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Tetracycline absorbed onto nitrilotriacetic acid-functionalized magnetic graphene oxide: Influencing factors and uptake mechanism

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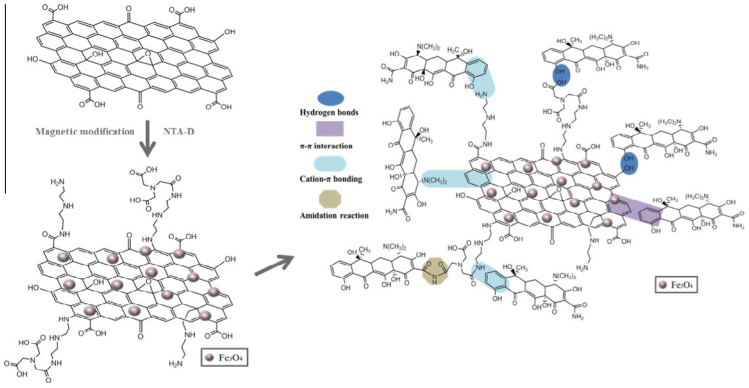
GRAPHICAL ABSTRACT



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ABSTRACT

A novel magnetic nanomaterial was synthesized by grafting nitrilotriacetic acid to magnetic graphene oxide (NDMGO), which was applied as an adsorbent for removing tetracycline (TC) from aqueous solutions. The nanomaterial was characterized using TG-DTA, SEM, TEM, XRD, VSM, XPS, Raman, BET surface area and zeta potential measurements. Several experimental conditions (solution pH, adsorption time, temperature, ionic strength and foreign ions) affecting the adsorption process were investigated. The results showed that the TC adsorption capacity could be affected by solution pH. The adsorption capacity of TC increased rapidly in the initial 20 min and finally reached equilibrium was about 600 min. The pseudo-second-order kinetics provided the better correlation for the experiment data. Various thermodynamic parameters indicated that the adsorption was a spontaneous and endothermic process. The presence of NaCl and background electrolytes in the solution had a slight influence on TC adsorption. Hydrogen bonds, amidation reaction, π-π and cation-π interaction between NDMGO and TC could be used to explain the adsorption mechanism. The regeneration experiment demonstrated that this nanomaterial possessed an excellent regeneration performance. Based on the experimental results

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and comparative analysis with other adsorbents, the NDMGO was a high-efficiency and reusable adsorbent for TC pollution control.

1. Introduction

Antibiotics are increasingly being used in the world to resist disease and protect the health of humans and animals. In China, approximately 2.1×10^5 tons of antibiotics are produced per year, and 85% of which is utilized in animal agriculture and medicine [1]. Tetracycline (TC, $C_{22}H_{24}N_2O_8$), as a widely used antibiotics in the world, is used frequently in human therapy and livestock industry [2], resulting in approximately 50–80% of unmetabolized parent compounds entering into the environment [3]. In fact, large amounts of TC have been recently detected in surface water, ground water, and even drinking water [4,5], which may pose potential risks to aquatic ecological environment and human health via the endocrine disruption and promotion of antibiotic resistance genes (ARGs) transformation between nonpathogenic and pathogenic bacteria [6,7]. Consequently, it is imperative to find an efficient and feasible method to remove TC.

To date, many methods have been reported to decontaminate TC such as adsorption [8], biodegradation [9], photodegradation [10], hydrolysis and oxidative degradation [11]. Among these methods, adsorption has attracted special interest in the treatment of TC pollutants due to its accessibility, high efficiency and harmless to the environment. Various adsorbents have been applied to investigate the adsorption performance of TC, including aluminum oxide [12], clays [13], activated carbons [14], carbon nanotubes [2], and biochar [15,16]. However, these adsorbents suffer the problem of limited adsorption ability, high cost or poor regeneration performance. Hence, developing an adsorbent with high adsorption capacity, low production cost, excellent regeneration performance, and environment friendly for TC removal should be conducted and studied urgently.

