

The role of oxalate in the kinetics of 2,4-D oxidation over ferrous ion-supported catalysts

C.Y. Kwan, W. Chu*, W.S. Lam

Department of Civil and Structural Engineering, Research Centre for Environmental Technology and Management, The Hong Kong Polytechnic University, Hunghom, Kowloon, Hong Kong

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Abstract

The cation-exchange resin loaded with ferrous ion (CERF) catalyzes the photochemical oxidation of 2,4-D. The co-existence of UV light and oxalate is the key to initiating the attack by hydroxyl radicals of 2,4-D in the presence of CERF and H_2O_2 . In addition to oxalate, citrate and EDTA may also drive the CERF-induced photooxidation that is more favorable in an acidic environment. The solid catalyst can easily be separated from the solution by filtration after the reaction, and then reused. The removal rate of 2,4-D with the reused CERF was found to be faster than that with the fresh CERF. This can be explained by the presence of a higher amount of ferrous ions in the recycled resin, thus speeding up the production of hydroxyl radicals. The effect of oxalate concentration on the recycling efficiency of the catalyst was studied. For the first cycle, the rate constants increased as the oxalate concentration increased. The removal rate was strongly dependent on the concentration of the oxalate. For practical purposes, a model was derived to evaluate the capacity of the catalyst and to predict the cumulative mass of 2,4-D removed at any reaction time of any cycle. In a series of four runs conducted with the same catalyst, the optimal concentration of oxalate was found to be 2.4 mM, and 74.7% of 2,4-D (total 0.099468 mg) was transformed.

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1. Introduction

The ion-exchange process involves a physical–chemical reaction by which ions held by electrostatic forces to charged functional groups on the surfaces of a solid are exchanged for ions of like charge in a solution in contact with the solid [1]. An ion exchanger such as resin is used extensively for water treatment, including the production of high-quality boiler feed water for the power industries; pure water for the chemical, food, and beverage industries; ultra-pure water for the nuclear, semiconductor, and pharmaceutical industries [2]. Ion-exchange is also used for the treatment of a variety of industrial effluents to recover valuable materials or by-products, such as the ionic forms of gold, silver, platinum, chromium, and uranium [1]. The technique is becoming more extensively employed in controlling environmental pollution, to remove hardness

ions, toxic metals, and harmful organics from contaminated water. A wide range of commercial resins has been shown to remove iron from hydrochloric pickling liquor, which may be used in the metal finishing industry [3]. The adsorption of herbicides has been investigated by Kyriakopoulos et al. [4], who found that highly hydrophobic resin is more effective for use in hydrophobic herbicides such as alachlor, trifluralin, prometryn, and that the more hydrophilic adsorbent is preferable to the hydrophilic one (amitrole). The addition of combined resins in the stabilization–solidification of sludge samples obtained from incineration plant residues could reduce the release of not only trace metals but also polycyclic aromatics hydrocarbons [5].

Due to the limited lifetime of homogeneous catalysts, the use of solid catalysts has attracted much attention to modern wastewater treatment because of their high stability and because they are easy to handle and recycle. The recent trend in the development of heterogeneous catalysis is to immobilize the catalyst or the oxidant on a support such as clay, zeolite, and resin. For instance, a Fenton-type reaction can be induced by surface iron loaded

* Corresponding author. Tel.: +852 2766 6075; fax: +852 2334 6389.
E-mail address: cwchu@polyu.edu.hk (W. Chu).

on different materials. Studies have shown that 4-nitrophenol degrades when catalyzed by Fe-modified clay [6] and Fe-zeolite [7]. In addition, there have been many studies on iron-containing zeolites with regard to the oxidation of phenol [8], carboxylic acids [9], azo dye [10], and ethanol [11]. Although zeolite-based catalysts are effective and stable, there are a few drawbacks arising from the particle size of zeolite (powder form). The typical particle size of zeolite powder catalysts is about 1 μm [8]. They might not settle in the solution within a short time, and it would be very difficult to collect the particles for recycling. Hence, the separation of the catalyst suspension requires centrifugation or filtration of a size down to less than 1 μm . This may increase the consumption of power and the operation cost. Another disadvantage is that the wet zeolite particles become rigid cakes after drying. After-treatment, such as grinding the dried catalysts, is needed before they can be reused, leading to an excessive loss and destruction of catalysts.

The wet particle size of the resin used in this work ranged from 300 to 840 μm . At this size, the resin particles settle in the solution by gravity within a minute, and remain separated after drying. In the present study, the intention is to examine the use of a resin containing Fe on the degradation of 2,4-dichlorophenoxyacetic acid in the presence of hydrogen peroxide. The effects of UV light and organic ligands on the catalytic activity of the modified resin are investigated. The total capacity of the solid catalyst for a series of four runs is determined. A practical model is derived to evaluate the capacity of the catalyst.

