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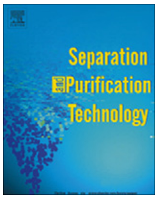

Short Communication

Preliminary study of ciprofloxacin (cip) removal by potassium ferrate(VI)

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ABSTRACT

Ciprofloxacin was identified among the top 10 of high priority pharmaceuticals detected in aquatic environment. Potassium ferrate(VI) is a strong oxidant which possesses very high redox potential and has been widely studied in water disinfection and removing organic and inorganic pollutants. There has been one published work to detail the removal of phosphorus as well as micro-pollutants including ciprofloxacin by ferrate in wastewater treatment. However, developing a simple ciprofloxacin detection method and study of feasibility of its treatment by ferrate was the objective of this work. Solid phase extraction (SPE) and UV/vis spectrophotometer at 280 nm was employed to analyse CIP. A series of jar test experiments was carried out to evaluate the ferrate performance for CIP reduction. Results demonstrated that a SPE coupled with simple UV/vis spectrophotometric method can detect CIP with detection limit of 10 μg/L for model wastewater samples. Ferrate can remove at least 60% of CIP from model wastewater even at very low ferrate doses (<0.3 mg/L). Besides, with increasing in ferrate dose up to 1 mg/L as Fe, the removal efficiency of CIP was higher than 80%. However, increasing ferrate dose further did not show significant increasing in CIP removal. Initial pH of CIP model wastewater samples has no obvious influence on CIP removal, while final solution pH (adjusted and after dosing ferrate) affected the performance of ferrate treatment significantly. CIP removal efficiency by ferrate decreased significantly if final pH of the waste water solution was greater than CIP's pK_a (i.e. pH > 8).

1. Introduction

There is growing concern about the occurrence of trace pharmaceutical residues in aquatic environment in recent years [1–6]. Fluoroquinolones (FQs) are among the most important synthetic antibiotics used in human and veterinary medicine, which show broader activity against Gram (−) and Gram (+) bacteria. Ciprofloxacin (CIP), one of the first generation FQs which came to the market in the 1980s [7], was identified among the top 10 of high priority pharmaceuticals relevant for the water cycle in general [8], it has been identified as a key priority substance for an EU project on the elimination of pharmaceutical residues from points sources in the healthcare sector and it has been detected in the environment with concentrations ranging from several of μg/L to 83 μg/L [9]. The property parameters of ciprofloxacin can be seen in Table 1.

Research on treating CIP has thus been carried out [10–16], and technologies studied include ozonation, photo catalytic degradation and other advanced oxidation process (AOPs). Recently, ferrate(VI) chemicals have been studied extensively which could offer alternatives to the AOPs to treat pharmaceuticals in wastewater. Ferrate(VI) is a strong oxidant. Under acidic conditions, the redox potential of ferrate(VI) ions is greater than that of ozone and is the strongest of all the oxidants/disinfectants commonly used for water and wastewater treatment [17]. Moreover, during the oxidation/disinfection process, ferrate(VI) ions will be reduced to Fe (III) ions or ferric hydroxide, which simultaneously generates a coagulant in a single dosing and mixing unit process. Thus, ferrate(VI) has been studied extensively in water disinfection [18,19], coagulation [20,21], degradation of organic and inorganic compounds [22–24] and reduction of organic micro-pollutants [25,26]. There has been one published work to detail the removal of phosphorus as well as micro-pollutants including ciprofloxacin by ferrate in wastewater treatment [27]. However, developing a simple ciprofloxacin detection method together with the investigation of the feasibility of treatment by ferrate was the objective of this work.

2. Experiment

2.1. Chemical reagents

Ciprofloxacin (≧98%, HPLC grade) and potassium ferrate(VI) (K_2FeO_4, 97%) were purchased from Sigma–Aldrich (UK). Methanol (MeOH, HPLC-grade), acetonitrile (ACN, HPLC-grade), formic acid (98%), kaolin (general purpose grade; $H_2Al_2Si_2O_8$–H_2O), sodium hydroxide (>97%), sulphuric acid (50% w/v; General purpose grade) and ferric chloride (FC) were obtained from Fisher Scientific (UK).

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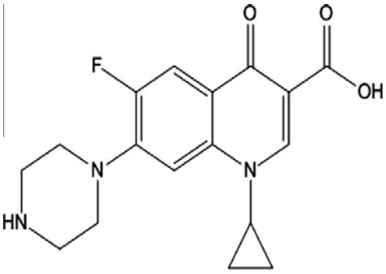
Table 1
Basic property data of ciprofloxacin.[*]

Compound	CAS No.	Chemical structure	Molecular weight (g mol^{-1})	pK_a	K_{ow}
Ciprofloxacin	85721-33-1		331.35	6.09[a] and 8.2[a]	0.28[b]

[*] From SRC.
[a] PhysProp Database.
[b] From Ref. [10].

