Science of the Total Environment 651 (2019) 580–590

Contents lists available at ScienceDirect

Science of the Total Environment

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

The residual tetracycline in pharmaceutical wastewater was effectively removed by using MnO_2/graphene nanocomposite

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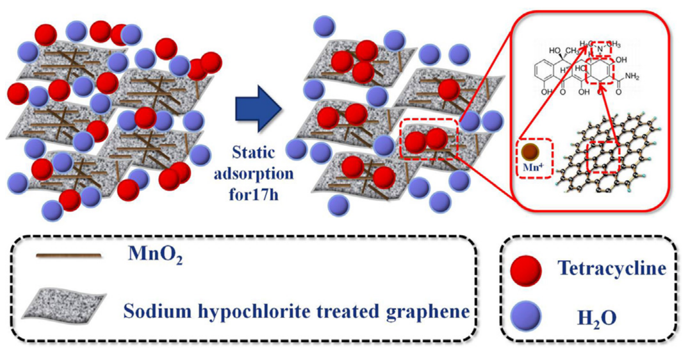
HIGHLIGHTS

- MnO_2/graphene nanocomposite with highly selective adsorption for TC was prepared.
- MnO_2/graphene nanocomposite has excellent water solubility.
- The nanocomposite could effectively remove 99.4% of TC from wastewater.
- MnO_2/graphene can be used for pharmaceutical wastewater treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 July 2018
Received in revised form 18 September 2018
Accepted 18 September 2018
Available online 19 September 2018

Editor: Paola Verlicchi

Keywords:
MnO_2/graphene
Adsorption
Tetracycline
Removal efficiency

ABSTRACT

The object of this study was to remove the tetracycline (TC) residue in pharmaceutical wastewater after flocculation treatment. MnO_2/graphene nanocomposite was synthesized by an in situ hydrothermal method and its TC removal rate was up to 99.4%. This nanocomposite had excellent water solubility. More importantly, the introduction of MnO_2 nanorods allowed the avoidance of excessive stacking of treated graphene sheets during the adsorption process, which made the TC molecules to have more opportunities to make contact with the adsorbents. In order to eliminate the interference factors, the adsorption isotherm, kinetics, thermodynamics and mechanism were all studied in TC aqueous solution. The influence of solution pH, contact time, MnO_2 loading amount, temperature and solution concentration on the adsorption process were also assessed. The main adsorption mechanism contributed to the complexation of Mn(IV) and π-π interactions of the benzene ring structure on treated graphene sheets with TC molecules.

1. Introduction

Since the advent of penicillin, great developments in antibiotics have been achieved, where pharmaceutical antibiotics have been used worldwide in the treatment of human and animal diseases (Yu et al., 2017; Wang et al., 2018; Aghagoli and Shemirani, 2017). Tetracycline (TC), the second most widely used antibiotics worldwide, has been extensively used as human medicine, as a veterinary drug, and as a growth promoter in animal cultivation, with little research carried out over the past few decades (Huang et al., 2017; Rattanachueskul et al., 2017). TC is poorly metabolized and absorbed by humans and animals, thus large fractions are excreted via urine and faeces (He et al., 2017). Therefore, TC has been frequently detected in soil, surface waters and even drinking water. However, it is very difficult to remove TC from water because of its variable state, low biodegradability and complex molecular

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https://doi.org/10.1016/j.scitotenv.2018.09.240

structure (Xiong et al., 2018). TC residues in the environment have caused a variety of potential adverse effects such as chronic toxicity and dissemination into antibiotic-resistant genes (Zhu et al., 2018). More importantly, the existence of TC residues can affect drinking water quality and create a potential risk for ecosystem and human health in the long term (Zhang et al., 2018; Yang et al., 2017; Thi and Lee, 2017). Thus, it is of great importance to develop effective and low-cost technologies for removal of TC from wastewater (Zhuang et al., 2017; Chao et al., 2017; Z. Li et al., 2017; Ahmed et al., 2017).

At present, there are many methods for the removal of TC, including adsorption (Zhang et al., 2015; Li et al., 2016), biodegradation (Ahmed et al., 2015), photodegradation (Liu et al., 2016; Chen and Liu, 2016; Norvill et al., 2017; Chen et al., 2017a, 2017b), and oxidative degradation (Ziółkowska et al., 2016; Khan et al., 2010). Of these, adsorption is a widely used effective technology, due to the advantages of easy operation, low-cost, high efficiency, and no risk of highly toxic byproduct (Yu et al., 2017). There are many different adsorbents used to adsorb and remove TC, including aluminium oxide (Guo et al., 2017; Chen and Huang, 2010), clays (Akhtar and Amin, 2015), activated carbons (Martins et al., 2015; Marzbali et al., 2016), carbon nanotubes (Zhang et al., 2011; Khan et al., 2017), and biochar (Zhou et al., 2017; H. Li et al., 2017). However, problems such as limited adsorption ability and high cost are associated with these adsorbents. Hence, development of an adsorbent with a high adsorption capacity, and low production cost, that is environmentally friendly, should be conducted and studied urgently (M. Li et al., 2017).

