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Evaluation of flurbiprofen removal from aqueous solution by electrosynthesized ferrate(VI) ion and electrocoagulation process

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HIGHLIGHTS

- Complete removal of FLU was achieved at pH 4 by applied ferrate(VI) ion.
- Removal decreased with the increase of pH for FLU.
- Oxidation power of ferrate(VI) was the main removal mechanism.
- Optimum conditions were current density of 2.5 mA/cm^2 and pH of 6.5 for EC process.
- Charge neutralization was the removal mechanism at optimum conditions in EC process.

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ABSTRACT

The removal of flurbiprofen (FLU) by electrosynthesized ferrate(VI) ion and electrocoagulation (EC) process was investigated. The degradation of FLU by ferrate(VI) was affected by pH, applied ferrate(VI) dose and initial drug concentration. Complete removal of FLU was achieved at pH 4 and applied ferrate(VI) dose was 1/1 in volume ratio for its initial concentration of 1 mg/L. Removal decreased with increasing pH. Increasing the ferrate(VI) dose increased the efficiency, but there was no significant difference between 3/1 and 1/1 (v/v) ferrate(VI) doses for FLU removal. The effect of current density and pH for the removal of FLU by EC process were investigated. The optimum conditions were current density of 2.5 mA/cm^2 and the solution pH of 6.5. Basic condition (pH 9) showed poor removal efficiency by EC process. Equilibrium concentration was reached within 20 min. TOC removal trends were also investigated for both process. While oxidation was the main mechanism for the removal of FLU by ferrate(VI), charge neutralization was the main removal mechanism by EC process.

1. Introduction

The global need for fresh water cannot be sustained by reducing water consumption alone; therefore most countries are exploring new developments to ensure water availability and quality through sustainable management of water resources. Particular attention is being paid to water reuse, including wastewater treatment, as a promising solution to the growing strain on water resources [1]. Yet the importance of wastewater reuse is not globally recognized due to the challenges of insufficient public participation, poor reuse guidelines and the presence of fairly toxic and non-biodegradable emergent pollutants in wastewater.

Prescription drugs are some of the most persistent and toxic contaminants and thus of interest to environmental specialists [2]. It is of critical importance to understand the behavior and degradation rate of prescription drugs during wastewater treatment, because municipal wastewater treatment plants (WWTPs) are the main points of entry for this type of chemical into surface waters [3,4]. Consumption of prescription drugs is continuously increasing, so more and more pharmaceuticals are being released into wastewater via wash-off, urine, and faeces, as parent compounds, conjugates or metabolites [5]. This is of grave concern due to the fact that certain pharmaceuticals are persistent, non-biodegradable and can potentially impact on health and ecology. Adverse effects from the presence of pharmaceuticals in the aquatic environment have been reported for bacterial, invertebrate, aquatic vertebrate and algal populations in the receiving waters of wastewater treatment systems [6,7]. Therefore it is vital to determine the occurrence and degradation ratio of pharmaceuticals during wastewater treatment. WWTPs are designed to remove oxygen demand, suspended solids, pathogens, and nutrients from

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wastewater, but there is no specific unit required for the removal of drugs. It has been reported that pharmaceuticals are not completely removed during wastewater treatment since they are detected in effluents [8].

The consumption of drugs is related to specific sales and practices in each country. For example, non-steroidal anti-inflammatory drugs (NSAIDs) are the families of drugs with major consumption in Turkey, according to the National Health System. NSAIDs are a class of drugs with analgesic and antipyretic (fever-reducing) effects, and, in higher doses, anti-inflammatory effects. Flurbiprofen (FLU) is a member of the phenylalkanoic acid derivative family and was chosen as representative of NSAID group for this study. FLU is a cyclooxygenase (COX) inhibitor, which is an enzyme responsible for the conversion of arachidonic acid to prostaglandin. The absorbance spectrum and molecular structure of FLU (the concentration of FLU was 5 mg/L for the measurement of UV spectra) can be seen in Fig. 1. FLU exhibited the maximum absorption at 247 nm [9].

A significant proportion of these drugs escape from WWTPs without being degraded, because they are usually soluble and are resistant to degradation through biological or conventional chemical processes. In addition, drugs entering into the soil system via sewage sludge and manure are not significantly adsorbed in the

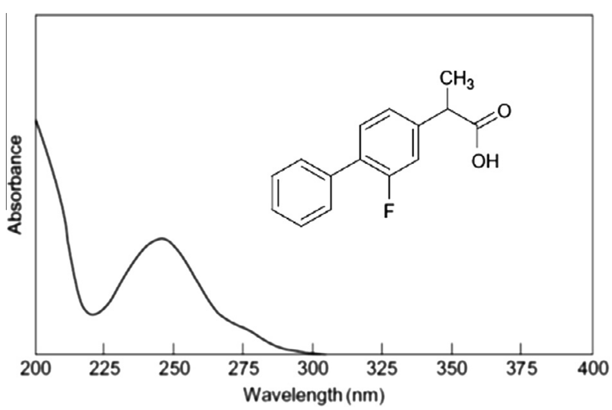

Fig. 1. The absorbance spectrum and molecular structure of FLU (the concentration of FLU was 5 mg/L for the measurement of UV spectra).

