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Removal of tetracycline from aqueous solution by MOF/graphite oxide pellets: Preparation, characteristic, adsorption performance and mechanism

Lin-ling Yu[a], Wen Cao[a], Shi-chuan Wu[a], Cao Yang[a], Jian-hua Cheng[a,b,*]

[a] Ministry of Education Key Laboratory of Pollution Control and Ecological Remediation for Industrial Agglomeration Area, College of Environment and Energy, South China University of Technology, Guangzhou 510006, China

[b] South China Institute of Collaboration innovation, Dongguan 523808, China

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ABSTRACT

Tetracycline (TC) as a typical antibiotic has been used extensively and detected in soil, surface water, ground water and drinking water, which results in toxic effect and bacterial resistance. In this study, aluminum-based metal organic framework/graphite oxide (MIL-68(Al)/GO) pellets were prepared through the addition of sodium alginate (SA), a natural crosslinking agent, and applied as a novel adsorbent for aqueous TC removal. The adsorption materials were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N_2 adsorption-desorption analysis and X-ray photoelectron spectroscopy (XPS). Results demonstrated that the pellets maintained similar chemical structure with parent MIL-68(Al)/GO powder. It is noted that the surface area and total volume of the pellets decreased obviously due to the disappearance of micropores. Besides, the efficiency of MIL-68(Al)/GO pellets for TC removal was evaluated by adsorption properties compared with parent powder, including key influential parameters, and adsorption isotherms, kinetics and mechanisms. It is found that the adsorption process was conformed to pseudo-first-order kinetics model and more suitably described through Langmuir isotherm model, with 228 mg g^{-1} of the maximum adsorption capacity. Moreover, these pellets which were separated easily and quickly presented high adsorption capacity and good stability in a wide pH range. The adsorption mechanism of the pellets may be ascribed to the complex interactions of hydrogen bonding, π-π stacking as well as Al-N covalent bonding. Overall, the MIL-68(Al)/GO pellets might be a promising adsorbent and show great potential for the removal of aqueous TC.

1. Introduction

Tetracyclines (TCs) as a typical antibiotic have been used extensively in human and veterinary medicines to control infections and keep healthy (Ahmed et al., 2017; Guo et al., 2017). It is reported that residues of TCs, discharged from municipal wastewater treatment plants and agricultural runoff, have been frequently detected in soil, surface water, ground water and drinking water (Miao et al., 2004). TCs are amphoteric molecules with multiple groups, containing phenol, amino and alcohol, which are expected to interact with cations and matters that are polar or charged. It is these complex chemical structures and properties that make it difficult to find universally applicable method for the TCs treatment (Ye et al., 2017). Additionally, the antibiotics often can not be fully metabolized by animals, and then most of the ingested antibiotics are excreted and discharged into the environment (Acosta et al., 2016). Long-term exposure of TCs to the environment has raised significant concerns of the toxic effect (Álvarez-Torrellas et al., 2016) and bacterial resistance, which results in ecological destruction and threaten human health through bioaccumulation in the food chain (Ahmed et al., 2017; Guo et al., 2017). Thus, it is of great importance to develop effective ways for the TCs removal from the aquatic environment.

To date, many methods, such as biodegradation, membrane filtration, photocatalytic degradation, chemical oxidation and adsorption, have been explored for the removal of antibiotics from aqueous solution (Acosta et al., 2016; Li et al., 2016). Among these technologies, adsorption technology has been considered as a simple, effective and economical way for TCs removal (Gao et al., 2012). As for the currently available adsorbents, it is found that the composites consisting of metal organic frameworks (MOFs) and graphite oxide (GO) have been studied

* Corresponding author at: Ministry of Education Key Laboratory of Pollution Control and Ecological Remediation for Industrial Agglomeration Area, College of Environment and Energy, South China University of Technology, Guangzhou 510006, China.

E-mail addresses: 1943406346@qq.com (L.-l. Yu), 1434857983@qq.com (W. Cao), 492754075@qq.com (S.-c. Wu), 997786113@qq.com (C. Yang), jhcheng@scut.edu.cn (J.-h. Cheng).

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greatly due to their outstanding properties such as ultrahigh surface area, adequate dispersion forces to adsorb small molecules, higher adjust ability and design ability of their structures and functions (Long and Yaghi, 2009; Wu et al., 2017). MOFs/GO composites have shown great applications in many fields, including water purification (Eda et al., 2008; Zhu et al., 2010), gas separation and storage (Getman et al., 2012), catalysis (Valtchev, 2009), etc. So far, some MOFs/GO composites have been reported, such as MIL-101(Cr)/GO (Zhou et al., 2014), MIL-53(Fe)/rGO (Yang et al., 2016), MIL-100(Fe)/GO, MOF-5/GO, and MOF-199/GO (Bandosz and Petit, 2011). However, these composites were rarely used in water adsorption. Recently, our group has developed a MOF/GO composite (MIL-68(Al)/GO) with good water stability, which was successfully applied for the efficient adsorption removal of aqueous methyl orange (Wu et al., 2017). Nevertheless, it is still a great challenge to separate the powdery MIL-68(Al)/GO composite in the practical application. Therefore, some shaping processes conducted by using an extrusion or a press method have been explored (Montazerolghaem et al., 2017). While the obtained pellets or granules through these methods were still unstable and easily dissolved in water, which led to the decrease of adsorption capacity (Kim et al., 2015; Permyakova et al., 2017). In order to overcome these obstacles and make further improvement, the powdery MIL-68(Al)/GO requires additional steps during the shaping processing to finally achieve superior adsorption and stability.

