

# Effect of ferrioxalate-exchanged resin on the removal of 2,4-D by a photocatalytic process

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Received 18 October 2005; received in revised form 10 March 2006; accepted 16 March 2006

Available online 22 May 2006

## Abstract

A new approach combining sorption and an advanced oxidation process has been developed for wastewater treatment.  $\text{Fe}^{3+}$  is incorporated into a cationic resin with or without the oxalate to afford two types of catalyst: ferrioxalate-exchanged resin (FOR) and ferric-exchange resin (FR), respectively. The removal of herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) by different resin-mediated processes including sole FOR, FOR/ $\text{H}_2\text{O}_2$ , UV/FOR, UV/R/ $\text{H}_2\text{O}_2$ , UV/FR/ $\text{H}_2\text{O}_2$ , UV/FOR/ $\text{H}_2\text{O}_2$  was investigated and compared. The optimal result was obtained in the treatment of 2,4-D with FOR when the system was irradiated at 350 nm with 1 mM  $\text{H}_2\text{O}_2$ ; 80% of the 2,4-D disappeared after an operation time of 60 min. In addition, two other organic pollutants, atrazine (ATZ) and 2-chloroaniline (2-CIA), were used as the starting materials to test the selectivity of the solid catalyst. The FOR was found to be a non-selective catalyst; pre-sorption on the surface of the resin was not an essential step for the photocatalysis. Sorption and radical oxidation were found to be the major reaction pathways for the removal of 2,4-D. The recycling of the FOR was easy and feasible.

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**Keywords:** 2,4-D; Ion exchange; Resin; Oxalate; Photocatalysis; Sorption

## 1. Introduction

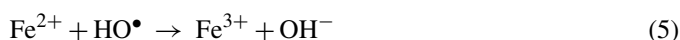
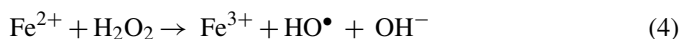
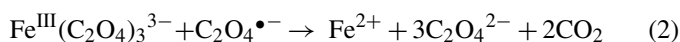
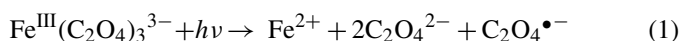
Ion-exchange resin is extensively used to remove ions of metal, and inorganic and organic compounds from wastewater and industrial effluents. For example, anion exchange resins were applied in the galvanizing process to remove Fe(III) and Zn(II) from acid pickling baths [1], where  $\text{Fe}^{3+}$  is adsorbed as  $\text{FeCl}_4^-$  on resins in a concentrated HCl media (12 M) [2]. To minimize the use of strong acid in a process, metal ions can be effectively sorbed on anion exchange resin through the formation of anionic complexes with chelating agents. For example,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  could be taken up by anion exchange resins in the form of Fe- and Cr-oxalate complexes [3]. In addition to inorganic ions, some carbonaceous resins are effective in removing organic compounds including phenols, pesticides, and some other chlorinated compounds. For instance, phenols were

efficiently adsorbed on non-ionic XAD-4 resin under acidic conditions where adsorption behavior was highly dependent on the solution pH because of the distribution of phenol compounds [4]. Moreover, an XAD-2 resin column was utilized in a dry/wet deposition sampler to extract 2,4-D from the particulate or rain samples, and to determine the ambient concentration of 2,4-D in the atmosphere and in wet precipitation [5,6]. Apart from sorption, resin may also immobilize oxidants for wastewater treatment. Fiorentino et al. [7] demonstrated that olive oil mill wastewater could be treated with two oxidation methods by using either periodate-supported anion-exchange resin or ferric-chloride-supported cation-exchange resin. They reported that the oxidation with the latter reagent was more efficient, resulting in a decrease of COD by 53% and a greater reduction of phenols. Given that the solid catalyst is easily handled, separated, and recycled, it is beneficial to use sorption and chemical oxidation together in treating wastewater. Aromatic amines have been shown to be sorbed on the anion-exchange resin and then oxidized by metal-oxalate complexes incorporated into the resin [8,9]. Moreover, the removal of 2-chlorophenol through the combination of adsorption on an organo-clay and  $\text{TiO}_2$ -based

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photocatalysis was reported to be efficient and cost-effective [10].

