Treatment of soil eluate containing nitro aromatic compounds by adsorption on activated coke (AC)

Yiping Zhang, Zhenming Jiang, Quanlin Zhao, Zhenzhong Zhang, Hongping Su, Xuewen Gao and Zhengfang Ye

ABSTRACT

Soil washing is a kind of physical method to remove organic matters from contaminated soil. However, its eluate after washing may result in secondary pollution to the environment. In this study, activated coke (AC) was used to remove organic pollutants from contaminated soil eluate. The effect of temperature, initial chemical oxygen demand (COD) and AC dosage on COD removal efficiency was investigated. The results showed that the organic matter can be removed in the eluate because the COD dropped a lot. When the AC dosage was 20 g·L⁻¹, 88.92% of COD decreased after 480 min of adsorption at 50°C. The process of adsorption can be described by the Redlich–Peterson isotherm. The adsorption was spontaneous and endothermic. The pseudo-second-order model can be used to describe the adsorption process. After adsorption, the acute toxicity of the eluate was reduced by 76%, and the water qualities were in agreement with Chinese discharge standard GB 14470.1-2002, which means the eluate could be discharged to the environment.

INTRODUCTION

2,4,6-Trinitrotoluene (TNT) is a kind of nitro aromatic compound, which can be used as a high explosive in many fields (Seok-Young Oh 2015). During its production and usage, large amounts of wastewater containing TNT and its transformation products are produced, which may infiltrate and contaminate the soils near the military sites (Via et al. 2014). The contaminated soils are toxic to plants and crops, and do harm to local residents (Lamichhane et al. 2012; Ungradova et al. 2013). Hence, it is important to remediate the contaminated soils effectively.

Soil washing is a kind of physical method that can remove heavy metals (Ye et al. 2015) and organic matters (Dadrasnia & Agamuthu 2013) effectively and conveniently from contaminated soil. However, the eluate remaining after washing results in secondary pollution to the environment and so should be further treated before its discharge. Adsorption is an efficient method to remove pollutants from wastewater, where activated carbon (Nie et al. 1998; Marinovic et al. 2005; Boddu et al. 2009), resin (Sklari et al. 2012; Ceglowski & Schroeder 2015; Du et al. 2015; Zglik before used as adsorbents. However, the high cost of adsorbents hinders the application of the adsorption method. A cheap and effective adsorbent is a prerequisite for its practical application.

Activated coke (AC) is a kind of substitute material for activated carbon, which is produced from naturally occurring carbonaceous materials like wood, lignite and petroleum coke (Tong et al. 2014) and is often used to treat gas purification because of its low cost and high adsorption capacity (Li et al. 2008; Wang et al. 2009; Ogriseck & Galindo Vanegas 2010; Sun et al. 2011; Jastrzab 2012; Schmauss & Keppler 2014; Wang et al. 2014). In our previous study, it was used to treat coking wastewater (Zhang et al. 2010) and red water (Zhang et al. 2011). To our knowledge, there are still few reports focused on treatment of contaminated soil eluate by AC. The objective of the present work was to investigate the feasibility of AC to remove organic pollutants from contaminated soil containing nitro aromatic compounds. The effect of temperature, initial chemical oxygen demand (COD), and AC dosage on COD removal efficiency was studied. In addition, the adsorption kinetics and thermodynamics were investigated.

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MATERIALS AND METHODS

Materials

The soil contaminated with explosives was provided by Gansu Yinguang Chemical Industry Group Co., Ltd. The soil eluate was obtained under the conditions of 1:1 water/soil ratio. It has an intense red color with a density of 0.99 g·mL⁻¹. Since its composition is complex with a high amount of COD, it was diluted 10 times with de-ionized water before treatment. The COD removal efficiency (R%) was used to evaluate the adsorption efficiency, which can be calculated by the equation:

\[ R\% = \left( \frac{COD_0 - COD_e}{COD_0} \right) \times 100 \]  

where \( COD_0 \) represents COD of eluate at contact time \( t \) and \( COD_e \) represents the initial COD of eluate.

AC was obtained from Datang Yima coke plant (Yima Coal Industry Group, Henan, China). The particle range was 0.45–0.90 mm, with a specific surface area of 408 m²·g⁻¹. The luminescent bacterium Vibrio qinghaiensis sp. nov. was provided by Beijing Hamamatsu Photon Techniques Inc., China.

