



## Steel dust catalysis for Fenton-like oxidation of polychlorinated dibenzo-*p*-dioxins

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### ABSTRACT

An advanced oxidation process (AOP) for degrading toxic contaminants, specifically polychlorinated dibenzo-*p*-dioxins (PCDDs), was developed to utilize steel dust, a steel industry by-product, as the heterogeneous catalyst for a Fenton-like oxidation. The steel dust was treated using a chemical acid etchant (HCl) and ultrasound to remove surface anchored groups, reduce aggregation, and thereby increase the specific surface areas, resulting in increased access to catalytic sites. The removal of PCDD was optimized through various reaction conditions. The removal percentage of 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxins (1,2,3,4-TCDD, 3.1  $\mu\text{M}$ ) after 3 h of Fenton-like oxidation under the conditions of 3 g/L (88 mM)  $\text{H}_2\text{O}_2$  and pH 3 was  $\sim 97\%$  with 10 g/L of steel dust, compared to  $\sim 99\%$  when 5 g/L metallic iron was used as a control. When a PCDD mixture (0.5–0.7 nM) was treated, 10 g/L (92 mM) steel dust achieved  $\sim 88\%$  removal, comparable to the removal with 5 g/L (89 mM) Fisher iron with 3 g/L (88 mM)  $\text{H}_2\text{O}_2$ . These results indicate that the steel dust is a potentially viable catalyst for removing PCDDs from contaminated water.

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### 1. Introduction

Advanced oxidation processes (AOPs) offer effective and rapid alternative treatments for various contaminants. One AOP investigated in numerous studies is the Fenton reaction with hydrogen peroxide and transitional metals, especially the ferrous ion, in an acidic aqueous system [1,2]. Hydrogen peroxide is a reactive and safe oxidant found in aqueous environments, and is preferable to ozone or chlorine based oxidants [3]. Ferrous ion is also a benign and cheap catalyst for performing the homogenous Fenton reaction. Homogenous reactions are an effective method for oxidizing a wide variety of hazardous contaminants in landfill leachates [4], drinking water [5], wastewater [6], soil/ashes [7], etc. However, this system generally offers effective contaminant removal only at high rates of hydrogen peroxide and soluble iron consumption due to the stoichiometric reaction [8,9]. The catalyst added as soluble salt causes the formation of sludge, which results in secondary pollution and treatment.

Currently, some research groups have reported heterogeneous Fenton systems offering significant advantages as well as solving problems. Heterogeneous iron makes the catalytic ion in solution, which properly generates the Fenton reaction without forming sludge. Even more, ions produced from minerals perform Fenton-

like oxidation. The role of mineral iron in promoting Fenton-like reactions has been reported and summarized in a critical review on Fenton-related reactions [2]. The Fenton-like reaction mechanism is still under investigation, but the fact is that it provides more efficiency to degrade stable toxic compounds. The success of these treatments is due to the catalytic decomposition of hydrogen peroxide in an acidic solution to form highly reactive hydroxyl radicals [10]. The Fenton-like reaction is observed for various types of mineral catalysts such as hematite [11,12], magnetite [13], ferrhydrite [14], goethite [15], lepidocrocite [16], mixed element oxides [17], and steel slag [18].

Steel dust is generated in considerable amounts by steelmaking processes. During the melting process in a furnace, certain elements form a fine dust which is collected in a baghouse in amounts of approximately 2% of the steel produced. In 2005, approximately 1129.4 million tones of steel were produced worldwide [19]. The dust was categorized as a hazardous waste by the US EPA in 1980 due to its chemical and physical properties [20]. If steel dust has zinc and lead levels higher than the regulation, it must be treated as a hazardous waste. It may be disposed of in a waste dump, or used as a secondary raw material in the production of zinc, iron, lead, etc. However, this general disposal or recycling is expensive and inefficient [21]. A previous study suggested that the most abundant elements in steel dust were iron and some transitional metals [22]. Because of the leaching potential of the heavy metals, especially zinc and lead, dust must be treated before utilization. However, the contents of toxic metals in dust vary owing to the raw materials

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and parts of the processes [19,23,24]. Reported data showed great differences among the studied countries and sampling locations [20,23–29]. Nevertheless, isolating the pure steel dust in steel making processes could provide an inexpensive and convenient mineral source for Fenton-type treatments.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) as well as polychlorinated dibenzofurans (PCDFs) are unwanted by-products from municipal and industrial waste incinerations [30], chemical and metal productions [30], pulp bleaching [31], and landfill leaching [32]. PCDD/Fs are released into the environment from various sources and present in all types of environmental media, not only the atmosphere but also the hydrosphere and terrasphere [33]. Since PCDD/Fs show extreme resistance to both abiotic and biotic degradation [30,34,35], their toxic effects can linger for long periods of time after contamination [30,31]. The concentration of PCDD/Fs in the hydrosphere is lower than in other environments due to their extremely low water solubility ( $10^{-4}$ – $10^{-8}$  ng/L) [36]. Though PCDD/Fs' physical data shows very low concentration in the hydrosphere, localized industrial wastewater or acids contain much higher concentrations of PCDD/Fs than estimates [37,38]. This is because they contain natural organic matters (NOMs) and particulate matters (PMs). NOMs, especially humic and fulvic acids, act as surfactants to enhance water solubility of organic pollutants [39,40]. PMs suspended in wastewater are one of the well-known sorption sites of hydrophobic compounds [41,42]. Therefore, an effective treatment for the removal of PCDD/Fs from contaminated water is needed for proper environmental management [30,34,35].

In this paper, PCDDs were chosen as the model chemicals because of their low degradability in water [42]. The factors that affect the oxidation efficiency were: hydrogen peroxide concentration, concentration of steel dust, pH, temperature, and concentrations of contaminants. The objectives of this study are (a) to treat PCDD/Fs-contaminated wastewater with mineral iron; (b) to optimize the oxidation reaction for various PCDD isomers; and (c) to evaluate the viability of the Fenton-like reaction using steel dust as the heterogeneous catalyst for wastewater treatment.