2. Methodologies

2.1. Preparation of the catalyst

The cation-exchange resin (CER) used in this work was Amberlite IR-120 (plus) in sodium form from Aldrich. The matrix was 8% cross-linked polystyrene and the matrix active group was sulfonic acid. The molecular structure of the cation-exchange resin is shown in Fig. 1, and the microscopic photography of the surface morphology of CER is shown in Photo 1. The cation-exchange resin was used as received. To immobilize ferrous ions on the CER, an aqueous solution of Fe^{2+} at 63 mg/100 mL was mixed with 2.4 g of resin to synthesize the catalyst, called the cation-exchange resin loaded with ferrous ions (referred to hereafter as CERF). The mixture was stirred for 24 h; the catalysts were then separated by filtration and thoroughly washed with deionized distilled water (DDW) until

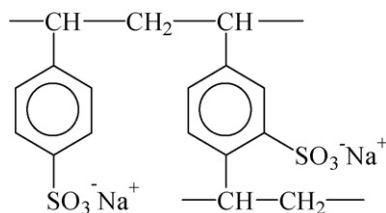


Fig. 1. The structural formula of the strongly basic cation-exchange resin in sodium form [19].

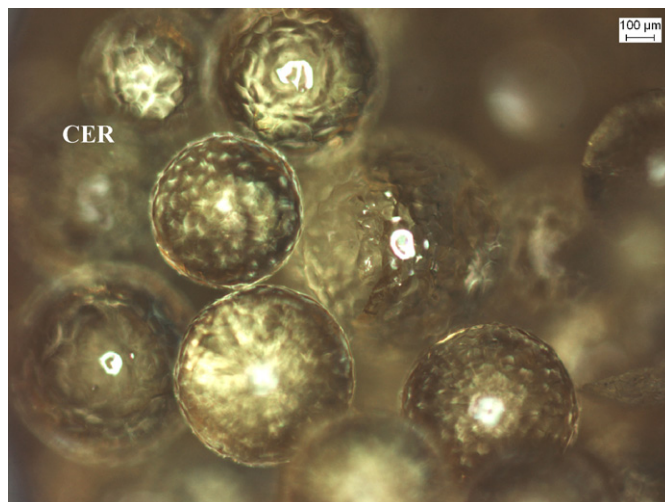


Photo 1. Microscopic image of the surface morphology of CER.

no ferrous ions were detected in the filtrate. After the sorption of Fe^{2+} , the surface of the resin turned from yellowish green to brown red. Photo 2 shows the microscopic surface morphology of CERF. To determine the amounts of Fe^{2+} exchanged onto the resin, the concentrations of aqueous ferrous ions were measured by a spectrophotometric method [12] before and after the ion-exchange process, and compared. Subsequently, the catalysts were dried and stored at room temperature in the desiccator, wrapped in aluminum foil. All of the spectrophotometric measurements were conducted by a Spectronic Genesys 2 UV–vis Spectrophotometer, and the photos of both CER and CERF were captured with an Olympus DP70 camera system operating on an Olympus BX60 microscope. The iron content of the catalysts was 26 mg Fe^{2+} /g CERF. The dominant species that conjugated with the cation-exchange resin (CER-Cl) in the solution should be the CER-Fe^{2+} , as indicated below:

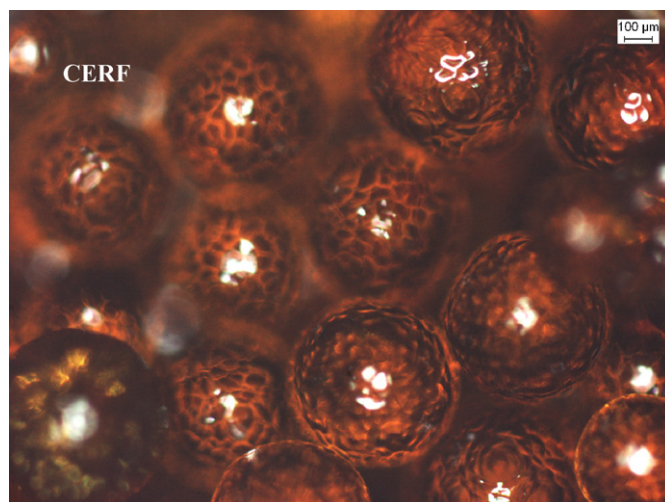
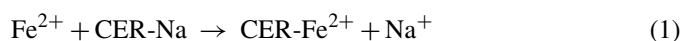


Photo 2. Microscopic image of the surface morphology of CERF.

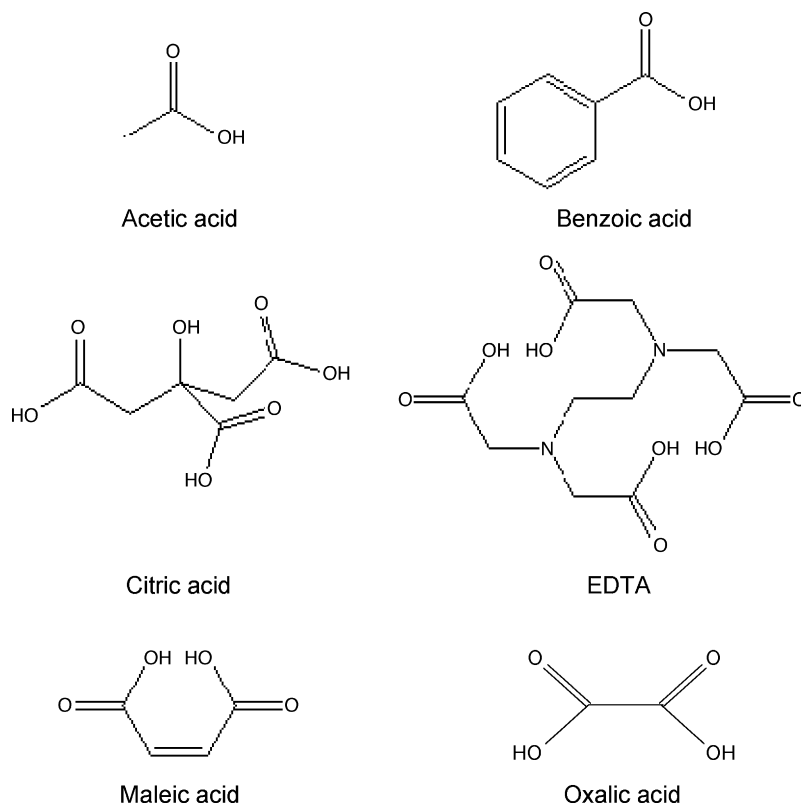


Fig. 2. The molecular structure of the organic acids.