Static adsorption test

The static adsorption test was used to study the effect of AC dosage, initial COD, and temperature on COD removal efficiency. The following equation was used to calculate the adsorption capacity of AC:

\[ q_e = \frac{(COD_0 - COD_e)V}{W} \]  

where \( q_e \) (mg·g⁻¹) is the adsorption capacity of AC at adsorption equilibrium, and \( COD_0 \) (mg·L⁻¹) and \( COD_e \) (mg·L⁻¹) are the initial and equilibrium COD of eluate, respectively. \( W \) (g) is the mass of AC and \( V \) (L) is the volume of eluate solution.

In the study of the effect of AC dosage on COD removal efficiency, weighed amounts of AC (0.5, 1, 2, 4, 6, 8, 10 g) were placed in a 100 mL flask containing 50 mL eluate samples with an initial COD of 424.65 mg·L⁻¹. The flasks were sealed and shaken at 50 °C and 200 rpm in a constant temperature oscillator (Taicang Laboratory Equipment Factory, Jiangsu Province, China). After the adsorption system reached equilibrium, 2.5 mL of the solution was withdrawn, and passed through a 0.45 μm membrane filter to test COD.

In the study of the effect of initial COD on COD removal efficiency, a weighed amount of AC (1 g) was placed in six 100 mL flasks containing 50 mL eluate samples in different dilutions. The initial COD was 111.72, 206.98, 293.44, 335.10, 378.75, and 424.65 mg·L⁻¹, respectively. The flasks were sealed and shaken at 50 °C and 200 rpm in a constant temperature oscillator. After the adsorption system reached equilibrium, 2.5 mL of the solution was withdrawn, and passed through a 0.45 μm membrane filter to test COD.

In the study of the effect of temperature on COD removal efficiency, a weighed amount of AC (1 g) was placed in ten 100 mL flasks containing 50 mL eluate samples with an initial COD of 424.65 mg·L⁻¹. The flasks were sealed and shaken at different temperatures (15, 20, 30, 40, 50 °C) in a constant temperature oscillator at 200 rpm. Take out one by one at 5, 10, 15, 30, 45, 60, 120, 180, 300, and 480 min, 2.5 mL of the solution was withdrawn, and passed through a 0.45 μm membrane filter to test COD.

Water quality detection

The water quality was detected according to different national standards. COD was determined by fast digestion of potassium dichromate (Hach heating system, Hach Corporation, USA) under 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 nitro compound content was detected by spectrophotometry (Shimadzu, UV-1800) according to Chinese standard GB 4819-1985. The acute toxicity of the eluate was determined by luminescent bacteria test (Zhao et al. 2013).

RESULTS AND DISCUSSION

Effect of contact time on COD removal efficiency

Figure 1 shows the effect of contact time on COD removal efficiency. The COD removal efficiency increased quickly from 0 to 76.65% in the first 60 min, and then leveled off afterwards. After 480 min, the COD removal remained almost unchanged, meaning that the adsorption process reached equilibrium. The equilibrium adsorption capacity of AC was 16.41 mg·g⁻¹. In the present study, a total contact time of 480 min was chosen to ensure the adsorption process reached equilibrium.
Effect of AC dosage on COD removal efficiency

Figure 2 presents the effect of AC dosage on COD removal efficiency. When AC dosage increased from 10 to 20 g·L⁻¹, COD removal efficiency increased rapidly from 68.91 to 88.92%; then it gradually increased to 95.22% up to an AC dosage of 200 g·L⁻¹. This is because the number of active sites and surface area increase with increasing AC dosage. It can also be noted that the adsorption capacity decreased from 29.3 to 2.0 mg·g⁻¹ when the AC dosage increased from 10 to 200 g·L⁻¹, suggesting that the higher the AC dosage, the lower the amount of AC taking part in the adsorption.

Effect of initial COD and temperature on COD removal efficiency

Figure 3 illustrates the effect of initial COD and temperature on COD removal efficiency. It can be observed that COD removal efficiency decreased with increasing initial COD. When the initial COD increased from 111.8 to 424.6 mg·L⁻¹ at 15 °C, COD removal efficiency dropped from 94.07 to 77.32%. It can also be noted that COD removal efficiency increased with increasing temperature. At the initial COD of 424.6 mg·L⁻¹, when the temperature rose from 15 to 50 °C, the COD removal efficiency increased from 77.3 to 89.4%, suggesting that the adsorption process may be endothermic.