## 2. Methods and materials

### 2.1. Materials

The following chemicals were prepared and used: 1,2,3,4-tetrachlorinated dibenzo-*p*-dioxin (1,2,3,4-TCDD; AccuStandard Inc., New Haven, CT), 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD), 1,2,3,7,8-pentachlorinated dibenzo-*p*-dioxin (1,2,3,7,8-PCDD), 1,2,3,4,7,8-hexachlorinated dibenzo-*p*-dioxin (HxCDD), 1,2,3,4,6,7,8-heptachlorinated dibenzo-*p*-dioxin (HpCDD), octachlorinated dibenzo-*p*-dioxin (OCDD) (Dioxin mixture; AccuStandard Inc., New Haven, CT), toluene (Merck, Germany), hydrogen peroxide (30%, Merck, Germany), acetone (Merck, Germany), and Fisher iron (100 mesh, metallic iron, Fisher Chemical, USA). pH was controlled with an alkali solution [1N NaOH (Merck, Germany)] and an acid solution [1N HCl (Merck, Germany)]. All aqueous stock solutions were prepared using N<sub>2</sub> purged DI water.

Steel dust was obtained from a steel manufacturing company in Korea. Mixed basic oxygen furnace and electric arc furnace dust was the predominant part, but small amounts of sintering dust and blast furnace flue dust cannot be neglected. The sampled dust had zinc and lead in minor components, however, these were lower than leachable zinc and lead limits by the EPA (4.30 and 0.75 mg/L, respectively) which regulate the utilization and application of the materials. After more than three sampling events, steel dust was mixed and homogenized using a jar-tester and a tubular mixer. Par-

ticles over 100 mesh were excluded by sieving. For investigation, samples were dried at 105 °C in an oven.

### 2.2. Characterization

Elemental chemical analysis was performed to determine the composition of sampled steel dust. The exact amount of each metal species was measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS-AP, Thermo Elemental) and classical chemical titration following the standard Korean analysis method.

The physical characteristics were also investigated. The reduction capacities were determined by the back count of chemical oxygen demand (COD) following the US EPA method 410.4 (Colorimetric Automated Manual). The pH of the studied samples was measured using a pH meter as others reported [43]. The surface organic content (SOC) was calculated by measuring the COD of supernatants following the APHA standard method No. 5220B (Examination of Waster and Wastewater).

The microstructures of samples were characterized using a field emission TEM (JEOL 4000FX), a normal TEM (Philips CM-200), and a SEM (Philips XL-30). The TEM was equipped with an Oxford INCA/ENERGY 350 microanalysis system.

### 2.3. Pretreatment

The metal dust particles were pretreated using ultrasound (~20 kHz) and a chemical acid etchant (0.1 M HCl). The excess etchant was removed by washing with carbonate buffer (pH 9.5), followed by clean up with a sodium sulfate (Kanto chemical, Japan) column. Before and after the pretreatment, the samples were washed three times with acetone and three times with distilled water, and then dried with N<sub>2</sub>. Subsequently, the prepared samples were stored in desiccators and maintained at 4 °C until used.

In order to get optimized conditions for the treatment procedure, different applied frequencies and chemical concentrations were checked with reaction time. The treatment was conducted with monitoring of pH and iron leaching. Because of the alkalinity of the steel dust, an elevated pH of the solution was observed [43]. According to the monitoring result (data not shown), different treatment times were applied to achieve reaction completion, but they were always less than 10 min.

In this investigation, surface modification and increased dispersion were used by following the sonochemical procedure [44]. A chemical acid etchant (HCl) with 20 kHz ultrasound produced surface-cleaned iron particles, less aggregated clusters and, therefore, increased catalytic active sites of the steel dust.

Surface-cleaned iron particles were investigated by powder X-ray diffraction patterns (XRD). XRD of solids were recorded in the  $2\theta$  range of 2–80° by a X-ray diffractometer (Rigaku, Japan) using filtered Cu K $\alpha$  radiation to show the crystallized particle composition change during pretreatment. JCPDS Data Cards (International Center of Diffraction Data, Swarthmore, PA, 1988) and RINT 2000 RISM processing software (Rigaku, Japan) identified the diffraction peaks of the sample. As reported by Machado et al., overlapped signals from different phases and signals considerably weaker than the basis could not be interpreted as defined crystallines [24].

Less aggregated cluster was investigated by a laser-type particle analyzer (Beckman Coulter). Particle analyzer checked size distributions in the over 1  $\mu$ m range by multi-tube overlap method using 30–100  $\mu$ m aperture sizes. An electrophoretical light scattering measurement (Photal, Otsuka Electronics) provided more specific particle size distributions in the submicron range.

Increased active sites were investigated by Brunauer–Emmett–Teller (BET) specific surface areas. BET surface areas were deter-

mined by physisorption of nitrogen at the liquid nitrogen boiling temperature (77 K) using a sorption apparatus (BELSORP-max; Japan).

#### 2.4. Reacting system and analysis

The concentration of the investigated PCDD chemicals in the pretreated steel dust was below detection. Preliminary experiments determined the optimum initial contaminants concentration on degradation. The reaction showed most stable and reliable results with 1.0 mg/L (3.1  $\mu$ M) of 1,2,3,4-TCDD solution. To obtain the optimum ratio of pollutant:Fe:H<sub>2</sub>O<sub>2</sub> for the Fenton-like reaction, the H<sub>2</sub>O<sub>2</sub> and Fe concentrations were varied while keeping the TCDD concentration constant. After these preliminary tests, a mixture of five PCDD homologues was used for the actual decomposition test. These homologues were 2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,7,8,9-HpCDD, and OCDD, each at a weight/volume ratio of 0.25  $\mu$ g/L (0.54–0.77 nM for each congener). PCDD stock solutions which consisted of toluene and acetone were employed to prepare the PCDD contaminated wastewater. However, direct spiking of target compounds on the catalyst could minimize the use of solvent. Therefore dissolving solvent (~0.1 mg/L) was negligible on the reaction compared to surface organics (~10 mg/L).

The reaction occurred in a 40 mL vial fitted with PTFE (polytetrafluoro-ethylene)-lined screw caps. All vials were placed on an orbital shaker operated at 200 rpm. Based on the fact that temperature significantly affects degradation results, ~298 K was maintained during the process. A continuous pH adjustment was performed to maintain the best reaction system (pH 3–4) and there was not further adjustment after the initiation of reaction [45]. The concentration of ferrous and ferric ions in solution was determined using Iron Test paper (Merck). This 2,2'-bipyridyl immobilized test paper is stable in the presence of up to 200 mg/L of ferrous ion and gives reliable data with an optimized analytical range of 1–100 mg/L, 5–20% R.S.D., and  $n = 3$  in the presence of various interference. We diluted samples 10–100 times. Un-dissolved particles were removed using a micropore-size fabric filter to protect against particle interference on test paper discoloration. All catalytic oxidation experiments were carried out in triplicate. At each sampling time, reaction vials were sacrificed for extraction and analysis of dioxin.

