Improving alachlor biodegradability by ferrate oxidation

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Abstract

Alachlor can be recalcitrant when present at high concentrations in wastewater. Ferrate oxidation was used as a pretreatment to improve its biodegradability and was evaluated by monitoring alachlor elimination and removal of COD_{Cr} (chemical oxygen demand determined by potassium dichromate) during the oxidation process up to a value compatible with biological treatment. Ferrate oxidation resulted in elimination of alachlor followed by degradation of its intermediates. High pH suppressed alachlor removal and COD_{Cr} removal due to the low redox potential of ferrate ions. Although alachlor can be totally eliminated within 10 min under optimized conditions (alachlor, 40 mg l^{-1}; ferrate:alachlor molar ratio, 2; and pH 7.0), its complete mineralization cannot be achieved by ferrate oxidation alone. Alachlor solution treated by ferrate for 10 min inhibited an up-flow biotreatment with activated sludge. The biodegradability of ferrate-pretreated solution improved when the treatment was increased to 20 min, at the point of which BOD_5/COD_{Cr} ratio of the treated solution was increased to 0.87 from 0.35 after 10 min treatment. Under optimized conditions, ferrate oxidation for 20 min resulted in total elimination of alachlor, partial removal of COD_{Cr} and the ferrate-treated solution could be effectively treated by the up-flow activated sludge process.
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1. Introduction

Acetanilide herbicides have been classified as the carcinogen of B2 group due to their strong carcinogenic effects of animals [1–3]. For example, alachlor (2-chloro-2′,6′-diethyl-*N*-methoxymethyl acetanilide), an acetanilide herbicide widely used and detected in groundwater and rivers in China, has been found to disrupt the endocrine system [3]. The allowed maximum level of alachlor for drinking water established by the United States Environmental Protection Agency is 2 µg l^{-1} [2–4]. With increased acetanilide herbicides use and stricter environmental regulations imposed, developing advanced and cost effective techniques to remove them from the aquatic environment becomes more critical.

Biological treatment of wastewater is often the most cost effective remediation method compared to other treatment

options [5–7]. Nevertheless, high concentrations of acetanilide herbicides in wastewater are known to be recalcitrant and biological processes are not efficient in these cases [8]. Traditionally, high-valent transition metal oxides such as manganese dioxide, potassium permanganate, chromium trioxide, potassium chromate, and potassium dichromate are frequently used for oxidation of organic compounds. However, in addition to their lack in selectivity and difficulty in controlling the experimental conditions, these reagents are corrosive and toxic to humans, make them unacceptable for industrial wastewater treatment [9,10]. Ferrate ($FeO_4{}^{2-}$), derived from mineral salts, is the strongest of all the oxidants used for remediation [11]. Ferrate ions can be reduced to non-toxic insoluble Fe(III) species, which can adsorb organic compounds and remove them from solution [11]. Recently, considerable attention has been paid to its dual-functions of oxidation and coagulation to treat wastewater.

Advanced oxidation processes (AOPs) have been used to enhance the biotreatability of wastewaters containing various organic compounds that are non-biodegradable and/or toxic to

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common microorganisms [12–15]. A promising alternative to complete oxidation of biorecalcitrant wastewater is the use of ferrate oxidation as a pretreatment to convert initially biorecalcitrant compounds to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water. This study focused on the removal of alachlor through integrated ferrate and biological oxidation. Our objectives were to: (a) characterize the biodegradability of alachlor in wastewater, (b) compare ferrate-treated solution and untreated solution based on removal of alachlor and COD_{Cr} (chemical oxygen demand determined by potassium dichromate), and (c) determine the feasibility of ferrate oxidation as a pretreatment to promote complete mineralization of alachlor.

2. Materials and methods

2.1. Chemicals, wastewater and organisms

Potassium ferrate (purity >96.2%) was prepared by the modified wet oxidation method via reacting OCl^- and $FeCl_3$ in strongly basic media and then isolation from the saturated KOH solution [16]. Alachlor (purity >96%) was purchased from Xinyi Zhongkai Agricultural and Chemical Co. Ltd. (Xinyi, China) and used as received. All other reagents were purchased from Sinopharm Chemicals (Shanghai, China) unless otherwise indicated.