2.2. Experimental procedures

In each experiment, 0.1 g of resin was immersed and stirred in DDW 1 day before the reaction to ensure that the resin was fully swollen. The initial solution pH was adjusted to 2.8 by diluted sulfuric acid. A certain amount of 2,4-D and diluted hydrogen peroxide (if necessary) was added to a 300 mL quartz reactor. If ligand was involved in the test, the solution of the ligand would be introduced to the reactor 15 min before the commencement of the reaction. Fig. 2 shows the molecular structure of the organic acids used in this study. The dark experiments were initiated by turning on the magnetic stirrer without using UV irradiation. For light-induced reactions, the irradiation source was four 350 nm phosphor-coated low-pressure mercury lamps placed inside an RPR-200 RayonetTM photochemical reactor equipped with a cooling fan. The initial concentration of the probe compound at time zero was determined from an unexposed sample. Likewise, the reactions were initiated by turning on the pre-warmed UV lamps and the magnetic stirrer simultaneously. The supported resin was easily separated from the aqueous phase by gravity, settling a few seconds after the stirrer had been turned off. Then, the sample was collected from the aqueous phase out of the reactor at pre-determined time intervals and methanol was added at a ratio of one to one (by volume) to quench the reaction. Finally, the target compounds were quantified by an LC analysis with a Restek column packed with pinnacle octylamine (5 μm , 0.46 cm \times 25 cm), in which, the mobile phase was a combination of 0.2% acetic acid and acetonitrile (50/50%, v/v) at a flow rate

of 1.0 mL/min. The oxalate concentration was measured through titration with permanganate of potassium.

2.3. Aqueous Fe concentration

The aqueous ferrous concentration (in both ionic and complex forms) was measured using a spectrophotometric method at 510 nm, because *o*-phenanthroline forms reddish complexes with Fe^{2+} but not with Fe^{3+} . The detection limit of this method for Fe^{2+} was 1.8×10^{-4} mM [13]. The aqueous ferric concentration (in both ionic and complex forms) was determined spectrophotometrically by a potassium thiocyanate method with a sensitivity of 0.25 μg for Fe^{3+} [12]. This method is used to determine the concentration of Fe^{3+} in the iron(II)/iron(III) mixture because iron(II) thiocyanate complexes are colorless.

3. Results and discussions

3.1. Catalyst performance

The catalytic activity of CERF for the removal of 2,4-D was studied in detail, and the results are shown in Fig. 3. The combinations of the following reagents or UV lamps, $[\text{H}_2\text{O}_2] = 1.0$ mM, $[\text{oxalate}] = 2.4$ mM, and $\text{UV}_\lambda = 350$ nm, established various operational conditions. In the control experiments, the degradation via CERF alone in the dark or under light was less than 1%. This indicates that the sorption of 2,4-D by CERF is infeasible and can be ignored, and that even

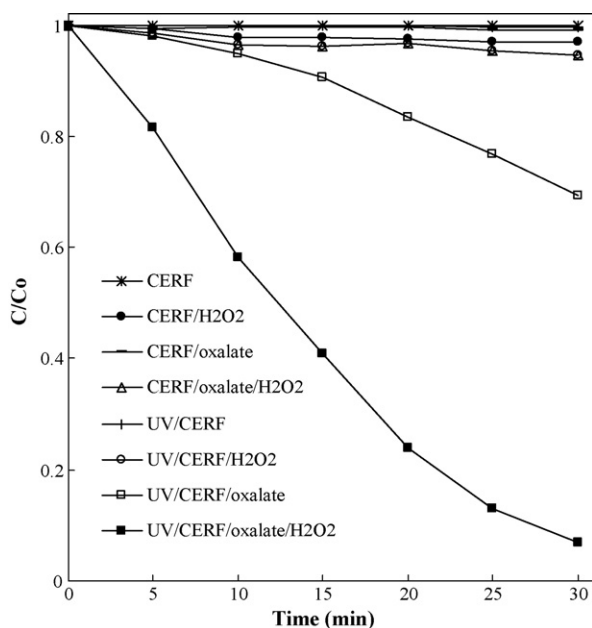


Fig. 3. The catalytic activity of CERF toward the removal of 0.5 mM of 2,4-D under different experimental conditions. Initial pH 2.8, $[\text{H}_2\text{O}_2] = 1.0$ mM, and $[\text{oxalate}] = 2.4$ mM.