Analysis of the PCDDs was performed using a Hewlett-Pakard 6890 gas chromatograph equipped with an electron capture detector (GC-ECD) and a 60 m  $\times$  0.25 mm DB-5 capillary column with a 0.25  $\mu$ m film. GC operating conditions were as follows: injector temperature of 300 °C, detector temperature of 300 °C, initial oven temperature of 100 °C, initial retention time of 2.0 min, program rate of 10 °C/min, and final temperature of 300 °C.

### 3. Results and discussion

#### 3.1. Characteristics of steel dust

Chemical and physical properties of steel dust investigated in this study are given in Table 1. Elemental chemical analysis showed that the major components of the steel dust were Fe, C, CaO, MgO, and SiO<sub>2</sub>. These results fell within the ranges typically observed: Fe 10–45%, Zn 2–46%, Pb 0.40–15.14%, Cr 0.2–11%, Cu < 3%, Si 1–5%, Ca 1–25%, Mg 1–12%, Al 0.1–1.5%, C 0.11–2.36% [20]. Machado et al. insist that a similar type of steel and similar dust-forming mechanisms result in values comparable to those found in the literature [24]. The percentage of iron in an advanced oxidation process using minerals has been reported to be an important factor for determining the efficiency of a Fenton reagent [46]. Our steel dust was more than half Fe, however this steel dust has low levels of some heavy metals compared to the literature values for Cd, Cu, Cr, Pb, etc. [20,23,24]. It should be noted that while these results showed that our steel dust sample easily passed Korean Environmental Regulations; other dusts must be individually tested and compared to local regulations. However, these results suggested that other steel dust could also be acceptable.

The steel dust, contained some moisture, probably owing to its reactive metal components such as Ca, Na, and K, which react readily with water. The SOC were evaluated. ~30 mg/L was the SOC value, which meant the dust contained a sparse layer of adsorbents. The pH of samples (Table 1) was higher than reported values; Leclerc et al. reported values of 9.3, 11.0, and 11.4 [47], Salihoglu et al., 10.50 [19], and Mecozzi et al., 8.57 [43]. As expected, the relatively high ratio of Ca contributed to the formation of alkali compounds. The reduction capacity of the dust is around one third that of commercial metallic Fe (99% Fe assay).

The microstructure of the steel dust was observed by TEM and SEM as shown in Fig. 1. These micrographs showed the various grain sizes, from 100 nm to 5  $\mu$ m, and highly agglomerated bunches of clusters, which were similar to other results as well as to the laser-type granule analysis results of 9.2  $\pm$  6.2  $\mu$ m in median and 3.3  $\pm$  1.1  $\mu$ m in average under the 5% consistent level [20,23,24,27]. The detailed image of the steel dust particles shows that spherical and quadrilateral shaped iron crystals form aggregated clusters. However, the dominant dendritic structure containing a spinel-type crystal region, which originates from rapid cooling, was hardly observed, unlike the results reported by Mantovani et al. [27].

The spherical particles forming the clusters had wrinkled surfaces and elongated (or attached) amorphous non-defined forms, after routine cleaning with distilled water and acetone, which might contribute to the diminished specific surface area. The lower values might originate from the blocking of micropores in inner spaces or of active sites on the surface by some undefined conglomerate substance. Salihoglu et al. also reported a diminished specific

**Table 1**  
Physical properties and chemical composition of the steel dust

Physical properties	Reduction capacity (mmol/g steel dust)		Surface organic content (mg/L)				Specific surface area (m <sup>2</sup> /g)	Water contents (%)	pH	
Before treatment	0.26 $\pm$ 0.02		31.6 $\pm$ 1.8				2.6 $\pm$ 0.1	10.3 $\pm$ 3.3	12.3 $\pm$ 0.3	
After treatment	0.32 $\pm$ 0.02		10.3 $\pm$ 0.8				10.8 $\pm$ 0.2	9.4 $\pm$ 4.1	11.7 $\pm$ 0.3	
Major component (w/w, %)	Tot-Fe	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	C	P	S	
Before treatment	61.2 $\pm$ 3.5	9.1 $\pm$ 0.3	5.5 $\pm$ 0.2	5.2 $\pm$ 0.2	2.3 $\pm$ 0.1	1.6 $\pm$ 0.1	10.6 $\pm$ 0.3	2.1 $\pm$ 0.2	0.4 $\pm$ 0.1	
After treatment	57.4 $\pm$ 6.8	5.8 $\pm$ 1.2	6.4 $\pm$ 1.2	9.4 $\pm$ 2.1	2.4 $\pm$ 0.3	2.0 $\pm$ 0.2	3.5 $\pm$ 1.6	1.8 $\pm$ 0.4	0.4 $\pm$ 0.1	
Minor component (mg/kg)	Zn	Pb	Ni		Cr	Cu		Cd	As	Hg
Before treatment	65.5 $\pm$ 15.3	20.9 $\pm$ 10.3	16.7 $\pm$ 9.7		61.6 $\pm$ 2.1	34.5 $\pm$ 15.2		n.d	n.d	n.d
After treatment	20.3 $\pm$ 4.9	15.4 $\pm$ 8.1	14.2 $\pm$ 8.6		40.3 $\pm$ 4.4	32.7 $\pm$ 14.3		–	–	–

