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Research article

Highly efficient magnetic chicken bone biochar for removal of tetracycline and fluorescent dye from wastewater: Two-stage adsorber analysis

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ABSTRACT

Magnetic chicken bone biochar (MCB) was fabricated and characterised. The specific surface area, magnetisation value and pH_{pzc} of the MCB were found to be 328 $m^2 g^{-1}$, 64.7 emu/g and 8.3 respectively. The adsorptive performance of MCB for rhodamine B dye (RB) and tetracycline (TC) removal in a single and two-stage stirred adsorber (TSA) was evaluated. The TSA reduced the pressure drops, mass transfer resistances, and fouling of the adsorbent. 63.0 g MCB is required to remove 75% of RB and TC in a single-stage system within 12 h. However, the optimised TSA confirmed that 33.2 g of MCB is needed to achieve 96% removal of TC and 22.2 g for RB within 180 min of 100 mgL^{-1} effluent solutions. The sorption was suitably described by the Freundlich mechanism. Based on the comparative performance, the MCB is considered a viable efficient and magnetically separable alternative adsorbent.

1. Introduction

In recent years, environmental pollution has attracted concerted attention due to increased release of toxic compounds, especially xenobiotics and recalcitrant dyes by pharmaceutical and leather industries into the environment and waters. The rapid development of various broad-spectrum antibiotics such as tetracyclines (TC) has led to increasing TC contamination of water streams and poses a serious risk to ecosystems (Chen et al., 2016; Oladipo et al., 2016). TC has been applied to humans and livestock for disease control due to their perceived therapeutic effects (Zhao et al., 2012). However, about 70% of TC is excreted through urine and faeces because it is poorly metabolised in the digestive tract (Leong et al., 2016). Hence, TC is frequently detected in soil, surface and drinking water and must be eliminated because it can develop microbial resistance genes and allergies in humans (Gao et al., 2012). Rhodamine B (RB) is a fluorescent-based xanthine dye and vastly used as a tracer in pharmaceutical industries (Oladipo and Gazi, 2016a). Studies have indicated that RB poses a significant health hazard on prolonged exposure even at a low, permissible concentration (Gad and El-Sayed, 2009; Santhi et al., 2014; Kooh et al., 2016). Numerous methods have been attempted for the treatment of dyes and antibiotic-containing effluents (Ayodele and Togunwa, 2014; Chen et al., 2016; Yang et al., 2016).

Conventional techniques are not effective for TC removals because TC molecules are dominantly neutral or negatively charged in industrial water (Li et al., 2016a, 2016b) and, also most xanthene dyes are stable to photo/bio-degradation. Advanced oxidation processes (AOP) have been reported for the degradation of TC (Brinzila et al., 2014; Li et al., 2016a, 2016b). However, the AOP may generate toxic intermediates. By contrast, adsorption process is an efficient, non-selective and low-cost method to remove dyes and TC from environmental water (Onundi et al., 2010; Zhao et al., 2012; Ngwabebhoh et al., 2016).

In adsorption process, the pollutants can be transferred from the solution phase to the adsorbent phase without the generation of toxic intermediates (Ngwabebhoh et al., 2016). Various materials (activated carbon, agricultural wastes, polymers and minerals, etc.) have been developed as adsorbents for the removal of TC and RB from wastewater. However, these materials are difficult to separate and recollect from the reaction medium after spent (Oladipo and

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Gazi, 2015), and their poor stability affects the adsorption capacity. To solve the separation and stability issues, fabrication of stable and low-cost magnetic adsorbents could be an efficient solution to the emerging threats.

Biochars have been increasingly applied as adsorbent due to their excellent selectivity and a strong affinity for contaminants in water (Chen et al., 2011; Wang et al., 2015). Biochar is eco-friendly and cost-effective with various surface oxygen-containing functional groups (Wang et al., 2015; Komkiene and Baltrenaite, 2016). Magnetic separation is a rapid, economical and efficient method for the separation of magnetic materials from the medium after treatment of pollutants (Duman et al., 2016; Oladipo et al., 2016). Here, waste chicken bones were selected as feedstock for fabrication of magnetic biochar (MCB). The influences of pH and sorption behaviour of MCB on TC and RB sorption were investigated.

The study deals specifically with the contact time and adsorbent optimisation via a two-stage stirred batch adsorber. Stirred adsorber offers numerous advantages in comparison to fixed-bed adsorber (non-stirred). In a stirred adsorber, the agitation increases the sorption rate, and thus reduces mass transfer resistances (Martino et al., 2015). Also, the pressure drops and fouling of adsorbents are reduced in stirred adsorber in comparison to a non-stirred system (Pirozzi and Sannino, 2014). Notwithstanding, a limited number of studies has been focused on the application of two-stage stirred batch adsorber for pollutants removal. Given the preceding information, this study contributes to cover the knowledge gap in the use of waste chicken bones as precursors for fabrication of high-performance adsorbents.

