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Decontamination of tetracycline by thiourea-dioxide–reduced magnetic graphene oxide: Effects of pH, ionic strength, and humic acid concentration

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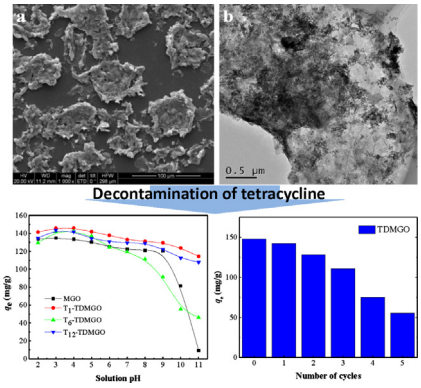
GRAPHICAL ABSTRACT



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ABSTRACT

Thiourea-dioxide–reduced magnetic graphene oxide (TDMGO) was successfully prepared as an efficient adsorbent for the removal of tetracycline (TC) from aqueous solutions via strong adsorptive interactions. The composite was characterized by SEM, TEM, EDS, TGA, FT-IR, XPS, XRD and VSM. The effects of variables such as the pH, TC concentration, and temperature were successfully analyzed. The kinetics and isothermal parameters were described well by pseudo-second-order and Langmuir isotherm models, respectively, and the maximum adsorption capacity (q_m) of TDMGO for TC calculated from the Langmuir isotherm was 1233 mg/g at 313 K. The removal of TC onto TDMGO, as indicated by the thermodynamic parameters, was spontaneous and endothermic. The removal performance was slightly affected by the solution pH. The presence of NaCl in the solution facilitated TC adsorption, and the optimum adsorption capacity was obtained when the NaCl concentration was >0.001 M. The adsorption capacity decreased slightly with increasing humic acid concentration. In addition, the adsorbent could be regenerated and reused. Based on these results, TDMGO is a promising adsorbent for the efficient removal of TC antibiotics from aquatic environments for pollution treatment.

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1. Introduction

Among pharmaceuticals and personal care products, antibiotics are an important group of compounds that are applied extensively for human treatment [1], livestock husbandry, and aquaculture [2]. Tetracycline (TC; $C_{22}H_{24}N_2O_8$) is one of the commonest broad-spectrum antibiotics [3,4]. The adverse effects of TC residuals, such as increased resistance of bacteria to drugs and widespread antibiotic-resistant genes [5,6], could ultimately threaten the health of human beings and safety of the ecosystem [7,8]. Thus, it is of great importance to understand the environmental behaviors of these compounds and investigate possible methods for their removal. Among the variety of treatment methods used for the removal of TC, adsorption is a promising procedure because it is cost-effective, has low energy requirements, and is environmentally benign [9].

Graphene and related materials are newly developed carbon-based materials that have been used for environmental remediation by the removal of antibiotics and other compounds such as tetracycline [10,11], sulfamethoxazole [12], ciprofloxacin [13], metronidazole, aspirin, acetaminophen, and caffeine [14] from aqueous solutions. Graphene oxide (GO), which is a two-dimensional nanomaterial, is prepared by the chemical oxidation of natural graphite [15]. Moreover, graphene oxide has attracted significant research interest because of its relatively high surface area and large number of oxygen-containing functional groups, such as epoxy (C—O—C) [16], hydroxyl (—OH) [17], carboxyl (—COOH) [18], and carbonyl (—C=O) [19]. The functional groups in GO or GO-based materials act as the platform for binding metals [20,21], radionuclides, and various other environmental contaminants via coordination and electrostatic interactions [16]; these materials have been applied with varying success. However, GO is difficult to separate from the solution using traditional separation methods after the adsorption process because of its hydrophilic nature, which increases the cost of industrial applications and/or environmental risks [22]. This problem can be solved using magnetic technology.

Magnetic nanomaterials, especially iron oxide (either Fe_3O_4 or γ-Fe_2O_3) and its nanocomposite with graphene oxide (Fe_3O_4/GO), have been suggested as efficient and environment-friendly adsorbents owing to their magnetic properties, which enable a large removal capacity, high separation efficiency, and fast kinetics [23]. Moreover, magnetic graphene oxide (MGO) can potentially be applied for enhanced optical limiting, magnetic resonance imaging (MRI), energy storage, drug delivery, and the removal of various toxic elements and compounds as well as radionuclides [24,25].