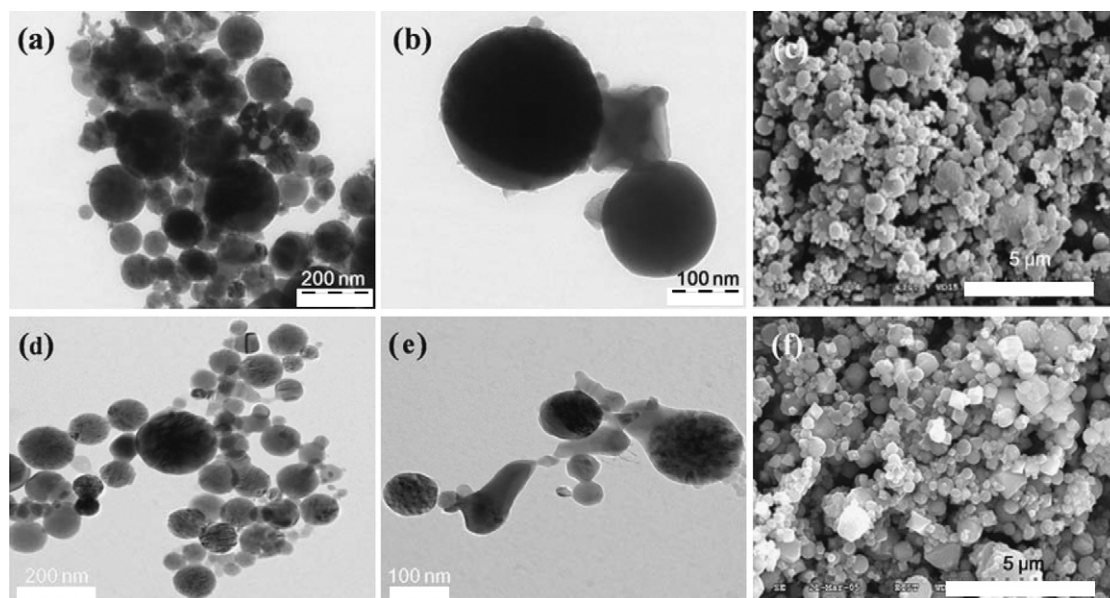


Fig. 1. Images of steel dust as received (a–c) and images of steel dust after treatment (d–f) using TEM and SEM.

surface area ( $0.16 \text{ m}^2/\text{g}$ ) of steel dust [19]. However, since others reported values of  $1\text{--}8 \text{ m}^2/\text{g}$  [48] and  $4.36\text{--}4.82 \text{ m}^2/\text{g}$  [28], the surface area of the steel dust could probably be further increased by an optimized process.

### 3.2. Effect of pretreatment on steel dust

The applied pretreatment system produced some slight changes in the physical properties and chemical composition. However, specific surface area and C in major phase were greatly changed. The pretreatment system was optimized to reduce surface organics. The contents of Zn, Cr and Pb of the steel dust were also reduced by the acidic treatment, similarly to Havlik et al. [49]. Though iron loss occurred during acid etching, no other significant change was observed except surface organics. Therefore, pretreatment of steel dust made a more stable iron leaching system on the Fenton-like reaction.

The aggregation of steel dust also determined the pretreatment to improve the catalytic activity. According to Guezennec et al. and Kashiwaya et al., agglomerations of dust particles develop in the in-fume extraction system which is required for steel making processes [25,26]. Kisfludi et al. reported that enhanced catalytic activity was obtained by hydrochloric acid treatment of amorphous iron based alloys [50]. Liu et al. used acid treatment to remove carbonaceous debris from nano-sized iron particles [51]. Gasgnier et al. reported on the effect of ultrasound on iron powder, which allowed the improvement of catalytic activity by decreasing the particle size [52]. Mantel et al. also employed a chemical etchant to pretreat steel surfaces [53]. And Uchida et al. insisted that surface modification of polishing particles could improve the utilization of OH radicals and that surface modification using a sonochemical method would maintain a good dispersity [44].

The morphology change was measured by electron microscope. Fig. 1(c) shows the SEM image ( $8000\times$ ) of a typical sample composed of many heterogeneous primary particles and cluster shapes. After treatment, the dynamic cluster shape changed negligibly, but a polished surface and reduced nano-size particles were revealed at  $\times 9000$  magnification, as shown in Fig. 1(f). Field emission TEM was carried out to closely observe the morphology and dispersion

of treated samples. A detail of a cluster is shown in Fig. 1(d and e), which shows that the entire structure of the aggregated or even agglomerated cluster is reduced into less massive clusters consisting of various ranges of spherical and quadrangular particles with smoothed surfaces.

EDX analysis provides a semi-quantitative composition of each region of the primary particles of pretreated dust. EDX analysis is reported in Fig. 2(b) together with TEM images, Fig. 2(a), indicating the investigated spots. These results imply that the dust particles have different compositions at different locations. The EDX spectra showed that the prevailing elements in the dark quadrangular particle (region 1) were Fe, Zn, Cr, Ni, and Si and those in the clear dendritic particles (region 2) were only Fe and Si. The dominant spherical particle (region 3) in pretreated steel dust was only Fe species. This is corroborated by other reported data [20]. A surface layer of carbon or non-metal compounds was not detected since it would have been removed during the pretreatment.

The results of X-ray diffraction phase analysis confirmed the surface changes of treated steel dust. Before the treatment, XRD patterns of the dust had one strong peak at  $26.6^\circ$ , indicating the existence of crystalline carbon, determined by qualitative software (RISM) to be graphite carbon-3R (JCPDS 26-1079). This corresponds to a chemical composition result (Table 1). Fig. 3 also shows the existence of crystallized metal diffraction peaks similar to those of other steel dust reported in the literature after reducing the graphite carbon [23,24,54,55]. The dramatically decreased graphite carbon line implies the detachment of crystallized entities and adsorbents.

Improved dispersion of steel dust after the treatment was measured using a light scattering system in a propyl alcohol solution. Particles over  $5 \mu\text{m}$  were not measured. As shown in Fig. 4, before sonication, the sample included approximately  $100 \text{ nm}$  to  $3 \mu\text{m}$  particles ( $\sim 50\%$  mass share from total granular dust), in agreement with published results [27,55]. Takano et al. reported a particle size distribution where 90% were less than  $10 \mu\text{m}$  in size [29]. Menad et al. reported an electric arc furnace dust which had 70% of particles below  $15 \mu\text{m}$  [55].

The sample collected after treatment showed an irregular granulometric distribution of dust, and downfield shift was observed.