UV light may not induce any reaction. The addition of the hydrogen peroxide system did not improve 2,4-D degradation under light illumination, in which a very small percentage of 2,4-D was transformed. CERF was activated by oxalate upon UV irradiation. The total removal percentage of 2,4-D by the UV/CERF/oxalate process was 31% after 30 min of reaction. When 1 mM of H_2O_2 was added to the system, the removal capacity increased by three times to 93%. It is believed that the aqueous Fe^{2+} reacts with hydrogen peroxide to produce hydroxyl radicals, accounting for the degradation of 2,4-D. The presence of ferrous ions in the aqueous phase implies that the ionic-bond between the immobilized ferrous ion and the surface of the resin is UV-light sensitive. Pulgarin et al. [7] used the light-induced dissolution of Fe^{3+} from the Fe-zeolite to catalyze the degradation of 4-nitrophenol. Hence, ferrous species may be released to the solution once the CERF is excited by UV, but only when oxalate is present. Previous studies found that the formation of iron-oxalate complex was stronger than the other complexation possibilities available in the solution [14,15]. It has been reported that oxalate facilitates the detachment of a central metal ion from different oxide minerals because the ligand brings electron density or negative charge into the coordination sphere of the central metal ion at the surface, lowering their Lewis acidity [16]. Our previous study showed that the photolysis of ferrous oxalate would generate hydrogen peroxide to induce photooxidation with another ferrous oxalate, yielding hydroxyl radicals [17]. This explained the modest reactivity of the UV/CERF/oxalate process (no spiked H_2O_2). On the other hand, the introduction of spiked H_2O_2 should further enhance the production of hydroxyl radicals and therefore, the transformation of 2,4-D. Nevertheless, the degradation taking place is light-induced and oxalate dependent.

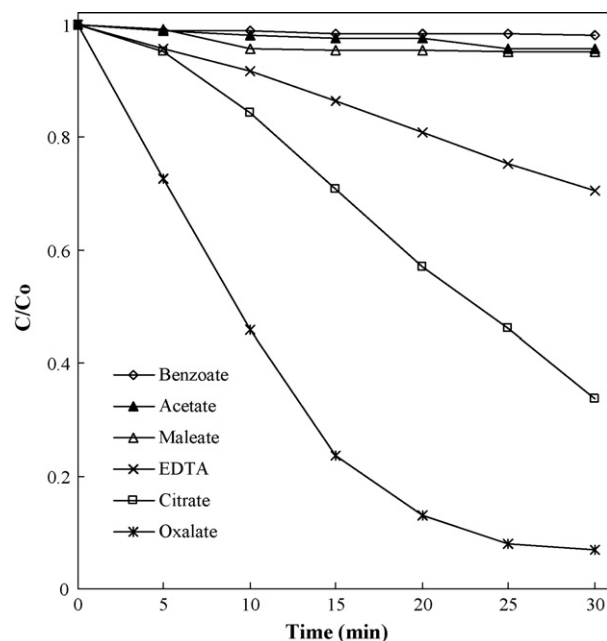


Fig. 4. The influence of ligand on the catalytic activity of CERF (0.1 g) at pH 2.8. $[\text{2,4-D}] = 0.5$ mM, $[\text{H}_2\text{O}_2] = 1.0$ mM, $[\text{ligand}] = 2.4$ mM.

To understand the effect of ligand on the catalytic activity of CERF, each ligand including acetate, benzoate, citrate, EDTA, maleate, and oxalate was irradiated with 2,4-D in a solution containing 1.0 mM of H_2O_2 and 0.1 g of CERF at an initial pH of 2.8 (Fig. 4) and 6.0 (Fig. 5), respectively. In our previous study [17], it was found that the ferrous complexes of citrate and EDTA catalyzed the decay of 2,4-D with or without the injection of spiked hydrogen peroxide upon UV illumination. However, only the ferrous oxalate showed acceleration and enhancement in the production of hydroxyl radicals. Kwan and Chu [17] reported that

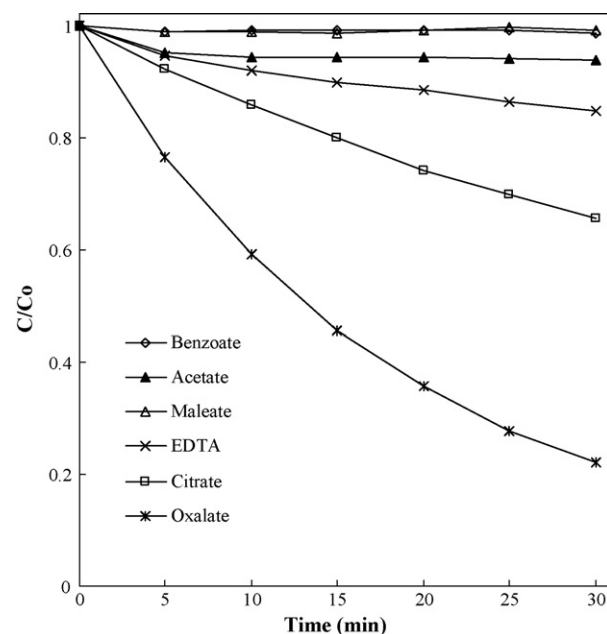
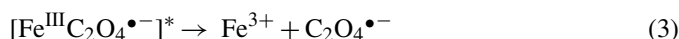
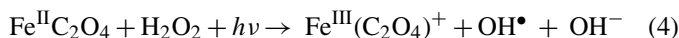


Fig. 5. The influence of ligand on the catalytic activity of CERF at pH 6.0. $[\text{2,4-D}] = 0.5$ mM, $[\text{H}_2\text{O}_2] = 1.0$ mM, $[\text{ligand}] = 2.4$ mM.