Graphene oxide (GO), a two-dimensional (2D) monolayer nanomaterial of sp^2-bonded carbon atoms packed densely in a hexagonal honeycomb lattice, is considered to be a superior adsorbent due to its chemical stability, large specific surface area, rich oxygen-containing groups and feasibility of mass production [17]. Currently, owing to its unique surface structure and hydrophilicity, GO serves as a promising adsorbent for the removal of organic aromatic compounds from aqueous solutions [18], such as polycyclic aromatic hydrocarbons [19], aromatic polyketide antibiotics [20], dyes [19], chlorinated aromatic hydrocarbons [18] and phenolic compounds [21]. TC is an amphoteric polyketides consisting of naphthacene ring structure and each ring includes phenol, alcohol, ketone and amino functional groups [22]. Therefore, TC could be removed by GO, which has been demonstrated by Gao et al. [5]. However, in practical application, GO is very hard to separate and recycle from aqueous solutions after the adsorption process [23]. Consequently, novel GO composite materials are required to be synthesized to overcome this drawback and improve the adsorption performance of GO for TC pollution control. Liu et al. [24] was reported that grafting magnetic nanoparticles to GO surface could provide convenience for the solid-liquid separation, but they would take up the adsorption sites on GO surface and were unfavorable to the adsorption [25]. Many researches showed that new chemical substances containing hydrophilic groups could be introduced to enhance the adsorption ability [26,27]. Like other multidentate chelating agents, nitrilotriacetic acid (NTA) is a well-known amino-carboxylic chelating agent possessing one amide group and three carboxyl groups, which can form stable chelates with most metals [26,28]. Besides, the nitrogen-containing functional groups have a relatively high reactivity and easily react with many chemicals [29]. Therefore, NTA is found to be an ideal choice for GO surface modification applications.

In this study, a novel magnetic composite was synthesized by grafting NTA to magnetic graphene oxide (MGO) through diethylenetriamine and applied to remove TC from aqueous solutions. The objectives of this work were to (1) optimize the adsorption conditions by investigating the effects of solution pH, contact time, temperature, ionic strength and background electrolytes; (2) probe the regeneration performance of NDMGO using desorption experiment; (3) evaluate the adsorption capacity of NDMGO by comparing with other adsorbents; and (4) discuss the adsorption mechanism between TC and NDMGO based on the kinetics, thermodynamic models, FTIR and XPS analysis.

2. Experimental section

2.1. Materials

The reagents such as 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS) were supplied by Shanghai Civi Chemical Technology Co., Ltd. Tetracycline hydrochloride (TC) was obtained from Hefei Bomei Biotechnology Co., Ltd. Graphite powder, NTA, diethylenetriamine, $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, 30% H_2O_2, 98% H_2SO_4 and some other chemicals used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Milli-Q water was used in all experiments.

2.2. Preparation of MGO

GO was prepared via oxidizing natural graphite powder following the modification of Hummers's method [30]. The specific synthesis methods of GO have been reported in the previous research [31]. Next, the magnetic graphene oxide (MGO) was prepared by co-precipitation method [32]. Briefly, 200 mL mixed solution of Fe^{3+} (0.1 mol L^{-1}) and Fe^{2+} (0.05 mol L^{-1}) was added to the 400 mL GO suspension (5 mg mL^{-1}) with addition of ammonia solution at 85 °C for 45 min to form Fe_3O_4-GO composite.

2.3. Preparation of NDMGO

NDMGO was obtained by reacting NTA with MGO through diethylenetriamine. EDC (0.4 g) and NHS (0.4 g) were added to the NTA (0.8 g) solution with continuous stirring for 2 h in order to activate the carboxyl groups of NTA [28,33,34]. Then the diethylenetriamine and MGO dispersion were added and reacted at room temperature. The mixed solution was continuously stirred at 80 °C for 6 h [25,28]. The obtained product was rinsed with Milli-Q water until the solution pH was about 7.0, and then stored at room temperature. The preparation sketch of NDMGO is shown in Fig. 1.

2.4. Characterization

TG and DTA curves were measured using thermoanalytical equipment (SDT Q600, USA) in nitrogen atmosphere from 0 to 1000 °C (heating rate was 10° min^{-1}). The BET specific surface area