Ferric ions undergo spontaneous-chelation with oxalate to form ferrioxalate complexes bearing either positive or negative charges, depending on the number of oxalate ligands bonded to the metal ion. The possible complexes are  $\text{Fe}(\text{C}_2\text{O}_4)^+$ ,  $\text{Fe}(\text{HC}_2\text{O}_4)^{2+}$ ,  $\text{Fe}(\text{C}_2\text{O}_4)_2^-$  and  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ , of which the Fe speciation depends on pH and the concentration of oxalate [11]. The ferrioxalate/ $\text{H}_2\text{O}_2$  system is a promising and effective advanced oxidation process (AOP) to photodegrade many organic contaminants including atrazine, 2,4-dichlorophenol (2,4-DCP), and dichloroacetic acid [12,13] in homogeneous systems. The photolysis of ferrioxalate indirectly generates hydroxyl radicals ( $\text{HO}^\bullet$ ), which through Fenton's reaction efficiently oxidize a great variety of organic compounds with a higher quantum yield (see Eqs. (1–5)) [11]:



The purpose of this project is to investigate the feasibility of using a pre-combined approach of sorption and AOP in one step for wastewater treatment. A cationic resin is exchanged with  $\text{Fe}^{3+}$  in the absence of or in the presence of oxalate to form a solid catalyst. The application of these iron-loaded resins on the removal of 2,4-D in the presence of hydrogen peroxide and UV light is examined. The reaction mechanism is investigated as well.

## 2. Methodologies

### 2.1. Materials

Atrazine (ATZ), 2,4-D, 2,4-dichlorophenol (2,4-DCP), ferrous sulfate-7-hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), and ferric sulfate hydrate were purchased from Riedel-de Haen, while 2-chloroaniline (2-CIA) was obtained from Fluka. Hydrogen peroxide (30%) and potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) were obtained from the British drug houses (BDH). All stock solutions were prepared in deionized and distilled water (DDW). Ferrous sulfate and ferric sulfate solutions were freshly made in diluted sulfuric acid. High-performance liquid chromatography (HPLC) grade acetonitrile (ACN), methanol, and acetic acid were bought from LAB-SCAN. All chemicals were used as received, without undergoing further purification. The anion-exchange resin used in this work was Amberlite IRA-416 in the chloride form (spherical-shaped beads of quaternary ammonium styrene divinylbenzene copolymer) from Fluka. Fig. 1 presents a structural formula of the strongly basic anion-exchange resin (type II) in the chloride form.

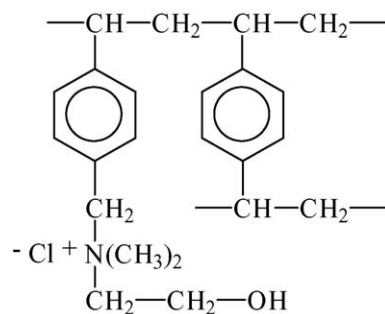


Fig. 1. The structural formula of the strongly basic anion-exchange resin (type II) in chloride form [14].

### 2.2. Catalyst preparation and characterization

Before being used, the anion-exchange resin was thoroughly washed with DDW and then dried in a desiccator at room temperature. The solid catalysts were prepared by introducing 3 g of the resin into 100 mL of aqueous solutions containing ferric sulfate and oxalate (Ox) at selected  $[\text{Fe}^{3+}]:[\text{Ox}]$  ratios: 1:0, 1:0.5, 1:1.5, 1:2.5, and 1:5. The mixture was stirred for 24 h, and then the catalysts were separated by filtration and thoroughly washed with DDW until no ferric sulfate and oxalate were detected in the washing solutions. To determine the amounts of ferric ions and oxalate exchanged onto the resin, the ferric and oxalate concentrations in the filtrates were measured by a spectrophotometric method and a potassium permanganate titration method, respectively [14]. Subsequently, the catalysts were dried and stored at room temperature in the desiccator, wrapped with aluminum foil. All of the spectrophotometric measurements were conducted by a Spectronic Genesys 2 UV-visible spectrophotometer.

