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Regeneration of sulfamethoxazole-saturated activated carbon using gamma irradiation

Libing Chu[a,b], Jianlong Wang[a,b,*]

[a] Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China
[b] Beijing Key Laboratory of Radioactive Waste Treatment, INET, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

Activated carbon (AC) has been widely used for reclamation and reuse of the effluent of wastewater treatment plant to further remove the emerging contaminants, such as PPCPs in recent years. How to regenerate the exhausted AC effectively and economically is still a challenge. In the present study, the regeneration of AC exhausted with SMX was performed by gamma irradiation to simultaneously recover the spent AC and degrade the pollutants. The results showed that the adsorption of SMX onto AC can be described by the Langmuir isotherm and the adsorption capacity was about 417 mg/g. SMX can be removed rapidly when exposed to gamma irradiation, with the initial concentration of 100 mg/L, more than 99% of SMX was removed at 5.0 kGy, while an extremely high dose (150 kGy) was needed to reach 80% mineralization ratio. The regeneration efficiency was about 21–30% at 50–200 kGy. The absorbed SMX and the intermediates formed during gamma irradiation were released into aqueous solution from AC and mineralized, leading to the partial regeneration of the adsorption capacity of AC. Further studies are needed to optimize the experimental conditions to increase the regeneration efficiency.

1. Introduction

In the last few decades, the occurrence of the organic micro-pollutants (OMPs), involving the pharmaceuticals, personal care products, steroid hormones, pesticides, industrial chemicals and other emerging contaminants in aquatic environment has gained growing concerns worldwide (Yoon et al., 2010; Luo et al., 2014; Barbosa et al., 2016). Although OMPs are commonly detected in waters at trace levels in the range of ng/L to μg/L, they are considered increasingly as a threat to aquatic ecosystem and human health owing to their toxicity, endocrine disrupting effects, and antibiotic resistance to bacteria strains and potential bioaccumulation (Fent et al., 2006; Bolong et al., 2009; Gavrilescu et al., 2015).

The wastewater treatment plants (WWTPs) are not effective in removing emerging contaminants, resulting in the release of these micro-pollutants into the aquatic environment (Reemtsma et al., 2006; Verlicchi et al., 2012; Aymerich et al., 2016). The implementation of the advanced treatment processes, such as adsorption on activated carbon (AC), advanced oxidation processes (AOPs) and membrane separation (nanofiltration and reverse osmosis) is necessary to reduce the discharge of emerging contaminants (Ikehata et al., 2006; Bolong et al., 2009; Sires and Brillas, 2012; Abdel daiem et al., 2013; Altmann et al., 2014; Wang and Wang, 2016).

Among the advanced treatment processes available, adsorption by AC is an effective and the most widely used technique to remove emerging contaminants from the effluent of WWTPs (Dabrowski et al., 2005; Boehler et al., 2012; Meinel et al., 2015). Generally, AC is in the form of powder (PAC) or granular (GAC). The exhausted PAC is typically incinerated or dumped, while the saturated AC could be regenerated for reuse which is an economically-efficient and environmentally-sustained option.

The regeneration of AC could be divided into two routs: desorption of the absorbed compounds by high-temperature thermal treatment or solvent extraction and decomposition of the pollutants adsorbed on AC by biodegradation and chemical oxidation, etc (Matatov-Meytal and Sheintuch, 2000; Aktas and Cecen, 2007; Zhan et al., 2016). Thermal regeneration, the most commonly used regeneration technique, is high-energy consuming and costly. Although the efficiency is relatively high, a large loss of AC (5–15%) was observed due to friction and washing during regeneration (Ania and Beguin, 2008). Regenerating AC by advanced oxidation processes (AOPs) seems to be attractive. Regeneration could be conducted in situ and is expected to be economically efficient. Moreover, the adsorbed pollutants are transformed into less toxic intermediate products and further mineralized to

* Corresponding author at: Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China.
E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

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CO_2 and H_2O, leading to the restoration of the AC adsorption capacity and the elimination of the potential risks related to the pollutants and intermediates. The regeneration methods by AOPs available include electrochemical, microbiological, chemical and ultrasound methods with the regeneration efficiency varying from 15% to 91% (Zanella et al., 2014). It is necessary to explore new regeneration methods.

Among the AOPs available, ionizing radiation is a promising alternative for degrading OMPs such as pharmaceuticals and herbicides in aqueous solution (Wang and Wang, 2007; Wang and Chu, 2016). Generally, the parent compounds removed fast by irradiation, but extremely high absorbed doses are needed for mineralization (Wojnarovits and Takacs, 2008). In addition, gamma irradiation with the good penetration might be beneficial for AC regeneration. In the present study, we proposed to regenerate the spent AC by gamma irradiation. The advantages of combining AC adsorption and regeneration by gamma irradiation include ambient-temperature operation, no need for added chemicals, and decomposition of the adsorbed organic compounds by reactive species formed in situ during water radiolysis.

The antibiotic sulfamethoxazole (SMX) was chosen as the target pollutant. As a widely used sulfonamide in human and veterinary medicine, SMX is highly resistant to biological degradation and has been detected in waters including the effluent of WWTP, surface water, groundwater and even drinking water in many countries (Luo et al., 2014; Sagi et al., 2016). Researches showed that both hydroxyl radicals and hydrated electrons formed in water radiolysis are responsible for the degradation of sulfonamides by gamma irradiation (Phillips et al., 1971, 1973), which has advantage over other AOPs that use hydroxyl radicals only (Mezyk et al., 2007; Kwon et al., 2012).