The adsorption kinetics

The pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Bangham models were used to fit the experimental data at different temperatures. The pseudo-first-order model (Bertoni et al. 2015) is expressed as:

$$\frac{dq_1}{dt} = k_1(q_{e1} - q_t)$$  (3)

Its integrated form is:

$$\log(q_{e1} - q_t) = \log q_{e1} - \frac{k_1 t}{2.303}$$  (4)

where $q_{e1}$ (mg·g⁻¹) is adsorption capacity of AC at equilibrium, $q_t$ (mg·g⁻¹) is the amount adsorbed at time $t$ (min), and $k_1$ (min⁻¹) is the rate constant. The parameters $k_1$ and $q_{e1}$ can be obtained from the slope and the intercept of the linear plots.

The pseudo-second-order model (Kuśmirek et al. 2015) is expressed as:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2$$  (5)

Its integrated form is:

$$\frac{t}{q_t} = \frac{1}{k_2q_{e2}} + \frac{1}{q_{e2}}$$  (6)
where \( q_e(\text{mg·g}^{-1}) \) is the adsorption capacity at equilibrium, and \( k_2 \) (g·mg\(^{-1}·\text{min}^{-1}) \) is the pseudo-second-order constant. The parameters \( q_{e2} \) and \( k_2 \) can be obtained from the slope and intercept of the linear plots of \( \ln q_t \) versus \( t \).

The intraparticle diffusion model (Arshadi et al. 2015) is expressed as:

\[
q_t = k_3 t^{0.5} + C
\]  
(7)

where \( k_3 \) (mg·g\(^{-1}·\text{min}^{-0.5}) \) is the particle internal diffusion rate constant. \( C \) (mg·g\(^{-1}) \) is the intercept of the equation, and is related to the thickness of the boundary layer. The higher the value, the bigger the boundary effects.

The linear equation of Bangham (Kaur et al. 2015) is expressed as:

\[
\ln \left( \frac{C_0}{C_0 q_m - q_m} \right) = \ln \frac{k_a m}{V} + a \ln t
\]  
(8)

where \( C_0 \) (mg·L\(^{-1}) \) is the initial COD of the soil eluate, \( m \) (mg·L\(^{-1}) \) is AC dose, \( V \) (mL) is the volume of the solution, \( q_t \) (mg·g\(^{-1}) \) is the amount adsorbed at time \( t \), and \( a \) (<1) and \( k_a \) are constants.

Table 1 lists the fitting results of the above-mentioned models at different temperatures. It can be seen that the correlation coefficient \( R^2 \) for the pseudo-second-order kinetic model is much higher than that for the other three kinetic models in the temperature range of 15–50 °C, and is higher than 0.995, indicating that the second-order kinetic model was more suitable to describe the adsorption process than the other three models. The adsorption capacity at calculated equilibrium \( (q_{e2}) \) shows propinquity with the experimental data \( (q_{exp}) \).

**Equilibrium isotherms**

An adsorption isotherm refers to the relationship of concentration between the two phases at adsorption equilibrium. The Langmuir equation is often used to describe the saturated monomolecular layer adsorption, which can be expressed as (Anisuzzaman et al. 2013):

\[
q_e = \frac{q_m K_a C_e}{1 + K_a C_e}
\]  
(9)

Its linear form is:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{1}{q_m K_a C_e}
\]  
(10)

where \( K_a \) (L·mg\(^{-1}) \) is the adsorption equilibrium constant, \( C_e \) is the COD of eluate at reaction equilibrium and \( q_m \)

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**Table 1: Fitting results of kinetics parameters for the adsorption of COD onto AC**

- **q_e**: adsorption capacity, **m**: AC dose, **V**: volume of solution, **C_e**: COD of eluate at reaction equilibrium, **q_m**: adsorption capacity at equilibrium.
- **k_1**, **k_2**: pseudo-first-order and pseudo-second-order rate constants, respectively.
- **W**: intraparticle diffusion model constant.
- **a**: initial release rate. For temperatures up to 30 °C, the reaction is exothermic and is lower than for temperatures above 30 °C, when the desorption rate is also high.
(mg·g\(^{-1}\)) is the maximum amount of COD adsorbed per unit mass by the AC.

The Freundlich equation (Li et al. 2015) is an empirical formula based on the adsorption between the different surfaces, which can be expressed as:

\[ q_e = K_f C_e^{1/n} \quad (11) \]

Its linear form is:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (12) \]

where \( K_f \) is Freundlich constant and \( n \) is adsorption intensity.