soil particles due to their polar structure. Therefore they have the greatest potential to reach significant levels in the environment. Ground water for drinking water production may be recharged downstream from WWTPs by eliminating this type of compound [10–12]. Consequently, it is reported that NSAIDs are detected in the effluent of sewage treatment plants and river water [13,14]. All the above-mentioned discharge pathways act as points of entry for pharmaceuticals into surface waters and potable water supplies [15].

Since WWTPs do not seem to eliminate pharmaceuticals completely, a number of recent studies have been carried out to determine the most suitable technologies to treat pharmaceutical residuals from water and wastewater [16,17]. Ozonation was found to be effective in removing pharmaceuticals in municipal WWTPs [18,19]. Nanofiltration (NF) and reverse osmosis (RO) membrane filtration have been applied in bench, pilot and full scale investigations [20,21]. Adsorption [22–24] has also been proven as an efficient process for removing pharmaceuticals; the addition of 5 mg/L of powder activated carbon with a 4-h contact time removed 50% to >98% of the volatile PPCPs and 10% to >95% of the polar PPCPs [17].

Another promising technology means of removing pharmaceutical residues by a dual function (oxidant/coagulant) is ferrate(VI). Ferrate(VI) has high redox potential under acidic conditions, and thus it has been successfully applied in water remediation and treatment processes [25–27]. Currently there is not enough information available on the performance optimization of pharmaceutical treatment by electrosynthesized ferrate(VI) ion. This paper addresses this issue, focusing on NSAID removal for the first time.

Electrocoagulation (EC) can be another alternative process to remove emerging pollutants from fresh waters and wastewaters [28–31]. Various electrode types such as iron and aluminum can be used in EC process. When current is applied, the electrodes start to dissolve and cations such as Al^{3+}, Fe^{2+} and Fe^{3+} are produced. These cations then form metal hydroxides ($Al(OH)_3$, $Fe(OH)_2$ and $Fe(OH)_3$ etc.) in water. Metal hydroxide species are effective for destabilization of pollutants. Different mechanisms such as double layer compression, adsorption, charge neutralization and sweep coagulation take place in EC process. The mechanism of EC strongly depends on the pH of aqueous medium. Also current density and conductivity play an important role in EC process. In the study, NSAID removal by EC process was also investigated and optimum operating parameters were evaluated.

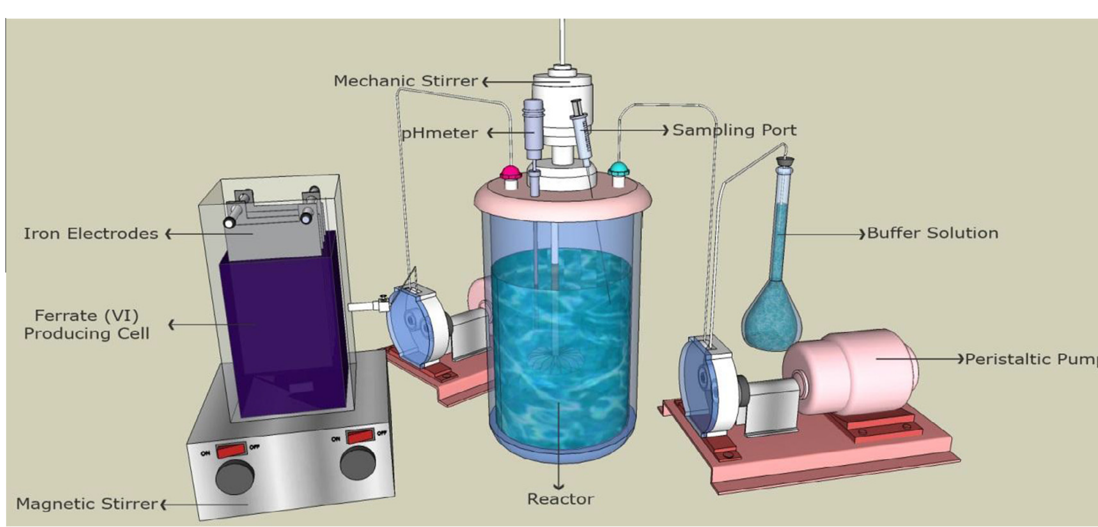

Fig. 2. Schematic diagram of ferrate(VI) process.