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Performance efficiency of electro-coagulation coupled electro-flotation process (EC-EF) versus adsorption process in doxycycline removal from aqueous solutions

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ABSTRACT

Two treatment methodologies such as electro-coagulation coupled electro-flotation (EC-EF) and adsorption have been adopted to remove doxycycline hyclate (DCH) from the aqueous solution. An electro-coagulation (EC) coupled electro-flotation (EF) system has been designed in a closed reactor with a capacity of 1.5 L on a laboratory scale. Electro-synthesis of alumina (electro-generated alumina, EGA) using aluminum electrodes with magnesium chloride as an electrolyte was achieved and used for the adsorption experiments. In both the treatment techniques, removal of DCH efficiency as a function of pH, initial DCH concentration and interfering electrolyte was studied. About 99% of DCH was removed at the end of 80 min in the range of pH 6–8 by EC-EF process whereas the adsorption technique achieved about 73% (73 mg g^{-1}) of DCH removal in the pH range of 3–9 at the equilibrium time of 150 min. Current density of 5.39 mS cm^{-2} and EGA dose of 4 g L^{-1} was optimized respectively for the EC-EF and adsorption processes. The presence of accompanying electrolyte (NaCl) with DCH solution in the EC-EF process increased the electrical conductivity of 1.78 mS cm^{-1} and could achieve about 90% of DCH removal in the first 30 min. On the other hand, in the adsorption process, the participation of chloride (NaCl) as an interfering ion decreased the DCH removal to about 76%. Kinetic and isotherm models fitting the DCH removal dynamics in both the techniques have been checked for their validation. Characterization studies which include FTIR, SEM and XRD have also been done to explore the functional groups, surface morphology and crystalline nature of the solid materials.

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1. Introduction

Pharmaceutical compounds even at very low concentrations can cause serious environmental damages and of great exigency to develop some efficient and cost-effective treatment technologies to remove such compounds. These compounds, particularly the antibiotics and growth hormones affect the quality of soil (O'Connor and Aga, 2007), surface and groundwater (Chang et al., 2009a,b; Tsai et al., 2010). Wan et al. (2010) reported that tetracycline is the second antibiotic in its production and usage across the world. Based on the report submitted by United States of Pharmacopeia (USP) Convention (1997) tetracycline causes a permanent discoloration of teeth, enamelhypoplasia and inhibition of skeletal growth in the fetus, infants and children up to 8 years of age. Doxycycline is a semi-synthetic form of tetracycline and an effective antibiotic against broad range of gram-positive, gram-negative and rickettsia. Due to its highly soluble nature, doxycycline exhibits high residual toxicity in surface and groundwater.

Various techniques for the tetracycline contaminated water are ozonation (Khan et al., 2010), Photo-Fenton process (Bautitz and Nogueira, 2007), photo electro-catalytic degradation (Liu et al., 2009), ion exchange (Wang et al., 2008) and adsorption (Reyes et al., 2006). Among the treatment processes, electro-coagulation has been reported to successfully treat wastewater containing fluoride, laundry-wastewater (Janpoor et al., 2011), municipal wastewater, baker's yeast wastewater, Stronium (Kamaraj and Vasudevan, 2015), heavy metal ions and electro-coagulation coupled to nano-filtration to treat wastewater containing metachlopramide was attempted by Chaabane et al. (2013). On the other hand, adsorption technique has also attracted the attention of researchers and includes the following adsorbents such as aluminum oxide (Chen and Huang, 2010), alumina (Zaidi et al., 2015), goethite (Zhao et al., 2011, 2014), montmorillonites (Zhao et al., 2012; Parolo et al., 2013; Chang et al., 2014) and palygorskite (Chang et al., 2009a,b) for the treatment of tetracycline contaminated wastewater. Although tetracycline removal is of great concern, researchers have contributed less amount of work in the removal of doxycycline by adsorption using graphene-like layered molybdenum disulfide (Chao et al., 2014), activated charcoal (Afonne et al., 2002), activated sludge (Yang et al., 2005), Spent black tea leaves/pomegranate peel wastes (Hassan and Ali, 2014) and Fe_3O_4 magnetic nanoparticles (Ghaemi and Absalan, 2014). Among the preferential adsorbents, aluminum oxide is of much interest as an adsorbent and has drawn attention in the treatment of water containing monothioarsenate (Xiao et al., 2015), dodecyl sulfate (Flilissa et al., 2013), fluoride (Tchomgui-Kamga et al., 2013) and organic acids (Xiao-hong et al., 2007).