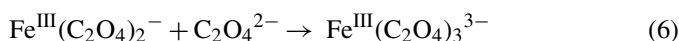
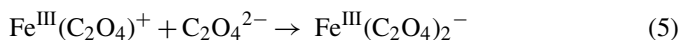
ferrous oxalate photooxidation in solution involves the initial excitation (Eq. (2)) via a metal-to-ligand charge-transfer transition, at which the electron goes from a metal-based orbital to a ligand-based orbital. Then, the dissociation of the excited complex yields a ferric ion and an oxalate radical ion (Eq. (3)).



In an oxygen-rich environment, the oxalate radical participates in the reduction of molecular oxygen to form the $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ pair for the generation of hydrogen peroxide. Consequently, ferrous oxalate is rapidly oxidized by H_2O_2 upon irradiation with UV, leading to the formation of hydroxyl radicals.



At high oxalate concentrations, i.e. $[\text{oxalate}] \gg [\text{Fe}^{2+}]$, $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^+$ may form photosensitive complexes with excess oxalate molecules (Eqs. (5) and (6)).



These ferrioxalate complexes would photolyze to another oxalate radical and Fe^{2+} to attain photo-Fenton reactions. In short, a hydroxyl radical attack initiated by the photogenerated hydrogen peroxide is responsible for the degradation of 2,4-D in the $\text{Fe}^{2+}/\text{oxalate}/\text{UV}$ system.

Hence, it is reasonable that lesser amounts of 2,4-D, 67% and 30%, were removed by the UV/CERF/ H_2O_2 process in the presence of citrate and EDTA, respectively. Nevertheless, acetate, benzoate, and maleate exhibited insignificant improvement in the disappearance of 2,4-D at both pHs. Similar phenomena have been observed in the dissolution of mineral oxides, at which ligands such as citrate, EDTA, and oxalate accelerate the detachment of metal ion while benzoate tends to inhibit the dissolution [16].

When the initial solution pH increased from 2.8 to 6.0, the total removal percentage of 2,4-D in the oxalate case was reduced to 78% and the performance of the citrate and EDTA systems was reduced by half. This indicates that the dissolution of ferrous ions and the ligand-mediated photochemical reaction are more favorable in an acidic environment. Given that UV/CERF/oxalate/ H_2O_2 was the fastest process observed in this study, such a combination would be selected for subsequent experiments.

3.2. Dissolution mechanism

It is known that oxalate and UV light are necessary to activate the catalyst. Mazellier and Sulzberger [18] reported that the adsorption of oxalate on the surface of the goethite ($\alpha\text{-FeOOH}$) is the first essential step in detaching Fe^{2+} from the crystal lattice into the solution.

To investigate the reaction mechanism of the CERF system, 0.1 g CERF was mixed with 6.0 mM of oxalate solution and

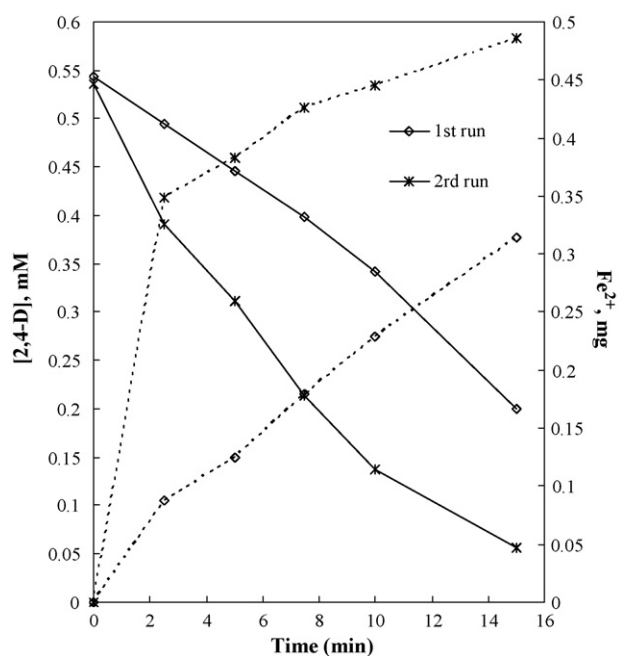


Fig. 6. Changes in the concentration of 2,4-D (mM) and ferrous ion (mg/225 mL) during the reactions.

stirred in the dark (data not shown). After an hour, the concentration of oxalate remained unchanged and the $[\text{Fe}^{2+}]$ in the solution was below its detection limit. This suggests that the pre-adsorption of oxalate on the surface of the resin is not an essential step for the dissociation of ferrous ions from the resin. Alternatively, the oxalate concentration dropped to 5.25 mM and a large amount of ferrous ions was detected in the solution after 15 min of illumination at 350 nm. It is thought that the ferrous species is released from the CERF as ferrous oxalate in UV light. Likewise, ferrous ions were detected in the cases of citrate and EDTA; therefore, these two ligands are believed to undergo a reaction mechanism similar to that of oxalate.

It was observed that the original light yellowish green CER (Photo 1) was turned into dark reddish brown CERF (Photo 2) when ferrous ions were exchanged onto the resin structure.

