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Removal of tetracycline by electrocoagulation: Kinetic and isotherm modeling through adsorption

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ABSTRACT

The use of antibiotics and growth hormones in human and veterinary medicine has a significant effect on the quality of surface and groundwater. The relevance of an electrocoagulation (EC) process for the removal of an antibiotic selected because of its wide application, high solubility in water, high residual toxicity and an absence of biodegradability, was examined in this study. Metal hydroxides generated during EC were used to remove tetracycline (TC) from aqueous solution. The knowledge regarding the removal mechanism of this substance has not been investigated up to now. Experiments were carried out in a batch electrochemical reactor using aluminum electrodes. The removal of TC was relatively fast and equilibrium was reached within 15 min. The effects of the main operating parameters were examined and showed that irrespective of the initial concentration and for pH ranging from 3 to 10, maximum removal efficiency remained close to 99%; while a sharp decrease was recorded at pH 2 (10% removal). The results of this study also showed that the removal of TC from water was strongly affected by the current intensity. The mechanism of electrocoagulation was modeled using isotherm models and showed that the Sips isotherm matched satisfactorily experimental data, suggesting monolayer coverage of adsorbed molecules and assumed a quasi-Gaussian distribution energy owing to the high correlation also found for the Toth model. In addition, adsorption kinetic studies showed that the EC process followed a pseudo-second-order kinetic model at the various current densities, pH and initial antibiotic concentrations considered.

Introduction

Traditionally, the impact of chemical pollution has focused almost exclusively on the conventional priority pollutants. However, the growing use of pharmaceuticals worldwide, classified as the so-called emerging pollutants, has become a new environmental problem, which has raised great concern among scientists in the last few years [1]. More than 3000 chemical products are used in human and veterinary medicine [2]. The use of antibiotics and growth hormones in human and veterinary has a significant effect on the quality of surface and ground water [3]. Among veterinary pharmaceuticals, antibiotics are widely prescribed with a prevalence of the tetracycline family; 50% of the antibiotics sold in France in 2004 [4]. At present, tetracycline antibiotics rank second in the production and usage of antibiotics worldwide [5]. It has been reported that TCs have been found in soils [6], surface water [7,8], and groundwater [8]. Frequent application of tetracycline antibiotics has given cause for concern about increased antibiotic resistance of microorganisms in the terrestrial environment and the effect of antibiotics on plant growth [5]. The presence of TC and other antibiotics in natural environments can cause bacteria to acquire and transmit antibiotic-resistant genes, which potentially threatens ecosystem functions and human health [9]. Even low concentrations of pharmaceuticals released from the environmental matrix into water can pose serious environmental damages. Thus, it is of great importance to develop some efficient and cost-effective treatment technologies to remove such compounds.

Various techniques such as ozonation [10], photo-Fenton process [11], photo electrocatalytic degradation [12], ion exchange [13] and adsorption [14] have been employed for the removal of tetracycline from water. Among these available methods,

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Nomenclature

α and β	constants in the Elovich model
b	the binding constant in the Langmuir model (L/mg)
C_0	the initial TC concentration (mg/L)
C_t	TC concentration at a given time t (mg/L)
K_1	the rate constant of adsorption (min^{-1})
K_2	the rate constant of the pseudo-second order equation (g/mg/min)
K_f	refers to the adsorption capacity in the Freundlich model
K, ν	constants in the Fractional Power model
M	the mass of electrode dissolved (g)
q_e	the adsorbed amount at equilibrium (mg/g)
q_t	the amount of tetracycline (TC) adsorbed per gram of medium (mg/g)
q_0	refers to the maximum adsorption capacity (mg/g)
n	refers to the intensity value in the Freundlich model
m	constant in the Toth model
V	the volume of solution (L)

adsorption is a widely used effective technology for the treatment of low concentration antibiotics. Recently, adsorption of tetracycline on sorbents based on metal or metal oxides such as montmorillonite [15], hydrous oxides of aluminum and iron [16,17] were reported.