The objective of this study was to generate the SMX-saturated AC by gamma irradiation, and special attention was paid to the effect of gamma irradiation on SMX degradation and regeneration efficiency of the spent AC.

2. Materials and methods

2.1. Chemicals

The AC employed was commercially available charcoal AC with grain size of about 2.5 mm (Merck, Germany). It has a huge specific surface area of 1233.7 m^2/g and a pore volume of 0.063 cm^3/g with an average pore diameter of 1.7026 nm. Before usage, the AC was washed by deionized water at 100 °C for three times and dried at 105 °C.

The SMX was purchased from the Aladdin Industrial Corporation (Shanghai, China) and used as received. SMX ($C_{10}H_{11}N_3O_3S$) has a molecular weight of 253.3. It is a slightly soluble nonpolar compound with the Log*Kow* value of 0.89. The chemical structure of SMX is as follows:

2.2. Adsorption experiments

Adsorption experiments were performed by adding AC at dose of 0.5*g*/L into glass flasks containing 100 mL of SMX solution with the concentrations of 50–500 mg/L. The flasks were shaken for up to 120 h at 150 rpm and room temperature of 27–29 °C. Samples of the supernatants were taken at predetermined time intervals to analyze the SMX concentration. All solutions were prepared with deionized water.

The adsorption equilibrium values of SMX (q_e, mg/g) were calculated according to the following equation.

$$q_e = (C_0 - C_e) \times V / m_{AC} \quad (1)$$

Where C_0 and C_e is the initial and equilibrium concentration of SMX (mg/L); V is the volume of SMX solution (L); m_{AC} is the mass of AC (g).

2.3. Irradiation and AC regeneration

Gamma irradiation was performed using a ^{60}Co source at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University. The radioactivity was 3.6×10^{14} Bq. Samples were prepared in 50 mL glass vessels. During irradiation the vessels were located near the centre from the gamma source. The dose rate was around 240.2 Gy/min on average. The desired series of absorbed doses were obtained by regulating the irradiation time. All the experiments were performed at least twice at ambient temperature of 24–25 °C and the mean values were given in the results.

The SMX stock solution (500 mg/L) was prepared by dissolving SMX in deionized water. For gamma radiolysis of SMX in aqueous solution, the SMX-containing solution was prepared by adding SMX stock into deionized water and irradiated directly. The detected parameters after irradiation include SMX concentration, TOC, absorbance at UV_{254} and intermediate products. For the regeneration experiments of AC, the SMX-saturated AC was sparged with N_2 for 5 min and then irradiated. After irradiation, the regenerated AC was dried at 70 °C and used for subsequent adsorption experiments. The regeneration efficiency (RE) was calculated according to the following equation:

$$RE = q_{e,r}/q_{e,o} \times 100\% \quad (2)$$

Where $q_{e,r}$ and $qe,_0$ (mg/g) represent the adsorption capacity of the regenerated and virgin AC.

2.4. Analytical methods

The SMX concentration was evaluated using a high-performance liquid chromatography (HPLC, Agilent 1200 Series, USA) equipped with a UV–Vis diode array detector and a reversed-phase column (XDB-C18, 4.6×150 mm). The mobile phase was a mixture of acetonitrile, water and formic acid at a ratio of 45:53.5:1.5 with the flow rate of 1.0 mL/min. The oven temperature and detection wavelength was 30 °C and 254 nm, respectively. Under the experimental conditions, the retention time of SMX is 1.97 min. The intermediate generated during gamma irradiation-induced degradation of SMX was analyzed by a LC-MS (2010EV, Shimazu, Japan) equipped with a photo diode array (PDA), an MS detector, and an atmospheric pressure chemical ionization (APCI) source. The scanned wavelength range of PDA was 190–800 nm with a bandwidth of 1.2 nm. The column, mobile phase and operation of LC are the same as that used in HPLC. Carboxylic acids formed from SMX decomposition were analyzed by an ion chromatograph (Dionex ICS 2100, Thermo Fisher, America).

The BET surface area, pore volume and size of the virgin, saturated and regenerated AC after gamma irradiation were analyzed by a surface area analyzer (Nova 3200e, Quantachrome, America). TOC was detected using a TOC analyzer (multi N/C 2100, Analytik Jena, Germany). pH was determined by a pH meter (model 8103BN, Thermo Orion, America). UV_{254} was measured using a UV–Vis spectrophotometer (Lambda 25, PerkinElmer, America).

3. Results and discussion

3.1. Adsorption isotherm and kinetics of SMX on AC

Fig. 1 depicts the adsorption behavior of SMX on AC. The Langmuir and Freundlich models were used to describe the adsorption isotherms of SMX (Table 1). The experimental data were better fit by the Langmuir model. The calculated adsorption capacity of SMX on AC according to Langmuir model was around 417 mg/g, which is close to the value deduced from extrapolation of the adsorption isotherms, suggesting that SMX adsorption onto AC surface is mono-layer coverage and there is no strong competition between the adsorbate and