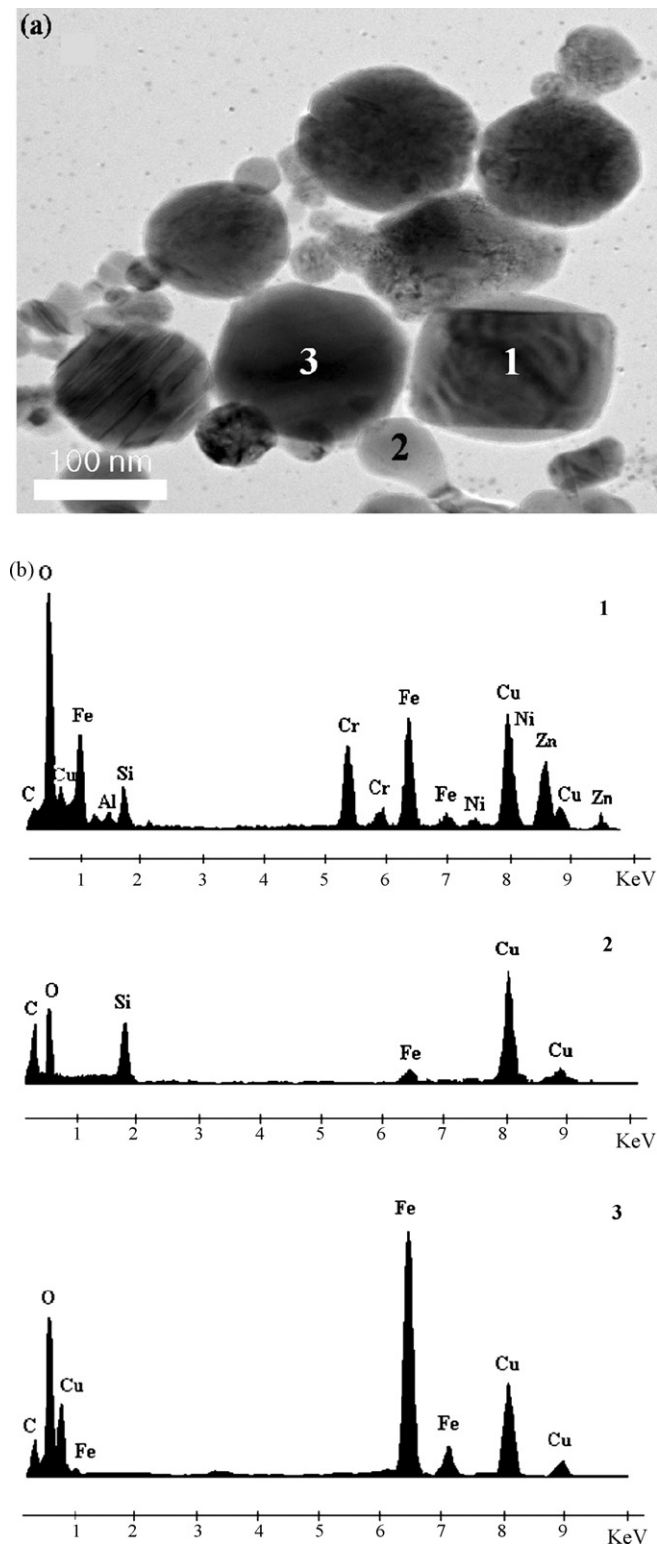


Fig. 2. TEM image (a) and EDX spectra (b) of pretreated dust particle.

Thus the sonochemical polishing of the sample affected the degree of cohesion among primary particles, which had submicron sizes. Probably, the irregular distribution is due to the change of the agglomerated state of particles because dust is known to have fine granules which tend to cluster together without control [56]. A decrease of grain size implies that the microspheres lose adsorbents, or separate to form reduced cluster structures.

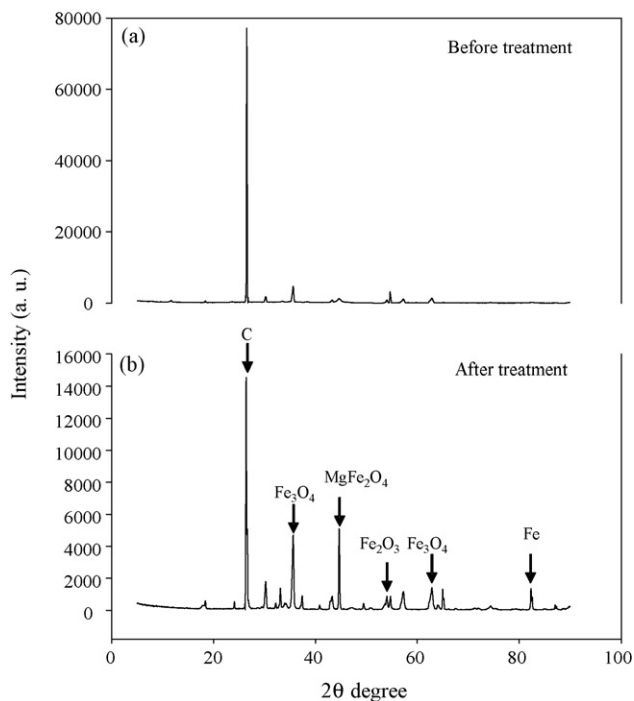


Fig. 3. X-ray powder diffraction patterns of steel dust (a) before treatment and (b) after treatment.

### 3.3. Influence of experimental conditions

#### 3.3.1. Effect of hydrogen peroxide on the removal of 1,2,3,4-TCDD

As the ratio of H<sub>2</sub>O<sub>2</sub> to pollutant increases, more OH radicals are available to attack target molecules, so the degradation reaction should be accelerated. However, researchers Li et al. reported that overdosage of H<sub>2</sub>O<sub>2</sub> could not make the best reaction conditions and they insisted that an optimal H<sub>2</sub>O<sub>2</sub> dosage should be determined in each reactor system [18]. They explained that the predominant hydrogen peroxide and hydroxyl radical suppressed the reaction between radicals and target molecules. These phenomena might originate from the inhibition of ferrous ions by excessive hydrogen peroxides. Nam et al. proved that increased H<sub>2</sub>O<sub>2</sub> consumption did not directly lead to radical production and insisted that over-dosed residual H<sub>2</sub>O<sub>2</sub> scavenged the hydroxyl radical [57]. Furthermore, instead of the Fenton chain reaction, excessive H<sub>2</sub>O<sub>2</sub> could cause an inverse reaction to form hydroxyl radicals [2].