3.3. Recycling with CERF

Resin can be easily separated from the solution by filtration after the reaction, then recycled. To examine the efficiency of the reused catalyst, the irradiated resin was collected after the treatment of 2,4-D with the UV/CERF/oxalate/ H_2O_2 process and then thoroughly rinsed with DDW. The washed resin was added to another batch of reaction solution containing 2,4-D (0.5 mM), hydrogen peroxide (1 mM), and oxalate (2.4 mM). The concentrations of 2,4-D and amounts of Fe^{2+} measured during the first and second runs are compared in Fig. 6. The removal rate of 2,4-D with the reused CERF was found to be faster than that with the fresh CERF. This can be explained by the presence of a higher amount of ferrous ions in the second test, speeding up the production of hydroxyl radicals. As discussed earlier, the bonds between the resin and ferrous ions are sensitive to light so that the irradiated CERF should more readily release ferrous ions

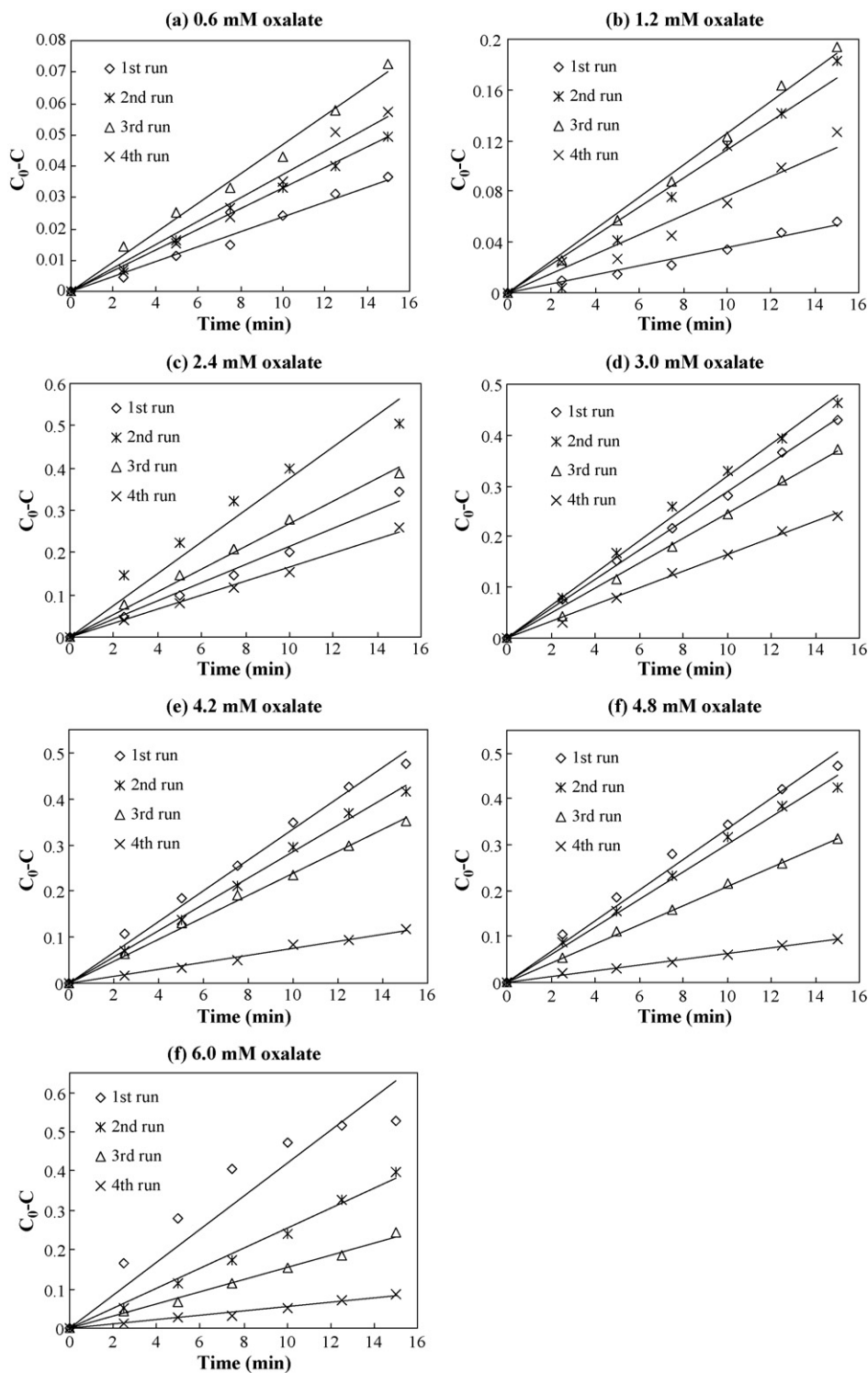


Fig. 7. Zero order plots for kinetics of 2,4-D in the presence of 0.1 g of CERF, 1.0 mM of H_2O_2 , and different amounts of oxalate (0.3–6.0 mM) under UV irradiation at 350 nm.

than the fresh CERF, where the activity depends on the amount of oxalate.

To study the influence of oxalate concentration on the recycling efficiency of the catalyst, the transformation of 2,4-D in four successive cycles of UV/CERF/ H_2O_2 processes in the presence of oxalate at concentrations ranging from 0.6 to 6.0 mM was conducted (i.e., the same CERF was reused three times).