After the sorption of  $\text{Fe}^{3+}$  or ferrioxalate, the surface of the resin became yellowish, and its color became deeper as the concentration of oxalate increased. The characteristics of the ferric-exchanged resin and ferrioxalate-exchanged resin are summarized in Table 1. The FR has the lowest Fe content in the resin which indicates the uptake of ferric ions by anion-exchange resin was not feasible due to the repulsion between the resin's cationic functional group and  $\text{Fe}^{3+}$ . When the [Ox] was increased slightly to 5.625 mM (i.e. FOR-0.5), the Fe content in resin increased dramatically by 18%. The Fe and Ox contents of the FOR generally increased as the initial oxalate concentration increased, but the exchange process started to level off after the  $[\text{Fe}]:[\text{Ox}]$  ratio reached 1:2.5 (i.e. FOR-2.5).

### 2.3. 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 or 3.0 by sulfuric acid. The reactor was a 300 mL quartz beaker covered with aluminum foil to minimize the unnecessary exposure of the mixture to light. A certain amount of the substrate and diluted hydrogen peroxide (if necessary) were added to the reactor. The dark experiments were initiated by turning on the magnetic stirrer without using UV irradiation. For light-induced reactions,

Table 1  
Characteristics of the Fe-exchanged resin (FR) and FeOx-exchanged resin (FOR)

Type	[Fe]:[Ox] ratio <sup>a</sup>	Initial Fe mass <sup>b</sup> (mg)	Final Fe mass <sup>c</sup> (mg)	Mass of Fe loaded on resin (mg)	Fe <sup>III</sup> content (mg/g resin)	Initial Ox mass <sup>b</sup> (mg)	Final Ox mass <sup>c</sup> (mg)	Mass of Ox loaded on resin (mg)
FR	1:0	62.83	61.44	1.40	0.47	0	0	0
FOR-0.5 <sup>a</sup>	1:0.5	62.83	36.04	26.79	8.85	49.52	26.41	23.11
FOR-1.5	1:1.5	62.83	14.60	48.23	15.82	148.56	30.81	117.75
FOR-2.5	1:2.5	62.83	0.82	62.01	20.25	247.60	30.81	216.79
FOR-5.0	1:5.0	62.83	0.31	62.52	20.41	495.20	214.01	281.19

<sup>a</sup> [Fe]:[Ox] molar ratio is the ratio of the initial concentrations of Fe and oxalate before the ion-exchange process. For each run, 100 mL of 11.25 mM Fe<sup>3+</sup> solution was stirred with 3.0 g of pretreated resins with or without oxalate.

<sup>b</sup> Initial mass is the mass measured before the ion-exchange process.

<sup>c</sup> Final mass is the mass measured after the ion-exchange process.

the irradiation source was four 350 nm phosphor-coated low-pressure mercury lamps placed inside an RPR-200 Rayonet<sup>TM</sup> 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 can easily be separated from the aqueous phase by gravity settling a few seconds after the stirrer is 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  $\mu$ m, 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. All of the experiments were conducted in duplicate. The variation of the duplicate samples was within 10% for each test and the mean of the two results was used to plot the curve in the figures.

#### 2.4. Aqueous Fe concentration

The aqueous ferrous concentration (in both ionic or complex forms) was measured using a spectrophotometric method at 510 nm, as *o*-phenanthroline forms reddish complexes with Fe<sup>2+</sup> but not with Fe<sup>3+</sup>. The detection limit of this method for Fe<sup>2+</sup> was  $1.8 \times 10^{-4}$  mM [15]. The aqueous ferric concentration (in both ionic and complex forms) was determined spectrophotometrically by a potassium thiocyanate method with a sensitivity of 0.25  $\mu$ g for Fe<sup>3+</sup> [16]. This method was used to determine the concentration of Fe<sup>3+</sup> in the iron(II)/iron(III) mixture because the iron(II) thiocyanate complex is colorless.

#### 2.5. Regeneration of resin

To verify the performance of resin regeneration, the recovery of adsorbed 2,4-D out of the used resin was examined by regenerating the resin with sodium chloride because chloride is the counterion of the resin. In this study, 225 mL of 1 mM 2,4-D was mixed for an hour with 0.1 g of unmodified resin. The used resin was then separated from the solution by vacuum filtration, followed by a few rinses with DDW. Next, the separated resin was immersed in 225 mL of 0.5 M NaCl solution and kept

stirring for 24 h at room temperature. The variation of 2,4-D in the solution was determined by LC analysis. 2,4-D was readily desorbed from the resin and above 90% of the 2,4-D was recovered after 3 h of contact with the NaCl solution (i.e. data not shown). In an independent blank test (no NaCl), no 2,4-D was detected when resins were regenerated in DDW. The maximum recovery efficiency of this method was 99% and, therefore, it was used to recover any 2,4-D sorbed by the resins in the further experiments, if necessary.