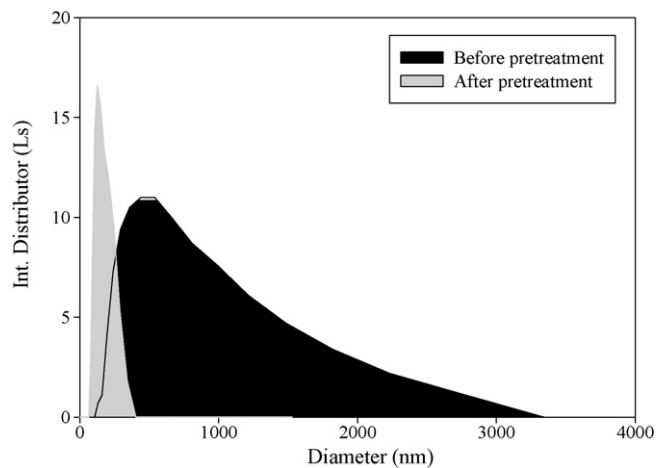
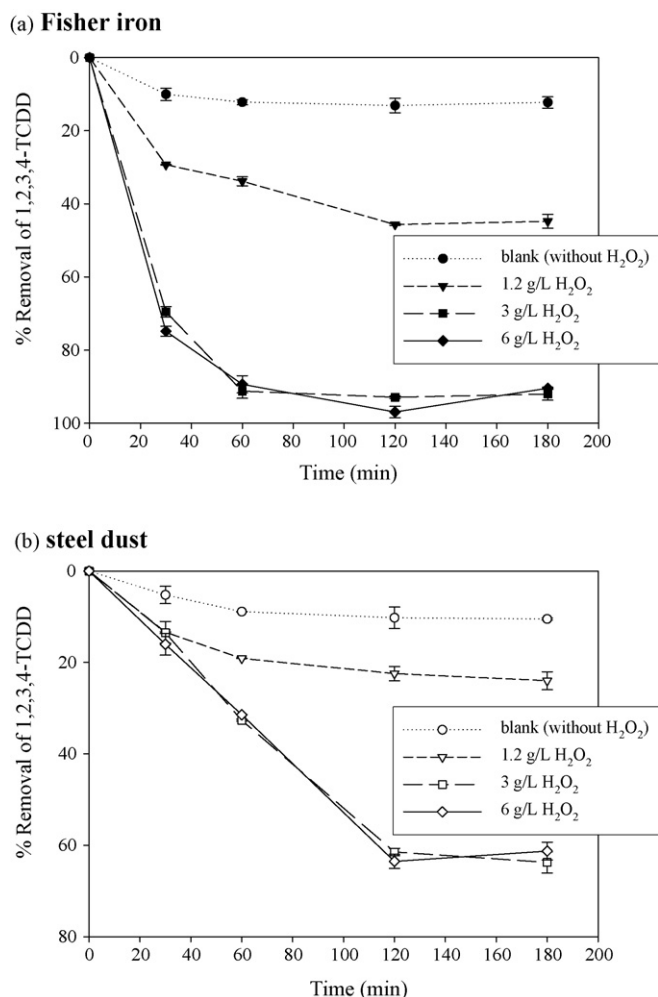


Fig. 4. Granulometric distribution of steel dust before treatment and after treatment.



**Fig. 5.** Effect of  $\text{H}_2\text{O}_2$  concentrations on the Fenton-like oxidation of 1,2,3,4-TCDD with (a) 5 g/L Fisher iron and (b) 5 g/L steel dust. Error bars indicate 1 standard deviation (some error bars are smaller than the data symbols). The initial 1,2,3,4-TCDD concentration was 1 mg/L (3.1  $\mu\text{M}$ ) in all cases: (●, ○) blank (without  $\text{H}_2\text{O}_2$ ), (▼, ▽) 1.2 g/L (35 mM)  $\text{H}_2\text{O}_2$ , (■, □) 3 (88 mM) g/L  $\text{H}_2\text{O}_2$ , (◆, ◇) 6 g/L (176 mM)  $\text{H}_2\text{O}_2$ .

In our experiment (Fig. 5), both the Fisher iron and steel dust had optimum removal of 1,2,3,4-TCDD at 3 g/L (88 mM)  $\text{H}_2\text{O}_2$ . Doubled  $\text{H}_2\text{O}_2$  diminished the removal percentage after optimization. Both the Fisher iron and steel dust systems with higher than 88 mM  $\text{H}_2\text{O}_2$  had lower removal percentages in agreement with previously reported results [7,10,18]. In the presence of Fisher iron, the removal rate was similar with 88 and 176 mM of  $\text{H}_2\text{O}_2$ , but the stabilized removal percentage (120 min) was highest at 88 mM  $\text{H}_2\text{O}_2$  (about 96%). The steel dust showed a similar trend, but the removal rate was much lower than Fisher iron. The stabilized removal was about 65% at 88 mM system.

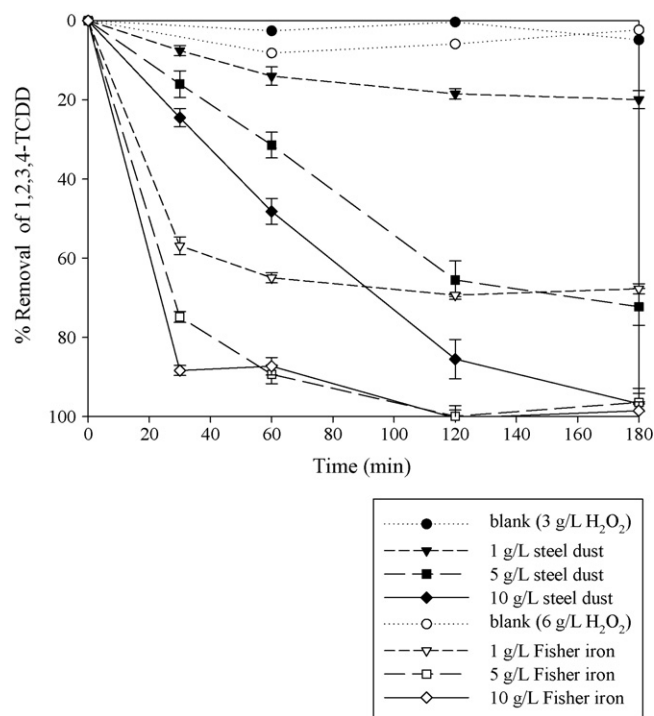
A very high ratio of  $\text{H}_2\text{O}_2$  was needed to increase the PCDDs degradation efficiency using recycled steel dust. PCDDs must be treated with great efficiency because they are toxic compounds covered by strict guidelines. The steel dust contains many other organics and inorganics which contribute to the wastewater. These interferences, organics associated with protons or inorganics, might retard iron leaching or radical generation. Furthermore, aromatic compounds with absorbable organics have resistance to radical induced oxidation, as reported by Lindsey and Tarr [58]. These interferences are realistic problem in wastewater treatment. This is one reason why we could not completely remove surface organic during the pretreatment step.

