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Bifunctional composite from spent "Cyprus coffee" for tetracycline removal and phenol degradation: Solar-Fenton process and artificial neural network

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ABSTRACT

Removals of tetracycline and photocatalytic degradation of phenol by Fe_3O_4/coffee residue (MCC) were investigated. Brunauer–Emmett–Teller (BET), vibrating sample magnetometer (VSM) and Boehm titration were employed to characterize MCC. Artificial neural network (ANN) model was developed to predict the tetracycline (TC) concentration in the column effluent. Maximum tetracycline adsorption capacity of 285.6 mg/g was observed in a batch system. High removal efficiency (87%) was obtained at 3.3 mL/min flow rate, 8.0 cm bed height and 50 mg/L influent TC concentration in a column system. Complete degradation of phenol by solar-Fenton was attained at 60 min irradiation time. Total organic carbon (TOC) removal increased to 63.3% in the presence of 1.0 g/L MCC, 1.2 g/L H_2O_2 and solar irradiation. MCC showed remarkable potential to remove antibiotics from wastewater even in the presence of heavy metal (Ni^{2+}) via magnetic separation.

1. Introduction

Phenol is frequently used as industrial raw material in the manufacture of pharmaceutical compounds. Therefore, effluents generated from pharmaceutical wastes have resulted in phenol-rich wastewater [1,2]. The increasing presences of phenolic compounds and antibiotics in the aquatic environment have been identified as emerging problems in environmental science [3]. Tetracycline (TC) is an important member of antibiotic families and second most widely used in livestock husbandry and human therapy [3,4]. Fractions of TC used in the livestock industry are absorbed in the digestive tract while large fractions are excreted as unmodified major compounds through urine and faeces [5,6].

The presence of TC and phenolic compounds in the aquatic environment may enhance the toxicological profile of the media and raise significant health risks due to the spread of antibiotic-resistant pathogens [7]. Conventional treatment methods have been applied to treat pharmaceutical effluents in a batch system using various adsorbents [8,9]. However, the use of some of these adsorbents has been limited due to separation difficulties, slow desorption kinetics and introduction of secondary pollution [3,7].

Inexpensive magnetic adsorbent has the potential to overcome the disadvantages of powdered adsorbents in a rapid and effective manner [10,11]. Also, advanced oxidation processes (AOPs) have been reported as efficient technologies for degradation and removal of bio-recalcitrant and persistent contaminants like tetracycline, dyes and phenolic compounds [10,12,13]. Fenton process is one of the most exhaustively studied AOPs due to its unique advantages including ease of operation, high degradation efficiency and benign process [1,10,12,13]. Conventional homogeneous Fenton process suffers several drawbacks including strict pH range and catalyst deactivation [12,13].

Heterogeneous Fenton-like and photo-Fenton processes have been developed to overcome drawbacks mentioned above. Various heterogeneous catalysts have been developed via incorporation of Fenton materials onto the surfaces of varieties of supports (diatomite coated Fe_2O_3, TiO_2/activated carbon and rice hull-based silica supported iron [1,10,14]). TiO_2 and ZnO nanoparticles have demonstrated better applications in wastewater treatment. However, these semiconductor have been limited by their wide band gaps (3.1–3.4 eV), radiation loss and separation difficulties after spent [10].

Fe_3O_4 is an environmentally benign *n*-type magnetic material with excellent physicochemical stability, high surface area, catalytic potential and has been applied in wastewater treatment [15,16]. High numbers of iron oxides are photoactive under solar illumination due to their narrow band gaps (2.0–2.4 eV). In addition, composites or photocatalysts containing Fe_3O_4 demonstrate

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Nomenclature

b	Related to heat of adsorption
B_T	Temkin adsorption constant (kJ mol^{-1})
C	Intraparticle diffusion model constant
k_1	Pseudo-first order kinetic rate constant (min^{-1})
k_2	Pseudo-second order kinetic rate constant (g mg^{-1} min^{-1})
K_L	Langmuir adsorption constant (L g^{-1})
K_F	Freundlich adsorption constant (L g^{-1})
K_T	Temkin model constant (L mg^{-1})
k_{AB}	Adams-Bohart kinetic constant (mL min^{-1} mg^{-1})
k_p	Intraparticle rate constant (mg g^{-1} min^{-1})
kTh	Thomas rate constant (mL min^{-1} mg^{-1})
kYN	Yoon-Nelson model rate constant (min^{-1})
q_T	Theoretical saturated adsorption capacity in Thomas model (mg g^{-1})
t	Time (min)

Greek letters

ε	Polanyi potential
α	Rate of chemisorption at zero coverage (mg g^{-1} min^{-1})
$\mho$	Time required for 50% adsorbate breakthrough (min)

excellent photoluminescence capability in both ultraviolet and visible regions compared with TiO_2 and ZnO [16].

Coffee is a popular, exciting beverage consumes in various parts of the world including Cyprus and as a consequence, large quantities of spent coffee are discharged into the environment [17]. It is essential to convert coffee wastes to a sustainable resource material. Spent coffee wastes have been used recently for various environmental applications [18–20]. However, to the best of our knowledge; application of Fe_3O_4/coffee composite as antibiotic adsorbent and heterogeneous catalyst for the photo-Fenton degradation of phenol has not been reported.