### 3. Results and discussions

#### 3.1. Catalyst performance

The probe 2,4-D was irradiated in solutions containing unmodified resin, FR, FOR, or blank at 350 nm with the same initial concentration of 2,4-D and hydrogen peroxide of 1.0 mM. It can be seen from Fig. 2 that less than 2% of the 2,4-D was

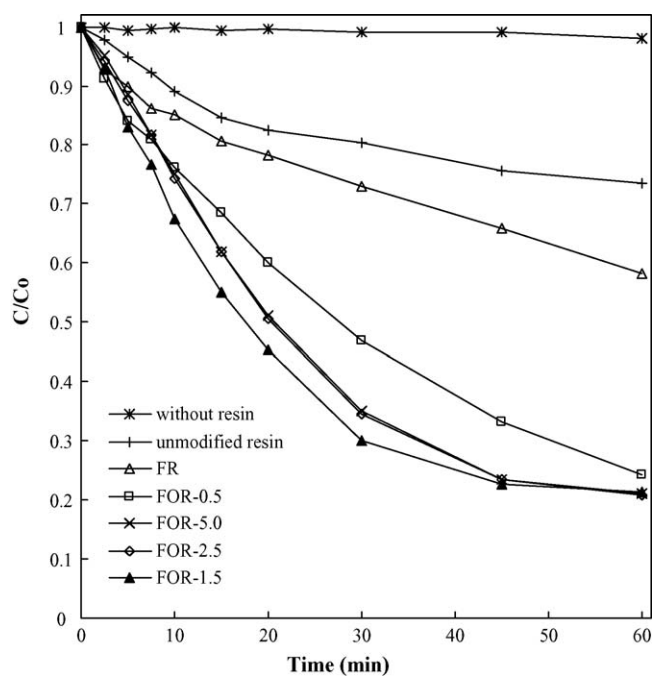


Fig. 2. Decay ratio ( $C/C_0$ ) of the removal of 2,4-D by different resins (0.1 g/225 mL) as a function of time in the presence of 1 mM of hydrogen peroxide and UV light (350 nm). Initial pH 2.8.

transformed by UV/H<sub>2</sub>O<sub>2</sub> in the absence of resin. The poor performance may be attributed to the low photo-reactivity of 2,4-D and hydrogen peroxide toward 350 nm UV light. This suggests direct photolysis and radical oxidation induced by the photodecomposition of hydrogen peroxide are not the major pathways responsible for the degradation of 2,4-D in such a UV-assisted system. When 0.1 g of unmodified resin was added to the system, the overall removal of 2,4-D increased by 14 times, likely due to the sorption of 2,4-D by the resin. It is known that the speciation of 2,4-D varies according to the solution pH; the distribution of the dissociated (ionic) and undissociated (molecular) forms of 2,4-D depends on the acid dissociation constant ( $pK_a$ ) and the solution pH. The 2,4-D has a  $pK_a$  of 2.9 [17], so about 56% of 2,4-D initially existed in anionic form at a pH of 2.8 (our reaction condition). Therefore, the negatively charged 2,4-D would be attracted to the cationic functional groups on the resin. As the resin was modified to FR, the ferric ions immobilized in the ferric-exchanged resin may help to degrade 2,4-D by initiating a photo-Fenton-like reaction, so the removal efficiency was further increased. It was interesting to find that the removal of 2,4-D was further enhanced by using the ferrioxalate-exchanged resins (FOR). After 60 min of treatment, 80% of the 2,4-D was removed in the reactions associated with the FOR-0.5, 1.5, 2.5, and 5.0, while the reaction rate was optimized at FOR-1.5. This is because the excess oxalate in FOR-2.5 and 5.0 may occupy exchange sites on the surface of the resin, and thus the reaction rate was reduced. The FOR-1.5 was therefore used exclusively for the remaining experiments in this study and is referred to as FOR from now on.