Buffers (0.1 M) included potassium dihydrogen orthophosphate–sodium hydroxide (pH 6.0–8.0); sodium tetraborate–sodium hydroxide (pH 9.0–10.5) and disodium hydrogen orthophosphate–sodium hydroxide (pH 11.0–12.0).

Activated sludge was collected directly from the aeration tank of Nanchang Chaoyang Municipal wastewater treatment Co. Ltd. (Nanchang, China). The inoculum of activated sludge with mixed liquid suspended solids (MLSS) of 44,760 mg l^{-1} was collected after centrifugation at 600 rpm for 15 min.

2.2. Biological treatment of alachlor

Two millilitres of activated sludge (MLSS, 44,954 mg l^{-1}) and 23 ml of normal municipal sewage (COD_{Cr}, 389.4 mg l^{-1}; total nitrogen (TN), 47.2 mg l^{-1}) supplemented with various concentrations of alachlor were mixed in 100 ml conical flasks under aerobic conditions on a mechanical shaker at 150 rpm to ensure homogeneous mixing of the solution for 6 h.

2.3. Ferrate oxidation

Fresh potassium ferrate solution was prepared with deionized distilled water and pH buffer solution immediately prior to each test to minimize its rapid decomposition. Oxidative reaction between ferrate and alachlor was conducted using 25 ml glass conical flasks in which buffered samples were agitated with magnetic stirrers coated with Teflon when aqueous ferrate solution was added. The flasks were mechanically stirred for selected time periods. For analysis, sodium sulfite (concentration equimolar with the initial alachlor concentration) was added into samples at selected intervals to quench residual fer-

rate. After the quenching, samples were centrifuged at 6000 rpm for 5 min.

Solution pH and ferrate:alachlor molar ratio were investigated for their effect on the oxidation performance in terms of COD_{Cr} and alachlor removal, defined as removal (%) = $(C_0 - C)/C_0 \times 100$, where C_0 is the initial COD_{Cr} or alachlor concentration.

2.4. Biological procedure

Under optimum conditions (ferrate:alachlor molar ratio, 2; pH 7.0), ferrate oxidation was applied to treat alachlor (40 mg l^{-1}) for various time using a batchwise mode.

To evaluate differences in the biodegradability of raw and ferrate pre-treated solutions, 2 ml of activated sludge (MLSS, 44,760 mg l^{-1}), 17 ml of normal municipal sewage (COD_{Cr}, 383.1 mg l^{-1}; TN, 47.6 mg l^{-1}) and 6 ml ferrate-treated solution with various oxidation durations in which ferrate was quenched by sodium sulfite (0.15 mM) were mixed in 100 ml conical flasks. The mixed wastewater was treated under aerobic conditions on a mechanical shaker at 150 rpm to ensure homogeneous mixing of the solution for 6 h. Then samples (5 ml each) were taken after centrifugation.

An activated sludge system was applied in an up-flow aeration glass-vessel (5 cm internal diameter; 5.8 cm external diameter; 25 cm height) with a total volume of about 500 ml. The treated wastewater was obtained by mixing municipal sewage (COD_{Cr}, 383.1 mg l^{-1}; total nitrogen (TN), 47.6 mg l^{-1}) and ferrate pre-treated solution (20 min oxidation) in which residual ferrate was quenched by 0.15 mM sodium sulfite at the volume ratio of 1:3. After mixed 35 ml of the inoculum of activated sludge (MLSS, 44,760 mg l^{-1}) and 365 ml of the treated wastewater, the system containing 4192 mg l^{-1} of MLSS was aerated using air pumps and diffusers coupled at the bottom of the reactors. The pH was controlled by a probe and maintained at 7.0 using H_2SO_4 or NaOH. Flow through the column was kept at 31 h^{-1} to assure a good contact between the solution and the biomass. The aeration was 45 l h^{-1}. All the experiments were carried out in triplicate and at room temperature (20–25 °C) by periods of 6 h. Physical characteristics of the sludge were periodically monitored by MLSS determination and microscopic observation. For COD_{Cr} determinations, samples (5 ml each) were taken every 1.2 h after centrifugation.