Generally, the reactions seemed to follow the zero order decay, and the removal rate (k) of 2,4-D could be obtained from Eq. (8).

$$C_t = C_0 - kt \quad (7)$$

$$C_0 - C_t = kt \quad (8)$$

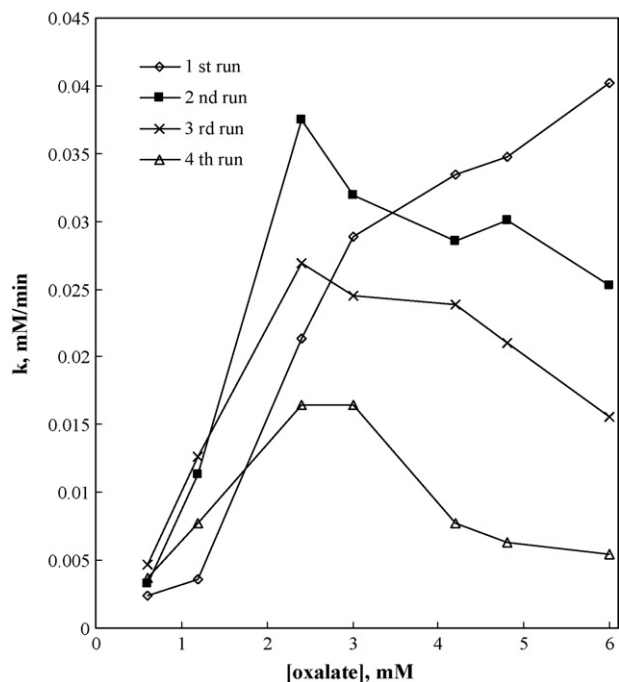


Fig. 8. The zero order rate constants (k) of the four consecutive runs are plotted as a function of time.

where C_t (M) is the concentration of 2,4-D in the system at time t (min), and C_0 (M) is the initial concentration of 2,4-D. The plots of the $(C_0 - C)$ values against the reaction time are displayed in Fig. 7. It can be seen that the curves are straight lines with very high r^2 values, except the first run with 6.0 mM of oxalate. The reaction with the addition of 6.0 mM oxalate was too fast to follow zero order decay, possibly due to overdose of oxalate. In spite of this, the good correlation indicates that the UV/CERF/oxalate/ H_2O_2 process can be described well by the zero order kinetics. It is worth noting that, at an oxalate concentration of below 4.2 mM, the catalytic activities of the CERF increased after recycling. In contrast, the performance of the CERF degraded slowly after each test when the [oxalate] was equal to or above 4.2 mM.

Fig. 8 illustrates the relationship between the reaction rate and the oxalate concentration, in which k_1 , k_2 , k_3 , and k_4 represent the decay rates of the first, second, third, and fourth runs, respectively. In the first runs, the rate constants increased sharply as the concentration of oxalate was increased to 3.0 mM, then gradually afterward. This suggests that the heterogeneous degradation is strongly dependent on the oxalate concentration.

With reference to the removal rates (k values), it is difficult to determine the optimum oxalate concentration for the CERF system in four consecutive cycles of runs. For practical purposes, a model is derived to help define the recycling efficiency of the catalyst in the UV/CERF/oxalate/ H_2O_2 process. This model is based on the reaction rate to predict the total mass of 2,4-D that can be transformed at any reaction time and at any cycle. By multiplying the solution volume at time t (V_t) to both sides of Eq. (8), the number of moles of 2,4-D removed at that time can

be obtained from Eq. (9):

$$(C_0 - C_t)V_t = ktV_t = \text{moles of 2, 4-D removed} \quad (9)$$

The removal mass of 2,4-D (m_t) at reaction time = t min can be obtained when Eq. (9) is multiplied by the molecular weight of 2,4-D (MW),

$$m_t = (C_0 - C_t)V_tMW = ktV_tMW \quad (10)$$

The removal masses of 2,4-D in the first, second, third, fourth and n th runs are shown in the following equations:

$$m_1 = (C_0 - C_1)V_{t1}MW = k_1t_1V_{t1}MW \quad (11)$$

$$m_2 = (C_0 - C_2)V_{t2}MW = k_2t_2V_{t2}MW \quad (12)$$

$$m_3 = (C_0 - C_3)V_{t3}MW = k_3t_3V_{t3}MW \quad (13)$$

$$m_4 = (C_0 - C_4)V_{t4}MW = k_4t_4V_{t4}MW \quad (14)$$

$$m_n = (C_0 - C_n)V_nMW = k_nt_nV_nMW \quad (15)$$

where n is the number of times that the catalyst CERF is used. The summation of the removal mass of each run leads to the proposed model:

$$\begin{aligned} \text{Cumulative mass} &= \sum_{i=1}^n (m_1 + m_2 + m_3 + \dots + m_n) \\ &= MW \sum_{i=1}^n (k_it_iV_i) \end{aligned} \quad (16)$$

The average mass of 2,4-D removed out of several runs using recycled CERF is given by dividing Eq. (16) by the number of runs:

$$\begin{aligned} \text{Average mass} &= \frac{\sum_{i=1}^n (m_1 + m_2 + m_3 + \dots + m_n)}{n} \\ &= \frac{MW \sum_{i=1}^n (k_it_iV_i)}{n} \end{aligned} \quad (17)$$

To verify the proposed model, the experimental data and predicted curves are compared in Fig. 9, where the curves show a good fit with the experimental data. As seen from the raw data, the removal mass of 2,4-D increased as the concentration of oxalate was increased in the first run. At 2.4 mM of initial oxalate concentration, the further addition of oxalate exhibited only an insignificant contribution to the removal of 2,4-D in the second run, but may retard the degradation in the third and fourth runs. This trend can also be seen in the average removal mass of 2,4-D. Out of the four runs (i.e., four equal portions of 2,4-D were inputted to the system), the maximum amount of 2,4-D removed was found to be 75.4% at [oxalate] = 3.0 mM. However, the optimal concentration of oxalate should be 2.4 mM because a similar total removal percentage (74.7%) can be achieved while less oxalate was used, which is probably more cost-effective in real applications.