In this work, the waste coffee residue (CC) coated with Fe_3O_4 nanoparticles was prepared, and its adsorptive potential was investigated for tetracycline removal. The catalytic degradation of phenol by MCC was examined and found to be very rapid under solar irradiation, suggesting a high catalytic efficiency of MCC. Finally, the magnetic separability and stability of MCC in fixed-bed system demonstrated that the synthesized material can be scaled up for industrial application.

2. Materials and methods

2.1. Chemicals and materials

The coffee wastes (CC) were collected from cafeterias in Gazimagusa, North Cyprus and were repeatedly washed with distilled water to remove soluble impurities, colour and dirt. The washed samples labelled CC were dried at 100 °C for 12 h, crushed and sieved using a standard sieve to a size ≤200 meshes. $Fe_2SO_4{\cdot}7H_2O$ (99% purity), $FeCl_3$ (99% purity), NaOH (purity > 96%), phenol and TC (purity ≥ 98%) were purchased from Merck (Germany) and used as received. Hydrogen peroxide (H_2O_2) reagent grade (30% w/v) from Merck (UK) was used.

2.2. Preparation of MCC

MCC was synthesized as earlier reported with slight modification [16]. Briefly, 50 mL of NaOH (5 mol/L) was added dropwise to 100 mL of solution containing $FeCl_3$ (0.036 mol) and $Fe_2SO_4{\cdot}7H_2O$ (0.02 mol) in a three-neck flask at 70 °C stirred continuously (100 rpm) for 60 min under nitrogen flow. The resultant dark precipitate (Fe_3O_4) was repeatedly washed with distilled water until the pH became neutral, separated with an external magnet and dried overnight.

The synthesized Fe_3O_4 (1.0 g) was dispersed in distilled water (200 mL) via ultrasonication for 30 min, dried CC (5.0 g) and glutaraldehyde solution (1.5%, w/w; V = 100 mL) were added to the suspension under constant stirring at room temperature. After 24 h, magnetic CC (MCC) was collected by external magnet from the solution, washed three times with distilled water, dried for 10 h in an oven, calcined in a muffle furnace at 300 °C for 2 h. Finally, Fe_3O_4/coffee composite was obtained and stored in a desiccator for further later use.

2.3. Adsorption Studies

Standard solutions of TC and phenol were prepared. The batch operations were conducted in 100 mL Erlenmeyer flasks agitated in temperature controlled shaker at 150 rpm. UV–vis spectrophotometer (UV-Win 5.0, Beijing, T80+) was used to analyse the residual TC concentration in the supernatant at the maximum wavelength (λ_{max}) of 354 nm. Solution pH was adjusted with the appropriate amount of NaOH and HCl. Effects of MCC dosage (0.5–8 g/L), influent TC concentration (50–200 mg/L), contact time (10–360 min), temperature (25–85 °C), co-existing ions (K^+, Ni^{2+}) and pH (1.0–12.0) on TC uptake by CC and MCC were investigated.

Column adsorption tests were conducted in a glass column (height; 40 cm and inner diameter; 2 cm) supported by glass beads and porous sheet at both ends. Column experiments were carried out at different bed heights (2–8 cm), flow rates (3.3–10 mL/min) and influent TC concentration (50–200 mg/L). The column operation was halted when the effluent TC concentration exceeded 94.9% of its influent concentration.

2.4. Photocatalytic experiments

The photocatalytic experiments were conducted using compound parabolic concentrator (CPC) tilted at latitude 35°09′ of the equator and longitude 33°22′ of Greenwich. The plain solar radiation intensity was measured by Apogee pyranometer (MP-200, USA) working on the photocell principle. The solar reactor consisted of single module (0.45 m^2) and six borosilicate glass tubes (outer diameter; 30 mm, thickness; 1.6 mm and length; 800 mm) mounted on aluminium reflector sheet (radius; 9.0 cm). Plastic joints connect the reactor with a continuously stirred tank containing phenol solution and reagents. The solution was circulated continuously in a closed cycle with a flow rate of 1.5 mL/min. The solar reactor was fed with 100 mg/L phenol solution and the reaction time is normalized to UV intensity of 30 W/m^2 according to Eq. 1 (1):

$$t_{30W,n} = t_{30w,n-1} + \Delta t_n \left(\frac{UV}{30}\right)\left(\frac{V_i}{V_t}\right), \Delta t_n = t_n - t_{n-1} \quad (1)$$

Where UV (W/m^2): the average solar ultraviolet radiation measured during Δt_n, t_n: observed experimental time, t_{30W}: the normalised illumination time (refers to a constant solar UV power (30 W/m^2) on a sunny noon), V_i (7.8 L): total irradiated volume and V_t (22.0 L): total solar reactor volume. Concentrations of phenol and its intermediates were quantified by HPLC (TOSOH) equipped with a UV–vis detector at a maximum wavelength of 270 nm.

2.5. Data evaluation

All the adsorption experiments were conducted in triplicate, and the average results were utilized in calculations. The following