To study the selectivity of the FOR based on its sorbing property, a nonionic and a cationic compound – atrazine (ATZ) and 2-chloroaniline (2-CIA) at pH 2.8 – were treated with the FOR, and the results are shown in Fig. 3. After 60 min of mixing with the FOR in the dark (to ensure that no photoreaction was involved), more than 95% of ATZ and 2-CIA remained in the solutions. This reveals that the sorption of nonionic and cationic compounds by FOR (anion-exchange) is insignificant and can be neglected. In contrast, when hydrogen peroxide and UV light were both present in the solution, 2-CIA and ATZ were completely degraded in 30 and 45 min, respectively. This suggests that the FOR is a non-selective catalyst and that pre-sorption on the surface of the resin is not an essential step for completing the reaction.

### 3.2. Reaction mechanism

To further investigate the reaction mechanism of the FOR system, the treatment of 2,4-D by four different FOR-related alternatives including sole FOR, FOR/H<sub>2</sub>O<sub>2</sub>, FOR/UV, and FOR/UV/H<sub>2</sub>O<sub>2</sub> was conducted under the same operational conditions at 1 mM [H<sub>2</sub>O<sub>2</sub>] (if applicable). The removal percentages of 2,4-D as a function of the reaction time for each system are presented in Fig. 4(a). The generation of 2,4-dichlorophenol (2,4-DCP), the main oxidation intermediate of 2,4-D upon the attack of hydroxyl radicals [18], was identified and quantified as illustrated in Fig. 4(b); hence, its presence may be an indicator of radical oxidation. The aqueous concentrations of Fe<sup>2+</sup> and

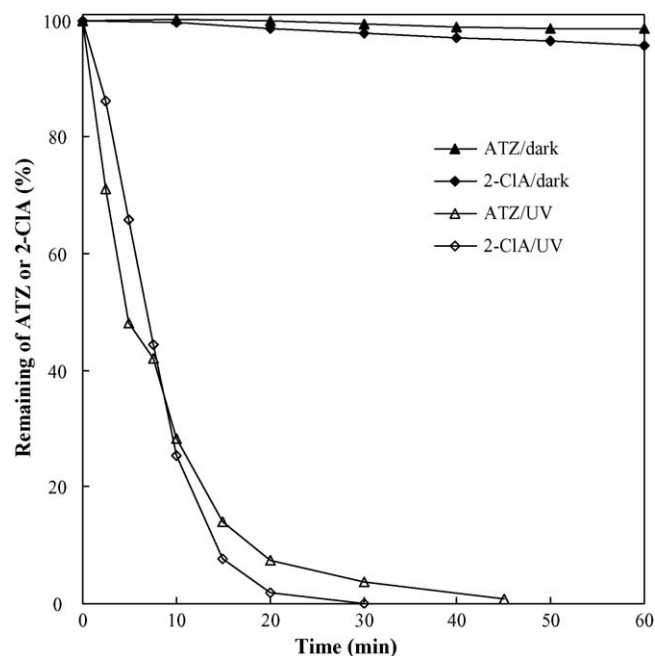


Fig. 3. Disappearance of 25.7  $\mu$ M ATZ and 63.2  $\mu$ M 2-CIA in the presence of 0.1 g of FOR (FOR-1.5) at an initial pH of 3. The closed markers refer to the experiments conducted in the dark and the open markers represent the experiments under UV irradiation at 350 nm with 1 mM of H<sub>2</sub>O<sub>2</sub>.

Fe<sup>3+</sup> were monitored as well during the reaction, as shown in Fig. 4(c), where the total Fe<sup>3+</sup> in the resin was 1.6 mg. From Fig. 4(a), the removal percentage of 2,4-D by the sole FOR (in the dark) was 27% in the absence of hydrogen peroxide. To verify the sorption effect, the FOR was separated from the aqueous phase after the reaction and rinsed with DDW. The resin was then regenerated with 0.5 M NaCl to determine the amount of 2,4-D desorbed in the resin (i.e. which is equal to the amount of 2,4-D removed by sorption). The disappearance of 2,4-D by either sorption or other reactions was analyzed in Fig. 5. For the sole FOR system, all the removed 2,4-D can be recovered from the resin after the regeneration, indicating that sorption was the dominant removal pathway. It should be noted that small amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> (~0.1 mg) were present in the solution before the reaction started. Such a minor leaching and occurred only during the swelling process, and not during the reaction, as their concentration did not change significantly.