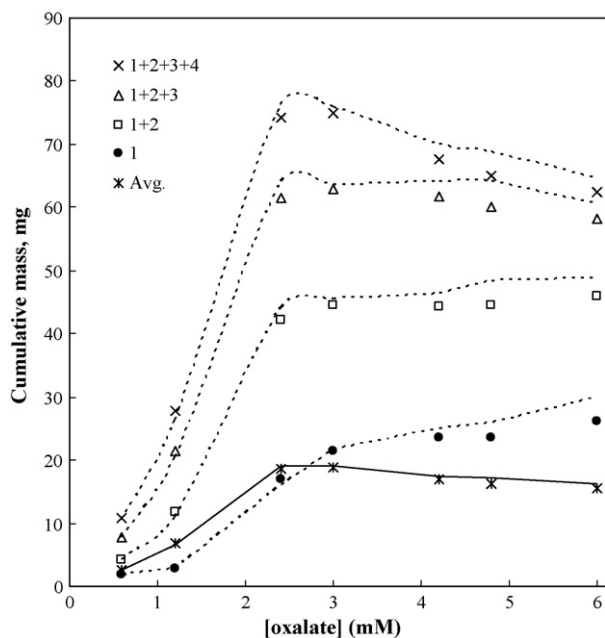


Fig. 9. Comparison of the experimental data (symbols) with the model calculation (dashed lines). The solid line is the average of the cumulative mass.

4. Conclusions

The cation-exchange resin loaded with ferrous ion (CERF) is capable of catalyzing and enhancing the decay of organic pollutants. The catalytic effectiveness of CERF is activated by the presence of organic ligands such as citrate, oxalate, and EDTA as well as UV light. An attack by hydroxyl radicals is the pathway to the degradation of 2,4-D in the CERF systems. This catalyst can be easily settled and collected after the reaction for recycling. The removal rate exhibits a strong dependence on oxalate concentration. The performance of the reused catalyst is better than that of the fresh catalyst in some situations, but the optimal concentration of oxalate should be 2.4 mM. Cation-exchange resin has been employed in real operations to remove Fe^{2+} and Fe^{3+} from effluents with high iron contents, and such Fe-loaded resin may end up as solid waste.

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References

- [1] J.M. Montgomery, *Water Treatment Principles and Design*, John Wiley & Sons, New York, 1985.
- [2] M. Streat, P.A. in, A. Williams, Dyer (Eds.), *Advances in Ion Exchange for Industry and Research*, The Royal Society of Chemistry, Cornwall, UK, 1998, pp. 3–11.
- [3] E. Marañón, Y. Fernández, F.J. Suárez, F.J. Alonso, H. Sastre, *Ind. Eng. Chem. Res.* 39 (2000) 3370.
- [4] G. Kyriakopoulos, D. Doulia, E. Anagnostopoulos, *Chem. Eng. Sci.* 60 (2005) 1177.
- [5] F. Bagnoli, A. Bianchi, A. Ceccarini, R. Fuoco, S. Giannarelli, *Microchem. J.* 79 (2005) 291.
- [6] L. Chirchi, A. Ghorbel, *Appl. Clay Sci.* 21 (2002) 271.
- [7] C. Pulgarin, P. Peringer, P. Albers, J. Kiwi, *J. Mol. Catal. A: Chem.* 95 (1995) 61.
- [8] K. Fajerweg, H. Debellefontaine, *Appl. Catal. Environ.* 10 (1996) L229.
- [9] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, *Catal. Today* 55 (2000) 61.
- [10] M. Neamțu, C. Zaharia, C. Catrinescu, A. Yediler, M. Macoveanu, A. Kettrup, *Appl. Catal. B* 48 (2004) 287.
- [11] E.V. Kuznetsova, E.N. Savinov, L.V. Vostrikova, V.N. Parmon, *Appl. Catal. B* 51 (2004) 165.
- [12] A.I. Vogel, *Vogel's Qualitative Inorganic Analysis*, seventh ed., Longman, Harlow, 1996.
- [13] H. Tamura, K. Goto, T. Yotsuyan, M. Nagayama, *Talanta* 21 (1974) 314.
- [14] V. Nadtochenko, J. Kiwi, *J. Chem. Soc., Faraday Trans.* 93 (14) (1997) 2373.
- [15] A. Bozzi, T. Yuranova, J. Mielczarski, J. Kiwi, *New J. Chem.* 28 (2004) 519.
- [16] W. Stumm, *Chemistry of the Solid–Water Interface*, Wiley-Interscience, New York, 1992.
- [17] C.Y. Kwan, W. Chu, *Chemosphere* 67 (2007) 1601.
- [18] P. Mazellier, B. Sulzberger, *Environ. Sci. Technol.* 35 (2001) 3314.
- [19] J. Korkisch, *Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry*, vol. I, CRC Press, Boca Raton, Florida, 1989.