More recently, nanomaterials show great promise in adsorbing antibiotics, due to the large surface area and controllable surface functionalities (Yu et al., 2017). Among them, graphene is a two-dimensional honeycomb lattice structure formed by the hybridization of a single layer of carbon atoms and possesses many excellent properties such as a huge surface area, flexibility, and good chemical stability. Based on the above advantages, graphene has great application potential in the adsorption field. On the one hand, under certain pH conditions, the metal oxide can form a strong coordination with the dimethylamino group in TC to achieve the purpose of adsorbing TC (Lv et al., 2015; Song et al., 2018). On the other hand, graphene composites combined with other materials can be applied in the adsorption of various pollutants from wastewater. In the work of Zhao et al. (2015), a TiO_2-graphene sponge (TiO_2-GS) was prepared by the deposition of amorphous TiO_2 on graphene oxide (GO) sheets for the adsorption of tetracycline antibiotics, where lyophilization was adopted to obtain the porous structure. Zhang et al. (2017) prepared a Fe_3O_4@graphene magnetic nanocomposite via an in situ precipitation method for the removal of oxytetracycline (OTC) and tetracycline (TC) from aqueous solution. The above results suggest that the prepared composite can be deemed as a promising material for the removal of TC antibiotics from aqueous solution. However, further research is needed in the study of pharmaceutical wastewater containing TC.

Herein, the MnO_2/graphene nanocomposite was synthesized via an in situ hydrothermal method. Adsorption behaviour and mechanism of materials on TC were studied in detail. The adsorption kinetics, isotherm, thermodynamics, and the impacts, such as, the MnO_2 loading amount, the solution pH, contact time and so on, were also studied. Based on the above experiments, this material was applied to remove TC residues in pharmaceutical wastewater after flocculation treatment.

2. Experimental

2.1. Materials

Tetracycline hydrochloride (AR, 98%) was purchased from QiYuanYaoYe Co., LTD in Ningxia, China. Pharmaceutical wastewater (pH = 5, C_0 = 200 mg L^{-1}) was provided by QiYuanYaoYe production line. We have obtained relevant water quality parameters from pharmaceutical companies (Table 1). NaOH (AR, 96%), HCl (AR, 36%), potassium permanganate (AR, 98%), polyaluminium chloride (AR, 98%) and polyferric sulfate (AR, 98%) were all purchased from Damao chemical reagent factory in Tianjin, China. Sodium hypochlorite (AR, 14%) was purchased from Aladdin Industrial Corporation. Graphene (CP) was purchased from TuLingJiHuaKeJi Co., LTD in Shenzhen, China.

Table 1
Water quality parameters of pharmaceutical wastewater and pharmaceutical wastewater after flocculation treatment.

Pharmaceutical wastewater		Pharmaceutical wastewater after flocculation treatment	
Parameters	Contents	Parameters	Contents
pH	5	pH	5
COD	2067 mg L^{-1}	COD	2003 mg L^{-1}
TOC	922 mg L^{-1}	TOC	894 mg L^{-1}
Protein	0.88 mg L^{-1}	Protein	–
Oxalate	4.5 mg mL^{-1}	Oxalate	–
Amino nitrogen	1.35 mg L^{-1}	Amino nitrogen	–
Reducing sugar	1.6 mg L^{-1}	Reducing sugar	–
Total sugar	3.2 mg L^{-1}	Total sugar	–
Tetracycline hydrochloride	200 mg L^{-1}	Tetracycline hydrochloride	180 mg L^{-1}
Pigment	Uncertain	Pigment	Uncertain
Inorganic ion	Uncertain	Inorganic ion	Uncertain
Microorganism	Uncertain	Microorganism	Uncertain

2.2. Preparation of MnO_2/graphene

The graphene (1 g) was placed in a beaker. Sodium hypochlorite (AR, 14%, graphene: sodium hypochlorite = 1 g: 120 mL) was then added to the beaker and thoroughly mixed. The mixture was stirred at 50 °C water bath for 24 h. The above product was washed with deionized water until the effluent was colourless and was then dried at 80 °C for 12 h. The pretreated graphene sample (3.5 g) was ultrasonically dispersed in deionized water (350 mL) for 2 h. Various amounts of $KMnO_4$ (i.e., 0.88 g, 2.33 g and 4.74 g) were added to the above mixture and stirred rapidly for 2 h. The mixture was transferred to a Teflon-lined stainless steel autoclave and reacted at 130 °C for 15 h. It was cooled to room temperature after the reaction was completed. The product was rinsed to neutral pH with deionized water and dried at 100 °C for 12 h. Finally, MnO_2/graphene powder was obtained (treated graphene is the abbreviation for sodium hypochlorite treated graphene in this paper; 40%MnO_2/graphene is the abbreviation of 40%MnO_2/sodium hypochlorite treated graphene in this paper; 40% refers to the loading amount of MnO_2).

2.3. Flocculation treatment of pharmaceutical wastewater

The flocculation process can effectively remove impurities in pharmaceutical wastewater and keep TC concentrations relatively stable. In this way, the adsorption mechanism of TC on MnO_2/graphene can be better studied. The flocculation treatment was carried out according to the wastewater treatment process provided by the pharmaceutical factory: The dosage of polyaluminium chloride (PAC) and polymeric ferric sulfate (PFS) was 0.175 g L^{-1}. The above two drugs were added to pharmaceutical wastewater and mixed. The rotation speed was 50 r min^{-1}. Both coagulation and settling time were 50 min. Finally, the pharmaceutical wastewater after flocculation treatment was obtained (pH = 5.0, C_0 = 180 mg L^{-1}).

2.4. Characterization

SEM, EDX (Hitachi S-4800) and TEM (FEI Tecnai G20) analyses were used to investigate the particle size, morphology and microstructure of the samples. The adsorption mechanism was studied by FT-IR (Bruker