When 1 mM of hydrogen peroxide was added to the system (i.e. FOR/H<sub>2</sub>O<sub>2</sub>), the observed removal of 2,4-D increased by a few percentages. In addition to the physical sorption, other chemical reactions may be present. The first possibility is the direct oxidation of 2,4-D by H<sub>2</sub>O<sub>2</sub>, which was suggested to be a slow process [19]. Fenton's and/or Fenton-like reactions could be insignificant as the aqueous [Fe<sup>3+</sup>] and [Fe<sup>2+</sup>] concentrations remained very low throughout the reaction (Fig. 4(c)). Hence, the major intermediate 2,4-DCP (from the decay of 2,4-D) was not detected because the two minor oxidation pathways were too slow to accumulate enough 2,4-DCP to a detectable level. As such, physical sorption is the dominant removal mechanism of 2,4-D in the sole FOR and FOR/H<sub>2</sub>O<sub>2</sub> systems.



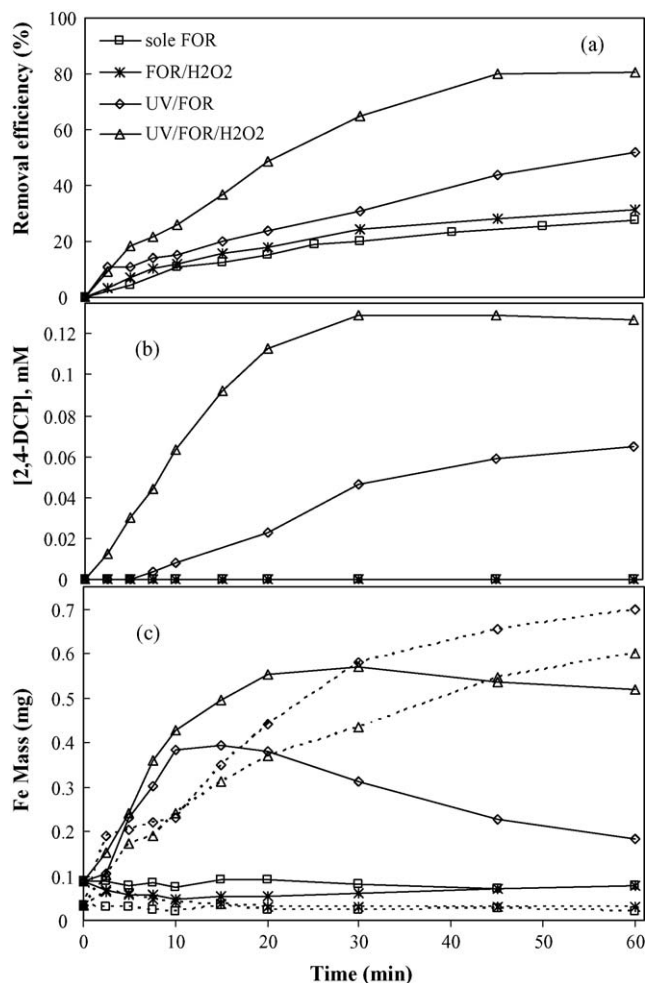


Fig. 4. (a) Removal of 2,4-D as a function of time under various resin treatments and two experimental conditions were monitored; (b) production of 2,4-DCP as the primary reaction intermediate; (c) concentrations of Fe<sup>2+</sup> (dash line) and Fe<sup>3+</sup> ions (solid line) in the solution. The legends for figure (a) are also eligible for figures (b) and (c). [H<sub>2</sub>O<sub>2</sub>] = 1 mM.