Deionised reagent water was prepared by ELGACAN B114 deioniser with C114 cartridge (ELGA LabWater). Ciprofloxacin stock solution (20 mg/L) for calibration was prepared in MeOH and stored in the freezer (at −18 °C), and was used within 2 weeks. Stock solutions for the treatment study (10 mg/L CIP) were prepared in deionised water and used within 1 week. Ferrate(VI) working solutions (1 g/L as Fe) were prepared by addition of solid K_2FeO_4 to 2 M NaOH solution and used within 30 min. A molar absorption coefficient of $\varepsilon_{505nm} = 1150\ M^{-1}\ cm^{-1}$ was used to determine ferrate(VI) concentration in the 2 M NaOH solution [28].

2.2. Jar test

A series of jar test experiments was carried out with a six-unit stirrer (Kemira flocculator 2000, Kemwater) to evaluate the ferrate performance for CIP reduction. The experiments were conducted using different ferrate doses from 0 to 4 mg/L as Fe. The jar test procedures were as follows: fast mixing for 1 min at 400 rpm; slow mixing for 20 min at 45 rpm; and then sedimentation for 60 min. Model wastewater samples was prepared by mixing ciprofloxacin with kaolin particles and tap water to make concentration of 100 μg/L CIP and that of 100 mg/L kaolin, which is identical to a previous study on ciprofloxacin removal [14]. The pH of stirred water samples was adjusted to 6–8 by addition of 0.1 M H_2SO_4 or 0.5 M NaOH.

The effect of pH on the CIP reduction was studied by two methods; (1) starting from an initial pH range between 4 and 8 and adjusting to a final pH of 6.5 (after fast mixing); (2) adjusted the initial pH to 6.0–6.1 for each sample and moving towards a final pH between 4 and 9.

2.3. CIP analytical procedures

After sedimentation, the upper 300 mL of supernatant was immediately filtered through 0.45 μm cellulose nitrate membrane filters (Millipore) with a vacuum filtration system (Sartorius Stedim Biotech 16309). Subsequently, the pH of filtered samples was adjusted to 6.5–7.5 for CIP measurement.

The analytical method of CIP by solid phase extraction (SPE) and UV/vis detection at 280 nm was employed which, based on a previous study, had an average recovery of 99.4 ± 11.8% for model wastewater samples. Solid phase extraction (SPE) cartridges employed were Strata-X 33 μm polymeric reversed phase (pore size 88 Å, surface area 818 m^2/g and particle size 28 μm; sorbent mass 200 mg/6 mL) bought from Phenomenex UK, which are suitable for extraction and enrichment of polar and non-polar neutral compounds. Each cartridge was pre-conditioned with 3 mL methanol (MeOH), followed by 5 mL pH 7.0 deionised water. Exactly 250 mL of waste water samples were extracted under vacuum through SPE cartridges at a flow rate of 5–10 mL/min. After extraction, cartridges were washed with 2 mL 50:50 (v/v) MeOH/H_2O, and then air dried for 15 min under vacuum. CIP in sorbents was eluted with 2:49:49 (v/v/v) formic acid/MeOH/acetonitrile (ACN). Elutes were re-constituted to 5 mL in volumetric flask for UV/vis spectrophotometer detection at 280 nm (Jenway 6505 with 10 mm light-path). The accuracy of the method was determined by recovery studies on the same cartridges by extraction of standard untreated CIP solutions.

2.4. Quantification

A six-point calibration curve was generated based on absorption of standard CIP solutions in 2:49:49 (v/v/v) formic acid/MeOH/ACN at 280 nm. Concentrations of CIP in model wastewater samples were calculated based on the absorbance reading and the established calibration curve.

3. Results and discussion

3.1. Spectra and calibration of ciprofloxacin

There were clear peaks of each concentration of ciprofloxacin at 280 nm which was chosen as the specific wavelength for the detection of ciprofloxacin. The calibration line of ciprofloxacin was developed for the concentration range of 0–6 mg/L, the mean linear regression equation was $y = 7.462x$ and the coefficient of correlation 0.998.

Using the established method, the recovery studies were conducted for a wide, low, concentration range, from 10 to 200 μg/L. The mean recoveries of ciprofloxacin were 93% and 108%, respectively, for various ciprofloxacin concentrations (Table 2).

In comparison with other studies using GC–MS or LC–MS, the established method shows good recoveries of ciprofloxacin. Though the analytical method has restrictions, especially in terms

Table 2
Recoveries of ciprofloxacin with different concentrations.

Ciprofloxacin Conc. (μg/L)	n	Recovery (%)	Mean (%)
200	2	103–112	108
100	4	88–96	93
50	4	88–120	101
20	3	91–115	105
10	3	83–111	95