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Cu and Co nanoparticles co-doped MIL-101 as a novel adsorbent for efficient removal of tetracycline from aqueous solutions

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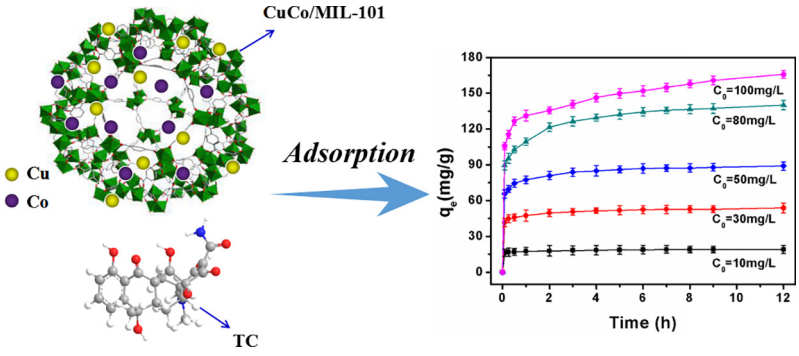
HIGHLIGHTS

- MIL-101 doped with Cu and Co bimetallic nanoparticles was utilized as an adsorbent to remove tetracycline for the first time.
- The synergistic effect between Cu and Co made the adsorption capacity of CuCo/MIL-101 significantly enhanced.
- Electrostatic interaction played an important role in the adsorption process.
- The good reusability and stability of CuCo/MIL-101 proved its potential to remove tetracycline from actual wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

Chromium metal-organic framework (MIL-101(Cr)) has been widely studied for removing organic contaminants from aqueous solutions due to its excellent water stability and giant pore size, but its low adsorption capacity limits the application. In this study, a new adsorbent MIL-101 loaded with CuCo bimetallic nanoparticles (CuCo/MIL-101) was successfully fabricated and applied in removal of tetracycline (TC) from aqueous solutions. The adsorption capacity of CuCo/MIL-101 for TC increased by 140% compared with that of pure MIL-101, which may be attributed to the chemical bonding between Cu and Co BNPs in MIL-101 and TC molecules. The effects of pH, ionic strength, humic acid and contact time on the adsorption were also discussed in detail. The results showed that the removal efficiency of TC solution with high concentration (100 mg L^{-1}) by CuCo/MIL-101 was still as high as 82.9%. The data of adsorption kinetics and isotherms could be well fitted by Elovich model and Freundlich model, respectively. According to the fitting parameters, the maximum adsorption capacity of CuCo/MIL-101 reached up to 225.179 mg g^{-1}. Additionally, the adsorption process of TC onto CuCo/MIL-101 was spontaneous and endothermic. Electrostatic interactions could play an important role in the adsorption process. The enhanced adsorption capacity, excellent reusability and water stability demonstrated the potential of CuCo/MIL-101 composite as a novel adsorbent for the removal of TC from aqueous solutions.

1. Introduction

Antibiotics are extensively used in the prevention and treatment of human and animal diseases, and as growth promoters for livestock,

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poultry and fish (Yang et al., 2011; Zhao et al., 2012). Among all antibiotics, tetracycline (TC) ranks second in usage amount in the world due to its broad-spectrum antibacterial activity, accounting for approximately one third of the production and consumption of antibiotics (Wang et al., 2018). However, since TC is difficult to be digested and absorbed by humans and animals, the pollutant is commonly discharged into the environment in its original form through feces or urine, causing serious environmental problems (Priya and Radha, 2014). The residues of TC can be detected in various receiving aquatic environment, even in drinking water (Kemper, 2008; Valcarcel et al., 2011). It was reported that TC concentrations in the sediments of the Yellow River, the Haihe River, the Liaohe River and the Pearl River are over 653 ng g^{-1} (Yang et al., 2010; Zhou et al., 2011). According to Deblonde et al., the concentration of TC in the effluent of the wastewater treatment plant (WWTP) is 2.375 μg L^{-1} (Deblonde et al., 2011). The extensive use and even abuse of TC cause significant risks to human health and the environment. Long-term enrichment of TC in the environment can lead to the microbial resistance to antibiotics and have toxicity to native microorganisms in the aquatic environment (Dantas et al., 2008; Xu et al., 2017). Therefore, it is urgent to remove TC from the environment, especially to minimize the adverse effect on the aquatic ecosystem.

Due to the variable form, low biodegradability, and complex molecular structure of TC, it is difficult to achieve complete removal of TC by conventional methods of wastewater treatment (Seo et al., 2017). Many researchers have employed some physical and chemical treatment methods to remove TC from aqueous solutions, such as adsorption, biodegradation, membrane separation, advanced oxidation, photocatalytic degradation and electrochemical processes (Michael et al., 2013; Wang et al., 2013; Song et al., 2017a; Xiong et al., 2017; Xu et al., 2018; Zhou et al., 2018). Among them, adsorption is superior to other treatment methods since the significant advantages such as simple operation, low cost, low energy requirements and no secondary pollution. Many adsorbents have been investigated for removal of TC from aqueous solutions such as activated carbon (Kim et al., 2010), graphene oxide (Gao et al., 2012), bio-char (Zhou et al., 2017b), clay (Chang et al., 2009), sludge (Ocampo-Pérez et al., 2012), and etc. Nevertheless, their applications are limited due to their relatively low adsorption capacity and poor reusability. Therefore, the development of high-performance and cost-effective adsorbents to remove antibiotics from aqueous solutions is needed.