The introduction of UV light to sole FOR or FOR/H<sub>2</sub>O<sub>2</sub> had a more significant effect than dark processes on the removal of 2,4-D (see Fig. 4(a)). At the same time, much less 2,4-D could be recovered from the resin in the UV-induced processes, particularly when hydrogen peroxide was added (Fig. 5). It is obvious

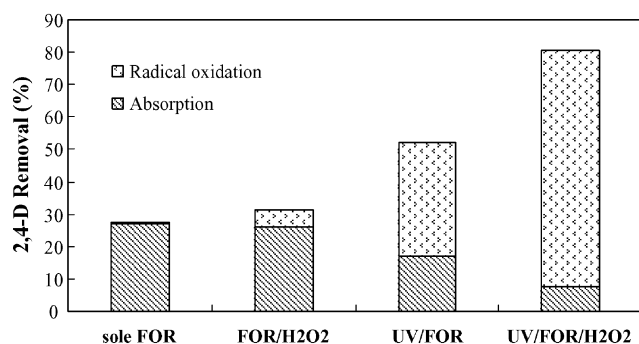


Fig. 5. Distribution of 2,4-D removed by sorption and the radical oxidation pathways in the FOR related systems. The H<sub>2</sub>O<sub>2</sub> concentration used was 1 mM.

that physical sorption became less substantial and some other chemical reactions became dominant, and therefore enhanced the process. UV radiation was clearly responsible for such an improvement in the decay rate. As mentioned above, 2,4-D was inactive toward direct photolysis at 350 nm or hydrogen peroxide so that these two pathways should have lower contribution in this respect. Another possibility could be the internal oxidation; for example, the heterogeneous oxidation of aromatic amines with metal–oxalate complexes in the solid phase had been reported [8,9]. To verify this, 0.3 g of FOR was stirred with 2,4-D for an hour without adjustment of pH. The resin was then rinsed and separated into three equal portions. The first portion of resin was regenerated with 0.5 M NaCl to determine the initial amount of 2,4-D that had been retained in the solid phase. The second and third portions were irradiated in 1 mM H<sub>2</sub>O<sub>2</sub> solutions for 15 and 30 min, respectively. The exposed resins were regenerated to determine the mass of 2,4-D left in the resins upon UV irradiation. The results showed that 17.5% and 22% of the 2,4-D sorbed on the resin were transformed in the 15 and 30 min reactions, respectively (data not shown). However, the internal oxidation was found to be a minor pathway because less than 20% of 2,4-D was sorbed and present in the solid phase.

The major difference between the light and dark processes was the iron level in the aqueous phase, where the iron concentrations were comparatively higher in the UV-assisted systems. This implies that the ionic-bonds between the ferrioxalate complexes and the surface of the resin is UV-light sensitive and that ferrioxalate or ferrous ions (if a surface reaction occurs, Eqs. (1) and (2)) could be released to the solutions when the FOR resin is irradiated by UV. From Fig. 4(c), the Fe species was released to the solution once the FOR resin absorbed UV light. Ferrous ions were then detected and accumulated in the solution due to the reduction of ferric ions in the complexes (see Eqs. (1) and (2)). It is known that Fe<sup>2+</sup> reacts with hydrogen peroxide to give ferric and hydroxyl radicals through the Fenton's reaction. This explains why the removal of 2,4-D by UV/FOR can be greatly accelerated by adding hydrogen peroxide. Another piece of evidence supporting radical oxidation is the high yield of 2,4-DCP (resulting from oxidation by hydroxyl radicals) in the UV-induced reactions (see Fig. 4(b)). The concentration of 2,4-DCP produced in the UV/FOR/H<sub>2</sub>O<sub>2</sub> process was two to three times higher than that in the UV/FOR. In addition, the former increased sharply in the beginning of the reaction and leveled off afterwards, justifying the deficiency of the consumable oxidant (i.e. hydrogen peroxide) at the end of the reaction.

Given that 2,4-DCP was also detected in the UV/FOR system without the use of H<sub>2</sub>O<sub>2</sub>, radical oxidation should not be excluded from the possible reaction pathways. It is believed that the ferrioxalate complexes may dissociate from the surface of the resin into the solution upon UV absorption. Then, the photolysis of ferrioxalate only acts as a source of hydroxyl radicals. It is known that the photochemical reduction of ferrioxalate leads to the formation of Fenton's reagent, Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> [20,21]. A longer time is required to form hydroxyl radicals because the above reaction is slower than the straight Fenton's process. A