In continuance to our previous exploration on the removal of doxycycline by electro-coagulation coupled electro-flotation process, the authors are interested to compare the efficiency of EC-EF process against the adsorption process using the electro-generated aluminum hydroxide.

2. Experimental

All reagents used in both the electro-chemical and adsorption processes are of analytical grade. The solutions were prepared using double distilled water. Doxycyclinehyclate [(4S,4aR,5S,5aR,6R,12aR)-4-(dimethylamino)-1,5,10,11,12a-pentahydroxy-6-methyl-3,12-dioxo-4a,5,5a,6-tetrahydro-4H-tetracene-2-carboxamidehydrochloride] was supplied by Sigma–Aldrich, Germany and the structural formula is shown in Fig. 1 (inserted at the bottom left).

2.1. *Electro-coagulation coupled electro-flotation process*

The experimental setup is as follows:

A coupled EC/EF system in a closed reactor through continuous mode electro-coagulation (EC) was set up. The reactor capacity with the volume of 1.5 L was built at a laboratory scale (Fig. 1). In this electro-coagulation coupled electro-floatation (EC/EF) pilot set-up, aluminum plates (as cathode and anode) of 11.9 cm × 4.7 cm × 0.4 cm dimension was designed to achieve the electro-coagulation process. The electro-flotation process was achieved using stainless steel anode and graphite cathode with dimensions of 11.0 cm × 4.7 cm × 1.0 cm. The electrodes were connected to a digital DC supply (2303 GPS-type) with voltage and current range of 0–32 V and 0–4 A respectively. A digital ammeter and voltmeter were used to regulate the current and voltage. After each run of experiments, the used aluminum electrodes were rubbed with glass paper followed by immersion in NaOH solution of 0.1 M for 10 min. These electrodes were then rinsed with distilled water and dried at 105 °C for 10 min before it is used for the next time. An ISMATEC (ISM 834C) peristaltic pump equipped with four channels is provided with Tygon® tubes of 0.8 mm internal diameter.

2.2. *Adsorption process*

2.2.1. *Electro-chemical synthesis of aluminum hydroxide (EGA)*

The electrolyte was hydrated magnesium chloride, $MgCl_2{\cdot}6H_2O$. The electro-chemical setup was constituted with two parallel aluminum rectangular plates of dimensions 164 mm × 29 mm × 2 mm and 198 mm × 40 mm × 0.5 mm for anode and cathode respectively. The electrodes were washed prior to electrolysis experiments with 0.1 M NaOH and rinsed with distilled water and then dried in an air-oven at 105 °C for1 h. The space between electrodes was 1 cm. The electrodes were immersed in a cell containing 0.1 mol L^{-1} electrolyte of 1 L (Tchomgui-Kamga et al., 2013) with magnetic stirring and controlled with an applied current of 0.7 A for 2 h using digital DC supply (2303 GPS type). At the end of the electrolysis, the wet mass of electro-generated aluminum hydroxide (EGA) was collected after precipitation, dried at 105 °C for 24 followed by rinsing with 200 mL of distilled water for about 1 h and again dried for at 105 °C for 24 h (Fig. 4B).

2.2.2. *Adsorption studies of DCH molecule onto EGA*

DCH solutions were prepared by diluting a home-made stock solution (200 mg L^{-1}). The adsorption of DCH experiments were carried out by the batch method at 25 ± 3 °C at pH 3.5 ± 0.2 for 240 min with an alumina dose of 1 g L^{-1} at first and then with an optimized dose of 4 g L^{-1} for the influencing parameters such as DCH concentration, temperature and ionic strength.

The residual doxycycline hyclate (DCH) concentration was determined by UV-visible spectrophotometer (Shimadzu UV-1800, Japan) at a wavelength of 350 nm and by HPLC (hp HEWLETT series, PACKARD 1100).