2.5. Analytical methods

The removal of COD_{Cr} and TN were two important indicators for treatment abilities of an activated sludge process. Determinations of COD_{Cr} and MLSS were carried out according to standard methods [17]. TN is a combination of nitrate/nitrite nitrogen and total Kjeldahl nitrogen (organic and reduced nitrogen). Total Kjeldahl nitrogen is measured using a digestion technique to convert organic nitrogen into ammonia [17]. After distilling, ammonia was measured using a standard colorimetric method [17]. UV–vis absorption was measured with a 762 spectrophotometer (Shanghai Precision Instruments) using 1-cm quartz cells. Biological oxygen demand (BOD) was measured

by means of a Hg-free ET99724A-12 BOD analyzer (Shanghai Precision Instruments, China) thermostated at 20 °C.

Alachlor was quantified by high performance liquid chromatography (HPLC) (Hewlett-Packard, HP series 1100) (CA, USA), comprising quaternary pumps with a 100 μl injector, a Waters^{TM} SYMMETRY 5 μm C_{18} (3.9 mm × 150 mm) column and a diode array detector (Hewlett-Packard) with quantitative detection at 265 nm [18]. Alachlor retention time was 5.63 min with a mobile phase consisting of 60% acetonitrile and 40% water (resistivity >18.2 MΩ cm^{-1}) prepared from Millipore Milli-Q 185 system at a flow rate of 1.0 ml/min.

2.6. Statistical method

Results were presented by mean ± standard deviation (M ± S.D.). Each result was statistically analyzed by the *t*-test. The values of $P < 0.05$ were considered statistically significant.

3. Results and discussion

3.1. Assessment of biological treatment of alachlor

Although biological treatment is often used for wastewater [5–7], its efficiency is often limited at high herbicide concentrations because most herbicides are recalcitrant in these cases [8]. As shown in Fig. 1, the COD_{Cr} and TN removal abilities of the activated sludge were remarkably restrained by the presence of alachlor. For example, when alachlor concentration was 60 mg l^{-1}, only 16.2% COD_{Cr} and 14.6% TN were removed, both of which were remarkably lower than the control test in which the removal of COD_{Cr} and TN were 93.9% and 85.2%, respectively. Moreover, less than 10% alachlor was removed under three alachlor concentrations investigated, indicating poor biodegradability. The reduced treatment activities of the activated sludge and the poor biodegradability of alachlor indicated the unfeasibility of utilizing municipal sewage treatment process to treat wastewaters containing alachlor. It is necessary to develop innovative techniques to remove alachlor from an aquatic environment.
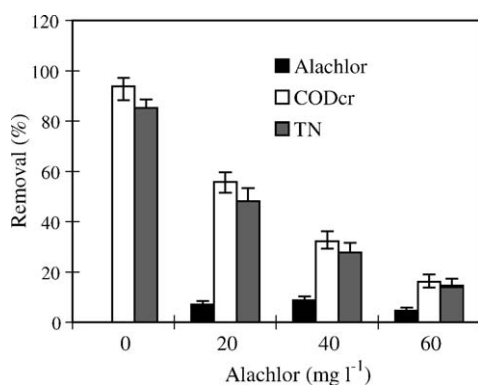

Fig. 1. Influence of alachlor on chemical oxygen demand (COD_{Cr}), total nitrogen (TN), and alachlor degradation under aerobic conditions (HRT = 6 h). The control consisted of municipal sewage without alachlor.
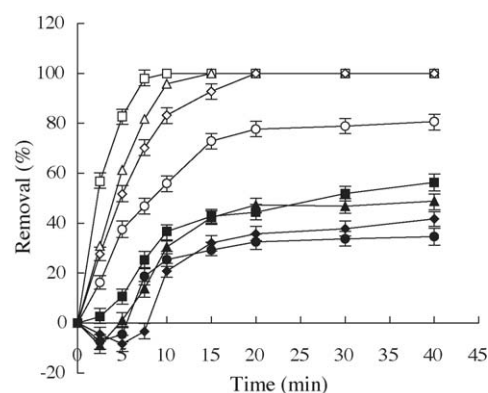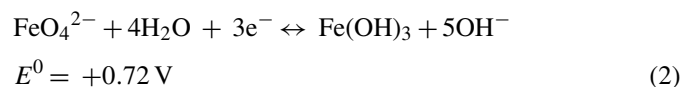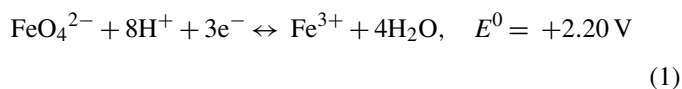

