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Development and physicochemical characterization of a new magnetic nanocomposite as an economic antibiotic remover

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ABSTRACT

Maghemite (Υ-Fe_2O_3) nanoparticles were impregnated to nanoporous carbon obtained from tomato waste (TWNC). The prepared magnetic composite (MTWNC) was characterized and used to remove tetracycline (TC) from water and then easily be separated from the medium by a magnetic technique. The morphologies and surface chemistries of both magnetic and non-magnetic nanoporous carbons were studied by FTIR, XRD, SEM, SEM-EDX, VSM, BET surface area, proximate and elemental analysis determinations. Batch adsorption studies were carried out and the effects of pH, initial TC concentration, adsorbent dose, ionic strength and temperature were investigated. The adsorption kinetics of TC on MTWNC could be expressed well by the pseudo-second order model, and sorption isotherms were described by Langmuir equation with maximum adsorption capacity of 60.60 mg/g at pH 4 and 50 °C. Thermodynamic parameters showed that the adsorption of TC onto MTWNC was feasible, spontaneous and endothermic. Furthermore, the recyclability of the adsorbent was tested with 0.01 M NaOH solution, and the results show that the synthesized composite adsorbent could be employed repeatedly in wastewater treatment.

Keywords: Nanoporous carbon; Magnetic nanocomposite; Tetracycline adsorption; Tomato waste; Regeneration; Wastewater treatment

1. Introduction

Pharmaceuticals present class of health care products that are intensively used worldwide to promote human health. Among pharmaceuticals, antibiotics are the most widely used drug for the prevention or treatment of bacterial infections in humans, animals and plants (Moussavi et al., 2013). It is reported that antibiotics cannot be completely absorbed by animals and 30–90% of antibiotics are excreted into the environment via urine or feces. Nowadays, the public are paying more and more attention to increased antibiotic resistance of microorganisms. It is generally accepted that the main factor causing this problem is frequent use of antibiotics (Liua et al., 2013). The tetracycline (TC) group is one of the most commonly used antibiotics worldwide, which finds wide applications in human therapy and the livestock industry, and is difficult to be metabolized. A large extent (up to 72%) of TC was excreted with unmetabolized form from human beings and animals. Due to its incomplete treatment in wastewater treatment plants, TC has been widely detected in soils, surface waters, ground water, and even drinking water (Liu et al., 2012). Effluent containing antibiotics needs to be treated chemically or physically to prevent the adverse effects from contaminated water. There are many techniques available for TC removal including adsorption, enzymatic degradation, oxidation, and photochemical degradation. Among these methods, adsorption technology provides a practical method for the removal of pollutants from wastewater in situ (Sun et al., 2012). Activated carbon is the most commonly used adsorbent for removing organic compounds from wastewater, but few

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studies have been carried out on its capacity for TC adsorption (Ocampo-Perez et al., 2012). Owing to the high surface area and adsorption properties of activated carbon, its pure and modified form has been extensively used for the removal of pollutants. However, after pollutant adsorption, the recovery of these materials is difficult and expensive. The use of magnetic materials, easily collected from wastewater using an external magnetic field, offers a solution to this problem. Magnetic separation could be cheaper than the classical separation methods and highly scalable (Gregory et al., 1988). In this paper, we report the use of a novel precursor, the tomato waste (TW), to prepare magnetically separable nanoporous carbon. Introducing magnetic medium (e.g. maghemite, Υ-Fe_2O_3) to the premade or commercial sorbent by chemical co-precipitation is an efficient method to enable the sorbent effectively separated by magnetic separating technique (Chen et al., 2011). Maghemite, a common magnetic material, is a promising adsorbent because it is inexpensive, readily available and can be easily separated and recovered (Jiang et al., 2013).In our previous works, we used TW as a new precursor to prepare nanoporous carbons (TWNC) for the adsorption of anionic and cationic dyes (Güzel et al., 2014; Güzel et al., 2013). In the present study, we successfully combined the magnetic properties of Υ-Fe_2O_3 nanoparticles with adsorption properties of activated carbon. In recent years, magnetic activated carbon composites have been used by researchers for different types of contaminant adsorptions such as multiwall carbon nanotube/iron oxide for Ni(II) and Sr(II) (Chen et al., 2009), magnetic cellulose/Fe_3O_4/activated carbon for Congo Red (Zhu et al., 2011), Oyster shell activated carbon/Υ-Fe_3O_4 for pesticides and heavy metals (Ohno et al., 2011), magnetic chitosan/graphene oxide for Methylene Blue (Fan et al., 2012) and $MnFe_2O_4$/activated carbon for tetracycline removal. To the best of our knowledge, the present paper is the first one to report the adsorption of TC by MTWNC. A low cost nanoporous carbon was prepared from TW, converted into magnetic nanoporous carbon and utilized for TC removal. The sorbent was characterized by FTIR, SEM, SEM-EDX, XRD, BET and VSM techniques. The effects of some physicochemical parameters such as pH, initial TC concentration, adsorbent dose, ionic strength and temperature were investigated. Next, TC adsorption was evaluated by examining kinetic and isotherm studies. Finally, in order to test the reusability of the sorbent, desorption studies were carried out.