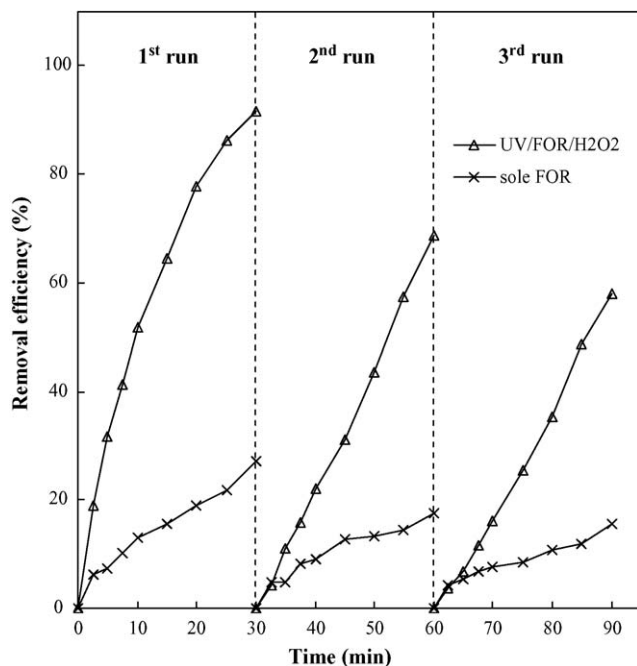


Fig. 6. Removal efficiencies of 2,4-D by sole FOR and UV/FOR/H<sub>2</sub>O<sub>2</sub> after three consecutive cycles of runs. The resin was separated by suction and then washed with DDW before being reused. [2,4-D] = 0.5 mM; [H<sub>2</sub>O<sub>2</sub>] = 3 mM.

lag phase was therefore observed in the formation of 2,4-DCP (Fig. 4(b)).

Based on the above observations, it is suggested that sorption and radical oxidation are two competitive pathways in the system. The former is dominant when sole FOR is used, and the addition of H<sub>2</sub>O<sub>2</sub> does not change this situation. When UV is involved, the latter immediately takes over the control of the process and becomes a much more effective pathway in removing 2,4-D, as illustrated in Fig. 5.

### 3.3. Recycling with FOR

Resin can be easily separated from the solution by filtration after the reaction, then reused. Fig. 6 shows the disappearance of 0.5 mM of 2,4-D in three successive cycles of either sole FOR or UV/FOR/H<sub>2</sub>O<sub>2</sub>. After each test, the irradiated resin was separated and rinsed with DDW before the addition of another batch of 2,4-D solution and hydrogen peroxide (if necessary). The performance of the FOR degraded slowly after each test in both treatments, where the FOR used in the photo-treatment showed a greater loss of activity mainly due to the dissolution of iron; however, a removal efficiency of 60% was still achieved by the UV/FOR/H<sub>2</sub>O<sub>2</sub> in the third run.

In the sole FOR, the removal of 2,4-D was comparatively low in each run (from 25% to 15%) due to the partition limitation, but such a barrier can be overcome by maximizing the adsorption capacity of resin in a continuous-flow tower reactor. The exhausted resin (containing 2,4-D) then can be treated and regenerated by adding UV/H<sub>2</sub>O<sub>2</sub> as a follow-up treatment (utilizing the high performance of the UV/FOR/H<sub>2</sub>O<sub>2</sub> process),

which can be done off-site with better flexibility in a real application.

## 4. Conclusions

The ferrioxalate-exchanged resin is a non-selective catalyst for the wastewater treatment of versatile organic contaminants such as 2,4-D (anionic) and 2-CIA (cationic), as well as ATZ (neutral). The rate of disappearance of 2,4-D catalyzed by FOR was significantly higher than that by unmodified or ferric-exchanged resin upon UV irradiation. The reaction mechanism involves sorption and radical oxidation, and they occur simultaneously when competing for 2,4-D. The former is a non-destructive process that can be used to sorb the target compounds; the exhausted resin can then be treated and regenerated off-site. The latter is a fast pathway whenever UV is involved in the process. This catalyst can be reused, but the effectiveness will be constrained by the dissolution of iron. Nevertheless, anion exchange resin has been employed in real operations to remove iron oxalate complexes from contaminated effluents, and such Fe-loaded resin may end up as waste. It is cost-effective and environmentally friendly to convert this solid waste to useful catalysts (FOR) which may then be applied to solve another environmental problem.

## Acknowledgment

The work described in this paper was fully supported by a grant from the University Grants Council of the Hong Kong Polytechnic University.

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