Fig. 2. Effect of initial pH on alachlor and COD_{Cr} removal (%). Alachlor concentration was 40 mg l^{-1}; ferrate:alachlor molar ratio was 2. Alachlor: (□) pH 7.0; (△) pH 8.0; (◇) pH 9.0; (○) pH 10.0. COD_{Cr}: (■) pH 7.0; (▲) pH 8.0; (♦) pH 9.0; (●) pH 10.0.

3.2. Optimization of ferrate oxidation

Ferrate species are strong oxidizing agents based on the reduction potentials of reactions (1) and (2) in acidic and alkaline solutions, respectively [11].

$$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O, \quad E^0 = +2.20\,V \tag{1}$$

$$FeO_4^{2-} + 4H_2O + 3e^- \leftrightarrow Fe(OH)_3 + 5OH^-$$
$$E^0 = +0.72\,V \tag{2}$$

The spontaneous oxidation of Fe(VI) in water forms molecular oxygen [11]

$$2FeO_4^{2-} + 5H_2O \leftrightarrow 2Fe^{3+} + 3/2O_2 + 10OH^- \tag{3}$$
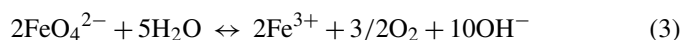
Consequently, the initial pH value will have a remarkable influence in the oxidative ability of ferrate.

Removal of alachlor was accelerated with decreasing pH (Fig. 2). At an initial pH of 7.0, all of the alachlor was removed within 10 min, but removal decreased to approximately 81% at the initial pH 10 even when the reaction time was as long as 40 min. Moreover, the removal of alachlor was different from that of COD_{Cr}. COD_{Cr} changed a little in the first several minutes, and then slowly decreased, showing a lag period (Fig. 2). Several papers have reported that the lag of COD_{Cr} removal behind parent molecules existed in other AOPs [15,19]. It is commonly thought that AOPs initially oxidize the parent molecules to intermediates, which are subsequently oxidized. Here, the duration of the lag period seems to be dependent on the initial pH because it determined the alachlor removal rate (Fig. 2). When the initial pH was 7.0, alachlor was rapidly removed and no lag period was detected. However, a lag period appeared when the initial pH values were above 8.0. Removal of COD_{Cr} was an important indicator of the degradation of organic matter. It varied with reaction time and initial pH (Fig. 2). At pH 7, only 56.3% of COD_{Cr} was removed after a 40 min oxidation. Moreover, removal decreased to 34.6% when pH was
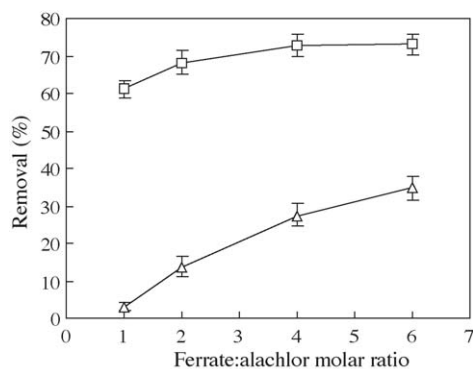
Fig. 3. Effect of initial ferrate:alachlor molar ratio on alachlor and COD_{Cr} removal (%). Alachlor concentration, $40\,mg\,l^{-1}$; pH, 7.0. ($\square$) Alachlor; ($\triangle$) COD_{Cr}.

increased to 10. Limited COD_{Cr} removal indicated that it is difficult to achieve complete mineralization by ferrate oxidation alone.