The present study proposes an electrocoagulation (EC) process for the removal of tetracycline, which was selected because of its wide application, high solubility in water, high residual toxicity and its absence of biodegradability. Recent research has demonstrated that electrocoagulation offers an attractive alternative method for treating water [18]. EC treatment is characterized by simple and easy operated equipment, short operation time, no addition of chemicals and low sludge production. Iron or aluminum is generally employed as a sacrificial electrode material in EC process but other anodes like magnesium alloy [19] and aluminum alloy [20] can also be used. The dissolved metal ions, at an appropriate pH, can form a wide range of hydro complex species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [21]. The anodic and cathodic reactions for aluminum electrodes can be written as [22,23]:

At the anode:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad (1)$$

At the cathode:

$$3H_2O + 3e^- \rightarrow 3/2H_2(g) + 3OH^- \quad (2)$$

The generated $Al_{(aq)}{}^{3+}$ ions combine with hydroxyl ions to form the metal hydroxydes which are partly soluble in the water under definite pH values. Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2{}^+$, $Al_2(OH)_2{}^{4+}$, $Al(OH)_4{}^-$, and polymeric species such as $Al_6(OH)_{15}{}^{3+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$ which transform finally into $Al(OH)_3(s)$ according to complex precipitation kinetics [21,24].

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3)$$

The polymeric aluminum complexes can have both positive and negative charges capable of attracting the opposite charge of polluting species and remove them from the solution. Electrocoagulation is a complex and interdependent process strongly dependent on the chemistry of the aqueous medium [25]. The electrolyte pH plays an important role in the separation of suspended particles; at low pH the separation is dominated by precipitation while adsorption dominates at high electrolyte pH [22]. The $Al(OH)_3(s)$ formed "sweep flocs" have large surface areas which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs can be easily removed from aqueous medium by sedimentation or H_2 flotation [24].

In this study, a series of batch experiments were conducted. The removal efficiency was investigated by a series of experiments under different experimental conditions such as reaction time, solution pH, initial tetracycline concentration and current intensity. To our knowledge, no report is available in the literature dealing with the reduction of TC concentration in water using the EC process.

Theoretical part

Electrocoagulation kinetics

The pollutant is generally adsorbed at the surface of the flocs electrochemically generated, following two consecutive separate processes: (i) An electrochemical process through which the metal flocs are generated; (ii) followed by a physicochemical process, namely adsorption on the surface of the flocs [22].

The removal of pollutant is similar to conventional adsorption except the generation of coagulants. The electrode consumption can be estimated according to Faraday's Law and the amount of flocs generated can be stoichiometrically estimated. The formed aluminum floc traps the pollutant present in the solution by adsorption mechanism: From this, pollutant removal can be modeled by adsorption phenomena and the amount of adsorbed pollutant is [22]:

$$q_t = \frac{V(C_0 - C_t)}{M} \quad (4)$$

where q_t is the amount of tetracycline (TC) adsorbed per gram of medium (mg/g), V is the volume of solution (L), M is the weight of electrode dissolved (g); C_0 and C_t are the initial concentration and the concentration of TC at any time t (mg/L), respectively.

In order to investigate the mechanisms of the OTC adsorption process, various kinetic models: pseudo-first-order, pseudo-second-order, Fractional Power and Elovich models were applied to describe the adsorption kinetics onto aluminum hydroxides. The most accurate model was selected according to the linear regression correlation coefficient values, R^2.

The pseudo-first order kinetic model can be given as [26]:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (5)$$

where K_1 (min^{-1}) is the constant rate of adsorption, q_t and q_e are the adsorbed amounts at a given time t and at equilibrium (mg/g) respectively. After integration between 0 and a given time t, it comes:

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -K_1 t \quad (6)$$

which can be rearranged to give:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$