In this work, we reported the preparation and characterization of the MIL-68(Al)/GO pellets, which were obtained through adding a natural cross-linking agent and then shaping in calcium chloride ($CaCl_2$) solution. The adsorption performance of those pellets for TC removal from aqueous solution was investigated. It was tested by comparing the behavior of powder and pellet adsorbents under different influence factors, including initial TC concentration, contact time, pH conditions, iron strength, and temperature. Additionally, the adsorption mechanisms were also discussed based on the obtained results.

2. Materials and methods

2.1. Materials

Graphite powder, aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$), terephthalic acid (H_2BDC), calconcarboxylic acid ($C_{21}H_{14}N_2O_7S$), tetracycline(TC), methyl alcohol (CH_3OH), sodium alginate ($(C_6H_7O_6Na)_n$, SA), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), phosphorus pentoxide (P_2O_5), potassium persulfate ($K_2S_2O_4$), potassium permanganate ($KMnO_4$), calcium chloride ($CaCl_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Shanghai Bio-Chem Technology Co., Ltd. (Shanghai, China). Deionized water (DW, 18.2 MΩ cm) was produced from a water purification system (EMD Millipore Corp., Merck KGaA, Darmstadt, Germany) and used in all experiments. All other reagents were analytical grade and used without further purification.

2.2. Synthesis of materials

GO was prepared on the basis of the Hummer's method (Lian et al., 2010). MIL-68(Al)/GO powder was obtained according to our previously described method with the mg (GO)/mL (DMF) ratio of 0.75 (Wu et al., 2017). MIL-68(Al)/GO pellets were synthesized by adding a certain amount of SA, a natural crosslinking agent. Briefly, MIL-68(Al)/GO powder (5.0 g) was dispersed in the deionized water (100 mL) and sonicated for 10 min. Then, the mixture was heated to 95 °C with stirring in the water bath and remained for 30 min. Next, some SA was slowly added to the suspension with vigorous stirring. After being stirred for 1 h in a water bath at 95 °C, the mixture was cooled to room temperature (RT) with stirring. Next, 200 mL of $CaCl_2$ solution (4 wt%) was placed in a 500 mL beaker, by then the mixture was added to the solution drop by drop with the pinhead syringe (10 mL). Then the obtained pellets were repeatedly washed with deionized water to remove residual $CaCl_2$ solution and freeze-dried for 24 h. Finally, the gray pellets were obtained. In this study, four groups of composite pellets were synthesized, with different mg (MIL-68(Al)/GO) /mg (SA) ratio of 10.00, 6.25, 4.17 and 3.33, respectively. These composites were marked as pellet-n (n = 1, 2, 3, 4).

2.3. Characterization methods

The surface morphologies of MIL-68(Al)/GO powder and pellet-n (n = 1, 2, 3, 4) were observed by SEM (Carl Zeiss Microscopy, GmbH, Jena, Germany) on a MERLIN Compact instrument, and it was well to be indicated that the pellets were tested after comminution. Data from N_2 adsorption-desorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were measured in a surface characterization analyzer from Micromeritics 3Flex (Micromeritics Instrument Corp., Norcross, GA, USA) at 77 K. Before analysis, samples were degassed at 333 K under vacuum for 12 h. Pore size distribution was analyzed by non-local density functional theory (NLDFT). XRD was carried on a Bruker D8 Advance XRD operated at 40 kV and 40 mA with Cu Kα radiation. FT-IR spectra were recorded in a Thermo-Nicolet spectrometer (CCR-1; Thermo Nicolet Corp., Madison, WI, USA). XPS measurements were performed on an ESCALAB250Xi spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with an Al Kα source (1361 eV). The internal reference was the C 1 s line at 284.6 eV.

2.4. Batch adsorption experiments

Batch experiments were carried out in a series of conical flasks (250 mL) covered with tin foil paper. In this work, the TC concentrations were no more than 60 mg L^{-1} in view of dissolvability. Fresh TC stock solution (60 mg L^{-1}) was prepared every time through adding a certain amount of TC into deionized water, and the TC standard solutions were made up just before use by the appropriate dilution of the stock solutions. The flasks were shaken in the constant temperature oscillator at a speed of 150 rpm for a predetermined adsorption time and performed in triplicate, with dosage of powder and pellets (0.2 g L^{-1}, calculated by pure MIL-68(Al)/GO powder). After adsorption, the powdery supernatant was obtained by centrifugation. For the pellets were used, the supernatant was collected directly using syringe. All supernatants were filtered by 0.22 μm membrane before test. The concentrations of TC were detected via high performance liquid chromatography (HPLC, Waters, USA), equipped with a photo-diode array (PDA) detector and an Xbridge BEH C18 column (250 mm × 4.6 mm). The mobile phase was acetonitrile/ultrapure water solution (20:80, v/v), delivered at 1.0 mL min^{-1}, and the injection volume of the samples was 10 μL. The detection wavelength used for quantification of TC was 355 nm, and the temperature of the column was 303 K. In this study, final results were performed in triplicate parallel experiments and the results were presented as average values.

The adsorption amount of TC onto different adsorbents at a predetermined time t, q_t (mg g^{-1}), was calculated based on Eq. (1):

$$q_t = (C_0 - C_t)V/M \quad (1)$$

The equilibrium adsorption amount for TC (q_e, mg g^{-1}) was calculated by Eq. (2):

$$q_e = (C_0 - C_e)V/M \quad (2)$$

where C_t is the residual concentration in the liquid phase at sampling time t (min); C_0 and C_e (mg L^{-1}) are the initial and equilibrium TC concentrations, respectively; V (L) is the volume of aqueous solution; M (g) is the dosage of adsorbent.