In recent years, metal-organic frameworks (MOFs), composed of metal ions or clusters and organic linkers, have attracted wide attention due to their special physical and chemical characteristics such as ultra-high surface area, tunable pore size, and easy chemical modifiability (Rowsell and Yaghi, 2004). MOFs have been applied in various fields, such as gas storage and separation, catalysis, sensing and adsorption (Barea et al., 2014). Besides, a great deal of studies have reported on the removal of organic pollutants from aqueous solutions by MOFs (Haque et al., 2010; Hasan et al., 2012; Jiang et al., 2013; Zhu et al., 2015; Xiong et al., 2018a; Xiong et al., 2018b). Due to the large size of TC molecule, a sufficiently large pore size of the adsorbent is the prerequisite to obtain a high adsorption capacity (Hu et al., 2016). However, most of MOFs materials are confined to their microporous structure, and their smaller pore size does not favor the diffusion and mass transfer process of large-sized molecules (Qiu et al., 2008). Among numerous MOFs materials, MIL-101 with mesoporous structure (MIL stands for Material of Institute Lavoisier) is attractive in liquid phase adsorption due to its excellent hydrothermal stability and large pore size. Besides, the coordinated unsaturated Cr^{3+} centers in the framework endow MIL-101 with Lewis acid properties, which contributes to the acid-alkaline interaction between Lewis open metal sites and other basic groups (Hu et al., 2016). Nevertheless, since pure MIL-101 has limited adsorption capacity for contaminants in water, it can be modified by incorporating some active species (such as various acidic or basic functional groups, metal nanoparticles, metal ions, metal oxides, metal salts, etc.) to optimize the performance (Khan et al., 2013). Metal nanoparticles (MNPs) have been widely used due to their higher surface energy, large surface area, small size, and high reactivity. These properties provide rapid adsorption rates and high adsorption capacity for eliminating pollutants in water. Transition metals such as Cu, Fe, Co and Ni have a slightly lower reactivity than noble metals (such as Au, Ag, Pd), but their low cost and wide availability make them alternatives for noble metals. Bimetallic nanoparticles (BNPs) exhibit remarkably enhanced physical and chemical properties over the monometallic NPs due to the synergistic effect between the two metals, and are widely used in various fields (Jiang and Xu, 2011). Incorporating BNPs into MOFs has been extensively used for synergistic catalysis, which seems to be an encouraging method of the modification for enhancing the adsorption performance in liquid phase (Chen et al., 2015; Qu et al., 2017). Therefore, it is considered to load CuCo BNPs on the MIL-101 to enhance the performance and availability of MIL-101. To our knowledge, currently there is no report about the removal of TC from aqueous solutions by CuCo/MIL-101 composite.

The focus of this study is to synthesize CuCo/MIL-101 composite and apply it to remove TC from aqueous solutions. The physical and chemical properties of prepared samples were characterized by various characterization methods including XRD, SEM, TEM, EDS, BET, FT-IR, TGA, XPS, zeta potential and particle size. The adsorption behavior of TC onto CuCo/MIL-101 was investigated systematically through batch adsorption experiments. Adsorption kinetics, isotherms and thermodynamics were also explored in detail. Meanwhile, the effects of pH, ionic strength, humic acid and contact time on TC adsorption were examined. Finally, the reusability of adsorbent was evaluated by recycle experiments.

2. Materials and methods

2.1. Chemicals

Chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%) was obtained from Xilong Chemical Co., Ltd. (Guangdong, China). *N*,*N*-dimethylformamide (DMF, 99.5%), 1,4-benzenedicarboxylic acid (H_2BDC, 99%), hydrofluoric acid (HF, 40%), ammonium fluoride (NH_4F, >96%), sodium borohydride ($NaBH_4$, >98%), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, >99%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, >99%) were purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Tetracycline hydrochloride ($C_{22}H_{24}N_2O_8 \cdot HCl$) was supplied by Bomei biotechnology Co., Ltd. (Hefei, China). All the reagents and solvents were in analytical grade and used without further purification. Ultrapure water (resistivity of 18.25 MΩ cm^{-1}) was used to prepare stock solutions and other solutions throughout the experiment.

2.2. Preparation of adsorbents

2.2.1. Synthesis of MIL-101

MIL-101 was prepared by a hydrothermal method according to the previous literature with some modifications (G. Férey et al., 2005). Typically, 4.2 g $Cr(NO_3)_3 \cdot 9H_2O$, 1.661 g H_2BDC, and 0.5 mL HF were added to 70 mL of water. The mixture was stirred for 15 min, then poured into a 100 mL Teflon-lined stainless steel autoclave and heated at 220 °C for 8 h. After being naturally cooled to room temperature, the resulting dark green mixture was filtered using a sand core funnel (G2) to remove unreacted terephthalic acid. The MIL-101 was purified as following steps. Firstly, the resulting material by centrifugation was washed three times with ethanol and DMF solutions, respectively. Secondly, the green solid was soaked in NH_4F solution and heated at 70 °C for 24 h in a thermostatic water bath. Finally, the obtained product was dried at 150 °C for 12 h under vacuum.