen and 95% of the COD, which was suggested that the treatment was highly efficient in terms of meeting the main associated environmental parameters. Maloney et al. [8] studied anaerobic treatment of pink water in a fluidized bed reactor containing granular activated carbon. They found that the main components, TNT and cyclo trimethylene trinitramine (RDX), can be effectively treated by anaerobic bacteria. TNT was transformed to triaminotoluene (TAT) and then degraded to undetectable end products. RDX was sequentially degraded to nitroso-, dinitroso-, trinitroso- and hydroxylaminodinitroso-RDX before the triazine ring was cleaved. The major end products were methanol and formaldehyde.

Red water is produced from purification stage of TNT production, which has an intense red color with high amount of COD. The main organic pollutants are dinitrotoluene sulfonates (DNTS), TNT, dinitrotoluene (DNT), monotoluene (MNT) and other nitrobenzene derivatives. It can be treated by chemical method such as wet air oxidation [9] and reduction [10]. However, the high cost and inconvenient operation hinders its large-scale application. Due to the high efficiency, low cost and operation convenience, adsorption method is widely used to treat wastewater, where granular activated carbon [11], resin [12,13] and silica [14] are often used as adsorbent. In our previous paper [15], we evaluated the acute toxicity of explosive wastewater by bacterial bioluminescence assays and found that macroporous polystyrene resin could reduce its acute toxicity obviously. The aim of the present work was to further study the feasibility of adsorption resin for COD removal from TNT red water. The effect of temperature, initial COD and resin dosage

---

[*] Corresponding author. Tel.: +86 10 62755914; fax: +86 10 62756526.
E-mail addresses: zhengfangye@163.com, yezhengfangiee@163.com (Z. Ye).

0042-207X/$ – see front matter
http://dx.doi.org/10.1016/j.vacuum.2013.02.016

on COD removal was studied. In addition, the adsorption kinetics and thermodynamics were also investigated.

2. Materials and methods

2.1. Materials

Red water was obtained from Dongfang Chemical Corporation, Hubei Province, China. It has an intense red color with the density of 1.101 g mL^{-1}. Since the composition of red water is complex with high amount of COD, it is diluted 10 times with de-ionized water before treatment. The COD removal R% was used to evaluate the adsorption efficiency, which can be calculated by the equation:

$$R\% = \frac{COD_0 - COD_t}{COD_0} \times 100 \quad (1)$$

where COD_t represents COD of red water at contact time t and COD_0 represents the initial COD of red water.

The polystyrene-based adsorption resin RS 50B used in our study was kindly provided by Xian Putian Biological Technology Co., Ltd. (Shanxi, China). The spherical particle size was in the range of 0.315–1.25 mm, with the specific surface area of 600 $m^2\ g^{-1}$.

2.2. Static adsorption test

The static adsorption test was used to investigate the influence of resin dosage, initial COD and temperature on COD removal. The pre-weighed amount of resin (1.0 g) was put into a 250 mL flask containing 50 mL red water samples. The flasks were sealed and shaken at different temperatures in a constant temperature oscillator (Taicang Laboratory Equipment Factory, Jiangsu Province, China). After the adsorption system reached equilibrium, the solution was withdrawn and filtered and then the COD was determined. The following equation was used to calculate the adsorption capacity of adsorption resin.

$$q_e = \frac{(COD_0 - COD_e)V}{W} \quad (2)$$

where q_e represents the adsorption capacity of adsorption resin at adsorption equilibrium, COD_0 and COD_e represent the initial and equilibrium COD of red water, respectively. W represents the mass of the resin and V represents the volume of red water solution.

2.3. Adsorption kinetics

For the adsorption kinetics test, 1.0 g adsorption resin was added to a stoppered flask containing 50 mL red water. At different time intervals, certain amount of solution was withdrawn and centrifugated for 10 min at 10,000 rpm. Then the COD of the supernatant was determined.

2.4. Adsorption isotherm

For the adsorption isotherm determination, 50 mL red water solution with different initial COD was added to 6 flasks, each of which containing 1.0 g resin. After the adsorption equilibrium had been achieved, the solution was withdrawn and filtered, and then the COD was determined.

2.5. Water quality detection

The water quality was detected by determining COD according to Chinese standard GB 11914-89. The chrominance was determined by dilution method until the water sample became colorless according to Chinese standard GB 11903-89. The concentrations of 2,4-dinitrotoluene-3-sulfonate (2,4-DNT-3-SO_3^-) and 2,4-dinitrotoluene-5-sulfonate (2,4-DNT-5-SO_3^-) in red water before and after adsorption were determined by HPLC [16].

2.6. UV–vis analysis

The UV–vis absorption of red water samples before and after adsorption was determined by using a UV1800 spectrophotometer (Shimadzu, Japan). The instrument uses a deuterium lamp and has a wavelength range of 190–1100 nm, with an accuracy of ±1 nm. A 1-cm quartz cell was used.

2.7. FTIR analysis

The chemical changes of resin before and after adsorption were monitored by Fourier Transform Infrared (FTIR) spectroscopy analysis using a Spectrum GX spectrometer (Perkin Elmer, England) with 16 scans and a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Effect of resin dosage on COD removal

Fig. 1 presents the effect of resin dosage on COD removal. It can be seen that with increasing resin dosage, COD removal increased quickly and then leveled off. When the resin dosage increased from 0 to 80 g L^{-1}, the removal efficiency of COD increased from 0 to 90%. When the dosage increased from 80 to 200 g L^{-1}, the COD removal changed a little, ranging from 90% to 94%. This is because adsorption site increases with increasing resin dosage. When the resin dosage is higher than 80 g L^{-1}, almost all organic components can be adsorbed, hence COD removal increased slowly.

3.2. Effect of initial COD and temperature on COD removal

Fig. 2 illustrates the effect of initial COD and temperature on COD removal. It can be observed that COD removal decreased with increasing initial COD. When the initial COD increased from 961 to 9610 mg L^{-1} at 30 °C, COD removal dropped from 89.51% to 38.81%. It can also be noted that COD removal increased with increasing temperature. At the initial COD of 3844 mg L^{-1}, when the temperature changed from 30 °C to 50 °C, the COD removal increased

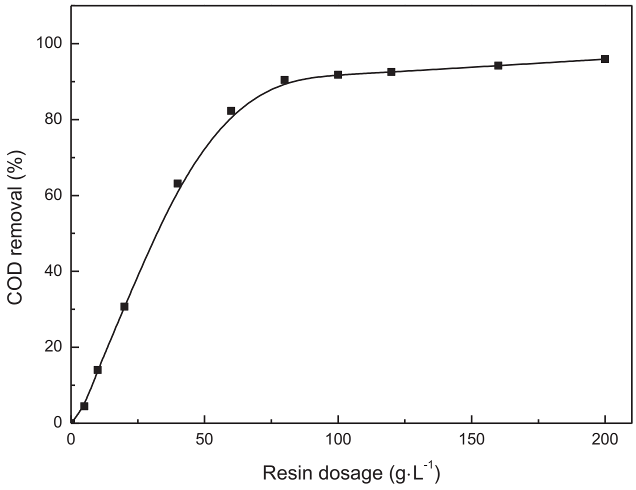

Fig. 1. Effect of resin dosage on COD removal.