Solution pH has two impacts on ferrate degradation of alachlor. Although ferrate ions possess good aqueous stability in high pH solution, its redox potential is low [20,21]. The high redox potential resulted from low pH value will improve the reactivity of ferrate to attack nitrogen atom in alachlor molecules [22] and further degrade alachlor by removing the alkyl groups linked to nitrogen [4]. Consequently, it is critical to control the initial pH to 6–7 to make full use of ferrate oxidation process in wastewater treatment.

Removal of COD_{Cr} increased significantly with increasing ferrate:alachlor molar ratio, while only a small increase in alachlor removal was observed (Fig. 3). The difference between alachlor and COD_{Cr} removal may be due to competition between alachlor and its intermediates [4,22]. Initially, ferrate preferentially attacked the nitrogen atom in alachlor molecules, resulting in rapid elimination. With the elimination of alachlor, intermediates accumulated in the solution and the removal of COD_{Cr} by ferrate oxidation was accelerated. However, from economical and engineering perspectives, increasing ferrate:alachlor molar

ratio is not a viable option to complete mineralization of alachlor due to the limited removal of COD_{Cr} (less than 35% even at the high ferrate:alachlor molar ratio of 6 and a reaction time of 5 min).

3.3. Biodegradability changes during ferrate oxidation

Ferrate oxidation resulted in almost complete elimination of alachlor and partial removal of COD_{Cr}. From an economical perspective, draining the ferrate-treated solution into municipal sewage treatment systems seems to be most promising for complete mineralization of its intermediates because it can utilize existing municipal sewage treatment facilities. However, the combination of ferrate oxidation and municipal biological process requires a low inhibitory effect of the ferrate-treated solution on the activated sludge as well as good biodegradability of the intermediates.

The evolution of COD_{Cr} (Fig. 2) does not indicate the inhibitory effect on microorganisms and biodegradability of the ferrate-treated solutions. Additional tests were carried out in 100-ml conical flasks under aerobic conditions to study the inhibitory effects of the ferrate-treated solutions and to determine optimum conditions for coupling ferrate oxidation with a biological treatment for complete mineralization of alachlor. The ferrate-treated solutions differentially affected the microorganisms (Table 1). In control 1, 94.9% of COD_{Cr} and 82.3% of TN was removed. The results of control 2 indicated that sodium sulfide added to quench residual ferrate after ferrate oxidation has no detrimental influence on activated sludge. When the solution treated by ferrate over 10 min was mixed with the municipal sewage, the removal of COD_{Cr} and TN decreased to 73.8% and 66.5%, respectively. This indicated that the intermediates have obviously inhibitory effects on treatment abilities of the activated sludge. It has also been reported that intermediates oxidized from pesticides (including alachlor) may be more toxic than their parent compounds on bacteria *Vibrio fisheri* [23]. In order to obtain a biocompatible solution, ferrate oxidation had to be carried out over 20 or 30 min. The increased removal

Table 1
Influence of ferrate-pretreated solution (initial alachlor concentration of $40\,mg\,l^{-1}$) on activated sludge

	Control 1[a]	Control 2[b]	Ferrate-pretreated solution		
			10 min	20 min	30 min
COD_{Cr}[c] $(mg\,l^{-1})$					
Influent	383.1 ± 4.3	356.2 ± 5.8	298.8 ± 4.1	287.9 ± 5.9	283.2 ± 4.7
Effluent	19.4 ± 1.3	22.7 ± 1.9	78.1 ± 2.3	10.8 ± 0.9	4.2 ± 0.8
Removal (%)	94.9	93.6	73.8	96.3	98.5
TN[d] $(mg\,l^{-1})$					
Influent	47.6 ± 1.3	50.1 ± 1.1	39.4 ± 1.1	40.6 ± 1.2	37.5 ± 0.9
Effluent	8.4 ± 0.8	7.3 ± 1.2	13.2 ± 1.3	2.9 ± 0.9	3.8 ± 1.1
Removal (%)	82.3	85.4	66.5	93.5	90.8