2. Experimental

2.1. Materials and chemicals

Waste chicken bones (CB) as feedstock for biochar were collected from a local restaurant in Gazimagusa, North Cyprus. Potassium permanganate (KM_nO_4) used for chemical activation of CB was obtained from Merck (Germany). Ferric sulphate ($FeCl_3.6H_2O$) and ferrous sulphate ($FeSO_4.7H_2O$) used as a precursor for preparation of magnetic particles were purchased from BDH Chemicals (England). RB and TC used as model pollutants, sodium hydroxide (NaOH) as precipitating agent were from Sigma-Aldrich (Germany). All the chemicals were of analytical grade.

2.2. Preparation of chicken bone biochar (CB)

The collected waste chicken bones were pre-treated as described in our earlier report (Oladipo et al., 2017). The air-dried bone samples were cut into pieces, activated by 0.1 M $KMnO_4$ solution and thoroughly washed with ethanol and distilled water after activation. CB was prepared according to the procedure described by (Wang et al., 2015) with a slight modification. The dried activated samples were placed in a ceramic crucible and thermally activated in a muffle furnace (Nabertherm; LE 1/11, Germany) at 100 °C for 1 h and then pyrolyzed under oxygen-limited conditions. The pyrolysis temperature of 500 °C was maintained for 2 h. Finally, the pyrolyzed samples (CB) were washed severally with distilled water, dried in an oven at 70 °C overnight and crushed to powder form.

2.3. Preparation of magnetite-modified chicken bone biochar (MCB)

To prepare MCB, dried CB was subjected to co-precipitation with a mixture of Fe^{3+} and Fe^{2+} salts (Oladipo and Gazi, 2015). Specifically, an aliquot of 10 g sieved (0.3 mm) CB was added into a 200 ml solution containing $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ (0.75 w/v %) at 1:2 M ratio. The suspension was stirred for 1 h at 40 °C. Afterwards, the pH value of the mixture was raised to 9–11 by the dropwise addition of NaOH solution (3.0 M). After stirring for 1 h, the black precipitate was separated from the solution by using an external magnet. Finally, the obtained MCB was washed severally with distilled water, dried at 70 °C and sieved to a uniform size before sorption experiments.

2.4. Characterization of CB and MCB

The surface chemistry and point zero charge (pHpzc) of the biochars were determined by the Boehm titration and pH drift method (Oladipo and Gazi, 2015). 0.1 g each of CB and MCB were dried in an oven at 105 °C for 5 h, and the moisture contents were determined by the difference between the weights of fresh CB/MCB and oven-dried CB/MCB. The ash contents were determined by combusting the CB and MCB at 900 °C for 3 h in slightly opened crucibles until a greyish white colour was obtained. The magnetic properties of MCB were measured by a vibrating sample magnetometer (VSM) at 300 K (7400-series, Lake Shore Cryotronics, Inc, USA). The specific surface areas, pore volumes and the particle diameter of the samples were calculated using multipoint Brunauer–Emmett–Teller (BET) analysis method after subjecting the samples to N_2 adsorption at 77 K (ASAP2020, Micromeritics, USA). The proximate and ultimate analysis was performed per the American Society for Testing and Materials (ASTM) standard using the elemental analyser.

2.5. Stirred batch sorption experiments

Stock solutions (1000 mg L^{-1}) were prepared by dissolving an appropriate amount of TC and RB in double distilled water and diluted to get the desired working concentrations. Calibration curves for TC and RB were prepared by measuring the absorbance of different concentrations (2.5–20 ppm). The sorption experiments were conducted at 26.0 ± 2 °C on a rotary shaker at 150 rpm using 200 mL capped flasks containing 20 mL of 20–100 mgL^{-1} of TC or RB solutions and 0.2 g of MCB for 24 h.

The experiments were performed to study the effect of some significant parameters such as pH (2–10) and contact time. The dosage optimisations were performed in a single stage and two-stage stirred adsorber systems. Periodically, aliquots of the sample were taken from the reaction flasks and analysed using a UV–vis spectrophotometer (T80 + PG Instruments Ltd., Leicestershire, UK) at 356 nm and 554 nm for TC and RB, respectively. Blanks experiments were performed to check MCB stability and sorption to flasks. The sorption isotherm was evaluated, and the amount of TC or RB adsorbed by MCB was calculated as the difference between loaded amount and quantity present at the equilibrium. For reproducibility, triplicate experiments were conducted under identical conditions, and the average values reported. The amount of adsorption per gram of MCB, q (mgg^{-1}), was calculated by:

$$q = \frac{V(C_o - C_t)}{1000W} \quad (1)$$

where V is the reaction volume (mL) and W (g) is the mass of MCB. The C_t and C_o (mgL^{-1}) denote the concentrations of adsorbate in the solution at any time t and time zero respectively.

2.6. Design of a single-stage and two-stage stirred batch adsorber

The feasibility of multi-stage treatment of the polluted wastewater is investigated via a two-stage stirred batch absorber to minimise the treatment time and cost (Özacar and Sengil, 2006;