The Redlich–Peterson isotherm (Foo & Hameed 2010) combines the features of Langmuir and Freundlich and can be applied either in homogeneous or heterogeneous systems due to its versatility. It approaches the Freundlich isotherm model at high concentration limit (as the exponent \( g \) tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the \( g \) values are all close to one). The specific form is:

\[ q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (13) \]

The parameters \( K_R \) (L·g\(^{-1}\)) and \( a_R \) (L·mg\(^{-1}\)) are constants and \( g \) \((0 < g < 1)\) is the exponent. Its linear form is:

\[ \ln \left( \frac{K_R C_e}{q_e} - 1 \right) = g \ln (C_e) + \ln (a_R) \quad (14) \]

where \( K_R, a_R, \) and \( g \) can obtained using the tool of origin.

Table 2 lists the fitting results of the three isotherms. It can be observed that the correlation coefficients of the three isotherms are mostly higher than 0.990. The best belong to the Redlich–Peterson isotherm. To compare the difference between theory and experiment, we calculate the \( q_e \) in theory in Table 2 as \( q_{\text{cal1}}, q_{\text{cal2}}, q_{\text{cal3}} \) and present the \( q_e \) in the experiment as \( q_{\text{exp}} \). Obviously, the \( q_{\text{cal3}} \) in the Redlich–Peterson isotherm is very near to \( q_{\text{exp}} \), meaning that the best fit is the Redlich–Peterson isotherm. It can also be noted that \( q_m \) increased with increasing temperature, indicating that the adsorption process may be endothermic.

**Adsorption thermodynamics**

In order to have a better understanding of the effect of temperature on the adsorption process, we calculated the thermodynamics parameters including changes of Gibbs free energy (\( \Delta G \)), enthalpy (\( \Delta H \)), and entropy (\( \Delta S \)) according
to the following equations (Ghiloufi et al. 2013):
\[
\Delta G = -RT \ln K_0
\]
(15)
\[
-RT \ln K_0 = \Delta H - T \Delta S
\]
(16)
where \( R \) is a constant with value of 8.314 J mol\(^{-1}\); \( T \) is temperature and \( K_0 \) is the thermodynamic equilibrium constant, which can be obtained from the intercept of the plots of \( \ln (q_e/C_0) \) versus \( q_e \) (Zhao et al. 2013). \( \Delta H \) and \( \Delta S \) can be calculated from the slope and intercept of the linear plots of \( \Delta G \) versus \( T \).

The Gibbs free energy varies at –12.02, –12.44, –13.19, –14.13 and –15.58 kJ mol\(^{-1}\), while the temperature varies at 15, 20, 30, 40 and 50 °C respectively, indicating that the adsorption process is spontaneous. The higher the temperature, the bigger the \( \Delta G \) absolute value and the easier the reaction (Basu & Suresh Kumar 2015). In general, \( \Delta H < 40 \) kJ mol\(^{-1}\) suggests absorption behaviour belongs to the physical function, and the value is 16.45 kJ mol\(^{-1}\) in our study, indicating that the adsorption is physical. A positive value means the process is endothermic. \( \Delta S \) is 98.40 J mol\(^{-1}\), illustrating the addition of the randomness of the system.

**Water quality analysis**

The change of eluate quality before and after adsorption was evaluated by determining pH, chrominance, COD, and suspended solids (SS). After the eluate had been adsorbed for 480 min at AC dosage of 20 g L\(^{-1}\), the pH value changed from 9 to 8. The chrominance decreased from 50 to 1°. The COD removal was 89.45%, reducing from 424.6 to 44.8 mg L\(^{-1}\). The SS decreased from 75 to 3 mg L\(^{-1}\). The total nitro compounds’ concentration decreased from 85.03 to 8.83 mg L\(^{-1}\). The parameters of the eluate are in agreement with Chinese discharge standard GB 14470.1-2002.

The acute toxicity of the eluate before and after adsorption was also evaluated by luminescence bacteria test. Before and after adsorption, the dilution ratio at 50% luminescence inhibition ratio was 5.00 and 1.20 times, respectively, indicating that the acute toxicity of eluate after adsorption was reduced by 76% after adsorption.

**Figure 4** shows the photographs of eluate sample before and after adsorption (50 °C, 480 min, 20 g L\(^{-1}\) AC dosage). It can be clearly seen that the soil eluate turned from being dark-colored and opaque to colorless and transparent after adsorption.

**CONCLUSIONS**

AC can be used to reduce COD from soil eluate. When the AC dosage was 20 g L\(^{-1}\), 89.45% COD could be removed after 480 min of adsorption at 50 °C. The adsorption of COD on AC can be described by the Redlich–Peterson isotherm. The adsorption was spontaneous and endothermic. The pseudo-second-order model can be used to describe the adsorption process. After adsorption, the acute toxicity of the eluate was reduced by 76%, and the water qualities were in agreement with Chinese discharge standard GB 14470.1-2002.

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