As Pignatello and Huang mentioned, to successfully degrade PCDD/Fs, a molar ratio of target compound:catalyst:oxidant = 1:10:200 was needed [59]. Teel et al. mentioned that mineral iron requires more  $\text{H}_2\text{O}_2$  than soluble iron [60]. They also reported that the standard Fenton procedure is impractical for hazardous and industrial waste treatment [60]. Standard Fenton process releases a low concentration of oxidants continuously which is of concern as limiting factor. An initial pulse input of  $\text{H}_2\text{O}_2$  was considered to be more suitable in mineral iron catalyst system since it can be better controlled. Dercova suggested that the oxidation effect of a Fenton-like reaction strongly increased with increasing molar ratio of catalyst and oxidants [61]. To solve these problems, excessive oxidants have been applying to get more efficiency in chemical treatment without direct photochemical or sonochemical assistance.

### 3.3.2. Effect of mineral iron on the degradation of 1,2,3,4-TCDD

In an acidic solution, minerals are ionized; the ferrous iron produced reacts with  $\text{H}_2\text{O}_2$ , producing hydroxyl radicals. As expected, under extreme acidic conditions, minerals are dissolved rapidly. Li and Kao reported that the  $\text{H}_2\text{O}_2$  within the Fenton reagent was most stable in the range of pH 3–4 [18,62]. In our investigation, pH 3.0 was better than pH 2 or 4 to remove 1,2,3,4-TCDD efficiently (data was not shown here).

The effect of mineral concentration on TCDD oxidation was investigated by adjusting the amounts of steel dust or Fisher iron as shown in Fig. 6. The removal percentage increases with increasing amounts of both Fisher iron and steel dust each up to 5 g/L. The increase of Fisher iron from 5 to 10 g/L did not elevate the removal percentage and removal rate. However, the increase of steel dust from 5 to 10 g/L elevated the removal percentage (~1.5-fold). This



**Fig. 6.** Effect of Fisher iron and Steel dust concentrations on the Fenton-like oxidation of 1,2,3,4-TCDD with 3 g/L (88 mM)  $\text{H}_2\text{O}_2$ . Error bars indicate 1 standard deviation (some error bars are smaller than the data symbols). The initial 1,2,3,4-TCDD concentration was 1 mg/L (3.1  $\mu\text{M}$ ) in all cases: (●) blank (3 g/L, 88 mM,  $\text{H}_2\text{O}_2$ , without mineral), (○) blank (6 g/L, 88 mM,  $\text{H}_2\text{O}_2$ , without mineral), (▼) 1 g/L Fisher iron, (□) 5 g/L Fisher iron, (◇) 10 g/L Fisher iron, (▽) 1 g/L steel dust, (■) 5 g/L steel dust, (◆) 10 g/L steel dust.

fact indicates that the iron contents in steel dust and Fisher iron affect the removal of this compound. Increasing the amount of mineral properly increases the production rate of the ferrous ion in an optimized Fenton reaction. However, when the Fe:H<sub>2</sub>O<sub>2</sub> ratio was higher than optimum, the quenching of reactive species and H<sub>2</sub>O<sub>2</sub> decomposition could occur. As Mecozzi et al. reported, excessive metal ions could cause undesired side reactions in the Fenton-like reaction [43]. But in this investigation, the reaction was not significantly retarded.

The difference in ion species between the same amounts of Fisher iron and steel dust also affected the removal reaction. The qualitative analysis program confirmed that the detected crystalline phases present in the steel dust showed great agreement not only with other XRD results but also with elementary and quantitative analysis data for basic species such as metallic iron (Fe: 06-0696), hematite (Fe<sub>2</sub>O<sub>3</sub>: JCPDS 33-0664), magnetite (Fe<sub>3</sub>O<sub>4</sub>: JCPDS 19-0629), and magnesioferrite (MgFe<sub>2</sub>O<sub>4</sub>: JCPDS 17-0464) [23,24]. The correlated composition data proved that the iron species in the steel dust made up the matrix and their mass share exceeded ~50%. Tarr summarized that hematite, magnetite and wustite as well as metallic iron had catalytic activity in a Fenton reaction; however, among the iron oxides, wustite, the less oxidized iron form, had the highest activity due to the high portion of ferrous ion in its crystal structure [46]. Ferrous and ferric ions are highly reversible in acidic solutions, but the formation of ferric ion can impede a rapid radical chain reaction [63].

Fisher iron provided comparative control data due to its uniform phase which conducts homogenous reactions. Although the Fisher iron can also perform a direct dechlorination as reported, increased granule size (104.52 ± 14.3 μm) and decreased specific surface area (0.069 m<sup>2</sup>/g) make this negligible on the view of kinetics of PCDD dechlorination [64,65]. Thus, the maximum efficiency of Fisher iron was ~50% higher than that of the steel dust. Furthermore, the reaction was faster. The steel dust contains not only metallic iron but also oxidized iron species which compete with the removal reaction. These adverse aspects decrease the removal percentage and rate, but the same concentration of ferrous or ferric ions might equalize the removal.

### 3.4. Decomposition of a PCDD mixture

The mixture of five PCDD congeners was decomposed at 0.25 μg/L (0.54–0.77 nM) of each congener concentration; 4-fold higher than the Universal Treatment Standards proposed by EPA). The Fisher iron and H<sub>2</sub>O<sub>2</sub> concentrations were 5 and 3 g/L, respectively, and the steel dust and H<sub>2</sub>O<sub>2</sub> concentrations were 10 and 3 g/L, which reflect the optimized Fe and H<sub>2</sub>O<sub>2</sub> levels for radical generation.

Fig. 7 shows the efficiencies for the overall removal of ∑PCDDs as a result of Fenton-like oxidation. Pollutant removal by adsorption (blank run in the same condition without H<sub>2</sub>O<sub>2</sub>) was not significant. After 4 h of oxidation, when the reaction showed no more progress, the total removal percentage was about 61% for the 5 g/L Fisher iron and 39% for 5 g/L steel dust. However, the reason why the Fisher iron had generally higher performance probably the difference in actual Fe concentration. Considering that the steel dust contains approximately 52% iron phase, the actual Fe concentration was adjusted by doubling the concentration. The measurements with iron test paper showed that the 5 g/L Fisher iron produced ~89 mM and the 10 g/L steel dust ~92 mM Fe ion concentrations. At the initial stage, the doubled steel dust had much lower iron leaching and slower removal rate than those of the Fisher iron. However, after system stabilized, the dust showed comparable results to the Fisher iron.