[a] Municipal sewage without alachlor and sodium sulfite.
[b] Municipal sewage containing 0.035 mM sodium sulfite without ferrate pretreated solution. Here, 0.035 mM was calculated from the amount of sodium sulfite used to quench residual ferrate and from the mixed volume ratio of ferrate treated solution to municipal wastewater (1:3).
[c] COD_{Cr}, chemical oxygen demand determined by potassium dichromate.
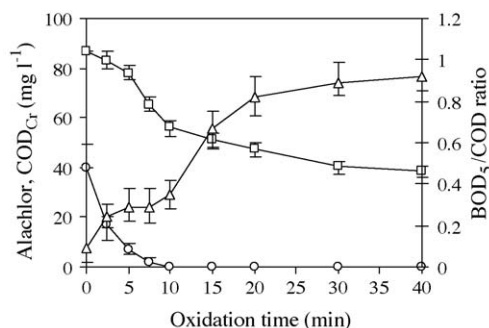[d] TN, total nitrogen.

Fig. 4. The BOD_5/COD ratio of ferrate-treated alachlor solution. Initial alachlor concentration, 40 mg l^{-1}; pH, 7.0; ferrate:alachlor molar ratio 2.

of COD_{Cr} might indicate the improved biodegradability of the ferrate-treated solution.

Biodegradability, as shown by the BOD_5/COD ratio, of the ferrate-treated solution was increased with the increase in oxidative reaction time (Fig. 4). The BOD_5/COD ratio of untreated alachlor solution was 0.09. Within 10 min, the BOD_5/COD ratio increased to 0.24–0.29. When all alachlor was eliminated at 10 min, the BOD_5/COD ratio reached a higher value of 0.35. After that, it increased abruptly, and an extremely high BOD_5/COD ratio (higher than 0.87) attained when the oxidation was over 20 min. The improved BOD_5/COD ratio of the ferrate-treated solution might be derived from the further oxidation of the biorecalcitrant intermediates into biocompatible intermediates after the elimination of alachlor. At this time, the ferrate-pretreated solution could be drained into the up-flow activated sludge process for the biological oxidation.

After treated by ferrate, the solution was equilibrated for 1 day for coagulation, which was accompanied by precipitation of $Fe(OH)_3$, and then the supernatant was collected to mix with normal sewage with the weight ratio of 1:3. Table 2 showed the removal of COD_{Cr} and TN in the up-flow bioreactor with the MLSS of 4,231 mg l^{-1} at HRT = 4, 6, 8 h, respectively. At HRT = 4 h, the removal of COD_{Cr} and TN were 76.4% and 40.4%, respectively, which were lower than that at HRT = 6 h, where 94.2% COD_{Cr} and 80.86% TN were removed. Compared with HRT = 6 h, the removal of contaminations was not improved significantly at HRT = 8 h, showing the optimal performance of the bioreactor at HRT = 6 h.

Table 2
Biological degradation of ferrate pretreated solution in the aerobic up-flow bioreactor

HRT	4 h	6 h	8 h
COD_{Cr} (mg l^{-1})			
Influent	308.3 ± 3.8	318.8 ± 4.2	302.9 ± 5.4
Effluent	72.6 ± 2.6	18.4 ± 1.2	9.6 ± 1.0
Removal (%)	76.4	94.2	96.8
TN (mg l^{-1})			
Influent	43.68 ± 1.1	40.73 ± 1.8	46.39 ± 1.9
Effluent	26.05 ± 1.2	7.39 ± 0.9	5.88 ± 1.3
Removal (%)	40.4	80.86	87.3

4. Conclusions

This study was intended to examine the feasibility of using ferrate oxidation to improve the biodegradability of wastewater containing a high concentration of alachlor, which is resistant to biological degradation. Ferrate oxidation of alachlor included elimination of alachlor and degradation of its intermediates. Alachlor can be totally removed within 10 min under optimized conditions; however, its complete mineralization was difficult to achieve by ferrate oxidation alone. When using an aerobic up-flow bioreactor to treat the ferrate-treated solutions, it was revealed that the ferrate-treated solution with short oxidation duration (10 min) exhibited obviously inhibitory effects on the activated sludge. Ferrate oxidation had to be carried out over 20 min in order to obtain a biocompatible solution for which almost all COD_{Cr} can be readily removed in the aerobic up-flow bioreactor. For this reason, the integrated ferrate oxidation-biological systems proposed here represented a suitable solution for the treatment of wastewater containing alachlor.

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