In recent years, the modification of graphene nanoparticles with a series of polymers and small organic compounds has been extensively researched. To produce gram quantities of chemically reduced graphene oxide, various reductants, such as sodium borohydride, hydrazine anhydrous, hydrazine monohydrate, and ascorbic acid [26], are typically applied. However, the adopted reductants are usually not appropriate for large-scale production because of their high cost and safety issues [27]. More specifically, the most commonly used compound, hydrazine, is highly unstable and carcinogenic, while sodium borohydride is very reactive and harmful to human health [28]. Thus, we were motivated to investigate new, cheaper, and safer reductants for the reduction of magnetic graphene oxide with high industrial scalability potential.

Thiourea dioxide has been utilized as a strong reductant for paper manufacturing, textile printing, photographic, and leather processing industries [29]. The amino group (—NH_2) on thiourea dioxide generates strong reducibility under highly alkaline conditions; this makes it suitable for the production of an ammoniated MGO composite. It has also been widely used in academic research towards the deoxygenation of a,b-epoxy ketones and reduction of ketones, aromatic nitro, azoxy, azo, hydrazo, and organo sulfur compounds [30–32]. The reduction of MGO using thiourea dioxide is easy to manage, scalable, and has the potential for commercialization and bulk production [33]. Thus, there is a strong impetus to investigate the reducing properties of thiourea dioxide and generate a novel reduction procedure to obtain high-quality, chemically reduced MGO for the adsorption of tetracycline (TC) from aqueous solutions prior to their discharge into the environment.

The objectives of this study were as follows: (1) prepare and characterize a thiourea-dioxide–reduced magnetic graphene oxide composite (TDMGO) and apply it as an adsorbent for the removal of TC residuals from aqueous solutions in a batch system; (2) investigate the effects of the process parameters on TC adsorption; (3) examine the molecular adsorption mechanisms using kinetic, isothermal, and thermodynamic models; and (4) assess the reusability of TDMGO.

2. Materials and methods

2.1. Materials

Graphite powder (particle size $\leqslant$ 30 μm) was obtained from Tianjin Hengxin Chemical Preparation Co., Ltd. Tetracycline hydrochloride ($C_{22}H_{24}N_2O_8HCl$, molecular weight (MW): 480.9 g/mol) was purchased from Sigma Corp. Formamidine sulfinic acid (thiourea dioxide, $CH_4N_2O_2S$, CAS: 1758-73-2, MW: 108.12 g/mol, 98% purity) and humic acid (HA) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl, 37%), sulfuric acid (95–98%), ethanol, sodium hydroxide (NaOH, AR grade), calcium chloride ($CaCl_2$, AR grade), sodium chloride (NaCl, AR grade), potassium chloride (KCl, AR grade), and hydrogen peroxide (H_2O_2, 30%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Only high-purity water (18.25 MΩ/cm) generated by a Millipore Milli-Q water purification system was used in the experiments.

GO was synthesized from natural flake graphite powder using a modified Hummers method [18]. Briefly, graphite powder, $K_2S_2O_8$, and P_2O_5 were first preoxidized using concentrated H_2SO_4. Next, concentrated H_2SO_4, $KMnO_4$, and $NaNO_3$ were used to further oxidize the preoxidized graphite, and H_2O_2 (30 wt.%) was added to eliminate any excess MnO_4^- anions; the resulting mixture was rinsed repeatedly with Milli-Q water and then sonicated at 323 K for 2 h.

MGO was prepared using the coprecipitation reaction method. Briefly, 0.05 M $FeCl_3{\cdot}6H_2O$ and 0.025 M $FeSO_4{\cdot}7H_2O$ were separately dissolved in 100 mL of Milli-Q water; the two solutions were then mixed with the GO solution under vigorous stirring at 450 rpm for 2 min. Then, 100 mL of NaOH solution (100 g/L) was added rapidly to adjust the pH to 10, and the mixture was stirred at 358 K at 350 rpm for 45 min. The MGO product was separated from the suspension using a magnet and then washed several times with Milli-Q water.

Reduced MGO was obtained from the reaction of thiourea dioxide with MGO. A 94.5 mL aliquot of MGO was added to 187 mL of ethanol and 10.4 g of NaOH, respectively. The components were then mixed with the addition of distilled water to reach 500 mL, and 14 g of thiourea dioxide was added slowly over 15 min. The mixture was refluxed at 363 K for 1, 6, or 12 h: These samples were labelled as T1-, T6-, and T12-TDMGO, respectively. The resultant paste was washed repeatedly until the pH was about 7.

The four adsorbents (i.e., MGO and T1-, T6-, and T12-TDMGO) were used in these experiments at a concentration of 3.50 ± 0.12 mg/mL. T1-TDMGO, which was determined to have the best adsorption capacity, was defined simply as TDMGO.

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