2. Materials and methods

2.1. Materials

TW was provided from tomato paste factory in Adana, Turkey. Firstly, the TW was washed and dried in an air oven at 70 °C for 24 h and then crushed and sieved to the desired particle size (between 0.177 mm and 0.4 mm) for using in the chemical activation experiment. Zinc chloride (purchased from Sigma-Aldrich) of purity 99.9% was used as chemical activator. HNO_3, $FeCl_3$ (99%), $FeCl_2{\cdot}4H_2O$ (98%), NH_4OH (25–30%) and HCl (37%) were used for preparation of the magnetic composite and were obtained from Fluka Company. TC (chemical formula: $C_{22}H_{24}N_2O_8$, molecular weight: 444.43 g/mol) was purchased from Sigma-Aldrich and stored at −8 °C, and used without further purification. Stock solution of TC was prepared by dissolving accurately weighed TC in ultrapure water to a concentration of 200 mg/L. The experimental solution of the desired concentrations was obtained by successive dilutions. Fresh dilutions were used in each experiment. The pH of TC solution was adjusted using 0.1 N HCl or NaOH. All chemicals used were of analytical grades.

2.2. Preparation of TWNC

30 g of TW was mixed with 30 g of zinc chloride (TW/$ZnCl_2$ weight ratio of 1:1) and 5 mL of distilled water was added to this mixture. Then, the mixture was dried at 105 °C in an air oven to obtain an impregnated sample. The impregnated sample was placed in a stainless-steel tubular reactor (7.0 cm diameter × 100 cm length), and then heated to the activation temperature of 500 °C for 1 h under nitrogen atmosphere (99.99%) flow (100 mL/min) at the rate of 10 °C/min. After the activation process, the obtain product was cooled down under nitrogen flow and then 0.2 N HCl was added on it. This mixture was filtered and washed with distilled water for several times to remove residual chemicals and chlorine until filtrated solution did not give any reaction with silver nitrate. It was dried at 105 °C for 24 h and ground and sieved to under 40–80 mesh sizes. Finally, the resulting product was stored in desiccators for further use in adsorption experiments. The yield was calculated as the ratio of the dry weight of resultant activated carbon to the weight of the air-dried of the raw precursor.

2.3. Preparation of MTWNC composite

MTWNC composite was prepared according to the procedure given in Darezereshki's study (Darezereshki et al., 2013). As a pre-treating step, 20 g of TWNC reacted with 150 mL 5 M HNO_3 solution and refluxed for 1 h at 70 °C to achieve treated TWNC (T-TWNC). The synthesis procedure for the nanocomposite was as follows: 4.2 g of T-TWNC, 13 g of $FeCl_3$ and 8 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 100 mL of 2 M HCl. The NH_4OH (2 M) solution was added to this solution (300 mL) with vigorous stirring at room temperature for 2 h. The dark brown precipitate was then collected by a magnet. After seven times of rinsing, the precipitate under deionized water and absolute ethanol, it was dried at 70 °C overnight.

2.4. Characterization of TWNC and MTWNC composite

The proximate analysis was conducted according to ASTM D 3172-3175 standards (ASTM D3173-3175, 1999) and the results were given as moisture, ash, volatile matter, and fixed carbon contents. To determine the contents of C, H and N in the TWNC and MTWNC, ultimate analysis was performed in an Elemental Analyzer (Thermo Scientific Flash 2000, CHNS Analyzer, Italy). Results were obtained as percentages of carbon, hydrogen, nitrogen, and the oxygen content was determined by difference.

The determination of surface acid functional groups (carboxyl, lactone and phenolic) of TWNC and MTWNC was based on the Boehm titration method (Boehm, 1994).

The surface physical morphologies of TWNC and MTWNC before and after TC adsorption were identified by using SEM technique (Jeol/jsm-6335F, USA).

Surface area and pore size distribution of TWNC and MTWNC were determined by nitrogen adsorption–desorption isotherms measured at 77 K (Micromeritics, ASAP 2020). Prior to the measurements, the TWNC and MTWNC were outgassed at 423 K under nitrogen flow for 4 h. The nitrogen