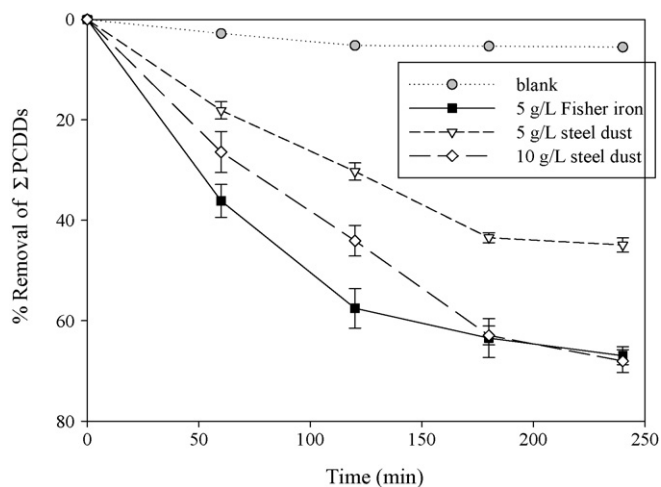


Fig. 7. Removal percentage of the PCDD mixture by Fenton-like oxidation (pH 3, 298 K, ∑PCDD = 1.25 μg/L, H<sub>2</sub>O<sub>2</sub> = 3 g/L, 88 mM, 200 rpm), (●) blank (5 g/L Fisher iron + 5 g/L steel dust without H<sub>2</sub>O<sub>2</sub>), (■) 5 g/L Fisher iron, (▽) 5 g/L steel dust, (◇) 10 g/L steel dust.

The removal of each significantly toxic homologue was examined for the Fisher iron and steel dust as shown in Fig. 8. Since the steel dust has a wide range of granular sizes and undetected rare metal compounds such as (Mn<sub>x</sub>Zn<sub>y</sub>Fe<sub>1-x-y</sub>)Fe<sub>2</sub>O<sub>4</sub> which might affect removal percentage or rate, the reaction is difficult to assess [23]. However, when the same concentrations were used, both the Fisher iron and the steel dust showed similar trends in the PCDDs removal test. 2,3,7,8-TCDD, the most toxic of these chemicals, was removed with a greater efficiency than any other homologue. OCDD showed promising results only for Fisher iron loading. OCDD is a common impurity in widely used biocides and is the thermodynamically stable homologue in the environment. However, OCDD itself is not an important homologue because its TEF value is only 0.001. Meanwhile, 2,3,7,8-TCDD is assigned a toxicity equivalent factor (TEF) of 1 [62]. The problem is generation of dechlorinated intermediates. Mechanistic studies about higher chlorinated compounds using radicals indicated the formation of less chlorinated compounds, which commonly resulted from reductive C–Cl bond cleavage [66]. In our experiment, the unusually low 1,2,3,7,8-

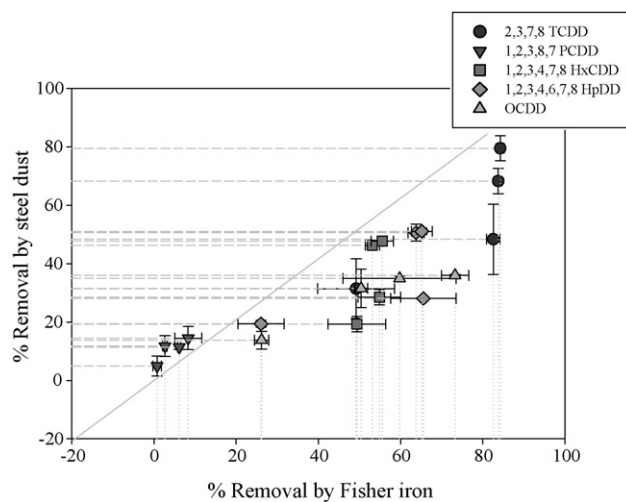


Fig. 8. Comparison of the PCDDs homologue removal patterns of Fisher iron (5 g/L) and steel dust (10 g/L) at pH 3, 298 K, ∑PCDD = 1.25 μg/L, H<sub>2</sub>O<sub>2</sub> = 3 g/L, 88 mM, 200 rpm, (●) 2,3,7,8-TCDD, (▽) 1,2,3,8,7-PCDD, (■) 1,2,3,4,7,8-HxCDD, (◇) 1,2,3,4,6,7,8-HpCDD, (▲) OCDD.

PCDD removal was probably due to the dechlorination of HxCDD, HpCDD, and OCDD, which kept the TEQ concentration elevated after treatment. However, these bench-scale results indicate that the oxidation of PCDDs with steel dust has the potential to be developed into a promising plant-scale application with assistance from light, electricity or biota.

#### 4. Conclusion

- These experiments demonstrate that the use of steel dust with hydrogen peroxide is a potentially viable remediation method for treating water contaminated with PCDDs.
- The characteristics of the steel dust, particularly its high iron contents, showed its possibility as a heterogeneous Fenton catalyst. If the iron contents of the dust can be separated from the impurities from steel making processes, it should increase the removal percentage in the mineral Fenton treatment.
- The surface area was increased and the primary particles dispersed by a simple pretreatment using a 0.1M of acid etchant and ~20 kHz ultrasound. Granular-metric analysis, micro-morphology measurement, X-ray powder diffraction analysis, and surface specific analysis confirmed the effect of the pretreatment.
- The removal reaction was optimized for the steel dust at 10 g/L (producing 92 mM ferrous ion) steel dust and 88 mM H<sub>2</sub>O<sub>2</sub> and for the Fisher iron 5 g/L (producing 89 mM ferrous ion) Fisher iron and 88 mM H<sub>2</sub>O<sub>2</sub> when the pH was 3, the temperature was 298 K and samples were agitated at 200 rpm. The same values of Fe concentration achieved similar removal percentages. However, the increased iron contents in particles could accelerate the removal reaction in the mineral Fenton treatment.
- The pretreated steel dust showed great activity in the Fenton-like oxidation of 2,3,7,8-TCDD; however, the decomposition reaction did not completely remove the PCDDs. In particular, the toxic 1,2,3,7,8-PCDD homologue might accumulate in the system. Nevertheless, steel dust could be used, after suitable pretreatment, as a practical catalyst in the remediation of toxic and persistent pollutants such as PCDDs in aqueous systems.

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