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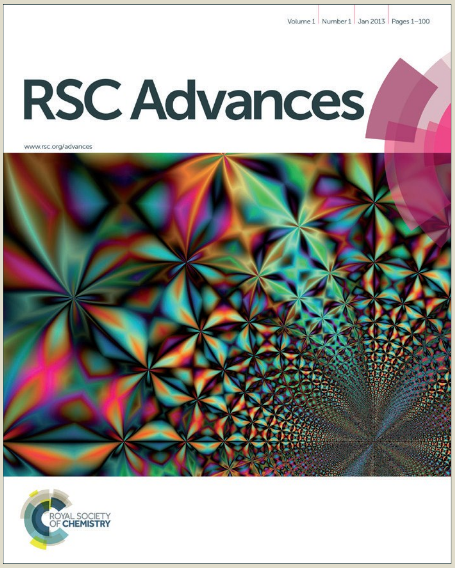

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Catalytic ozonation of 2, 4-dichlorophenoxyacetic acid over novel Fe-Ni/AC

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Abstract

Iron and nickel based bimetallic loaded activated carbon (Fe-Ni/AC) prepared by an impregnation method was employed as a heterogeneous catalyst for the ozonation of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution. The Fe-Ni/AC was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption-desorption, and atomic absorption spectrometer (AAS). The results indicated that the degradation and mineralization efficiencies of 2,4-D were considerably improved in the presence of Fe-Ni/AC. During the ozonation (50 mg h^{-1} ozone flow rate) of 2,4-D aqueous solution (10 mg L^{-1}, pH = 4.18) with the presence of Fe-Ni/AC, the TOC removal rate reached 72% at 60 min reaction time, while the rate was 60% with Fe/AC, 62% with Ni/AC, 50% with activated carbon (AC), and only 34% by ozonation alone. The 2,4-D removal process followed the pseudo first order reaction model well, its degradation rate constant with Fe-Ni/AC/O_3 was 1.6 times higher than that with AC/O_3, and 1.9 times than that by O_3 alone. The Fe-Ni/AC showed much better catalytic activity and stability based on the seven times repetition in the ozonation of 2,4-D. In addition, the effects of 2,4-D initial concentration, pH value and reaction temperature on catalytic ozonation of 2,4-D over Fe-Ni/AC were also investigated. The addition of tert-butanol (TBA) strongly inhibited the catalytic degradation of 2,4-D, which suggests that the degradation reaction follows the mechanism of hydroxyl radical ($HO^{\bullet}$) oxidation.

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D), an herbicide with potential toxicity for humans and animals, is used worldwide on a large scale for the selective control of weeds in gardens and farming[1,2]. Farmers rely profoundly on the use of herbicides and pesticides to maximize crop yields. This dependence on 2,4-D and other herbicides by the agricultural industry will not decline, guaranteeing the continued application of these compounds in large amounts (millions of pounds per year) [3]. Thus, due to its low soil sorption and high capacity of leaching, the removal of its residues in aquatic environment is inevitable[4]. However, 2,4-D's biodegradability is very poor [5]. Therefore, the heterogeneous catalytic ozonation, a novel alternative to traditional advanced oxidation processes (AOPs), has received wide interest as a promising technology for removing such environmental organic pollutants[5-7]. Metal or its oxide, such as Mn[8], Fe[1], Co[4], Ni[6], Ru[9], and Ce[10], has displayed a good activity in the heterogeneous catalytic ozonation. Meanwhile, activated carbon (AC) can promote the mass transfer between the pollutants and oxidants[6,9,10]. The degradation of organic pollutants by activated carbon loaded metal oxide has been described in recently reported studies[6,10-12], but there is little report on composite metal oxides supported on activated carbon.

Recently several reports have been published on the degradation of 2,4-D by AOPs like catalytic ozonation[1,13,14], photocatalysis[15—17], Fenton reaction[18], UV ozonation[16,19], electro-oxidation[20], or the combined systems[16,18,20]. These studies proposed the reaction mechanisms, determined the intermediates and efficiencies, aiming to select the most suitable process for 2,4-D mineralization.

As has been reported, iron or nickel oxide supported on AC or TiO_2[1,6] is believed to intensify the activation of the catalyst in the ozonation process by accelerating the decomposition of dissolved ozone into free hydroxyl radicals, strong oxidizing species capable of reacting rapidly with most of the water pollutants. On further thought, their composite oxides supported on AC could have synergic effect and might be capable of improving the mineralization efficiency than the monometallic oxide.

In this work, the iron-nickel composite oxides supported on AC (Fe-Ni/AC) were developed as a heterogeneous catalyst for the ozonation of 2,4-D in aqueous solution and were characterized by X-ray diffraction (XRD) and N_2 adsorption. Furthermore, their catalytic activity on the ozonation of 2,4-D degradation was studied.

2. Experimental

2.1 Materials

The coconut hull substratal activated carbon (industry grade) was supplied by Guangzhou Chemical Co., Ltd. (Guangzhou, China), and average particle size was about 0.45 mm. $Fe(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,4-D was supplied by Hervey Four Test chemical Co., Ltd (Shanghai, China). TBA, hydrochloric acid and sodium hydroxide were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Sodium thiosulphate was supplied by Tianjin Reagent Chemical Co., Ltd. (Tianjin, China). All chemicals were analytical grade except 2,4-D (chemical grade). Deionized water was used to prepare solutions. Hydrochloric acid and sodium hydroxide were added in aqueous solution to control its pH value.

2.2 Preparation of catalyst

Samples of Fe /AC, Ni/AC and Fe-Ni/AC were prepared by an impregnation method using $Fe(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ as Fe-Ni precursor. Activated carbon was added to the appropriate dose of nitrate solution (Fe:Ni = 3:1) to prepare Fe-Ni/AC (0.25 wt %). The samples were dispersed by ultrasound vibration for 90 min, dried at room temperature, then heated to 723 K at a rate of 3 K min^{-1} in N_2 flow (400 ml min^{-1}) and calcined at 723 K for 2 h to obtain the required catalyst. The actual content of metal in Fe-Ni/AC is 0.22 wt% (see table 1). Fe/AC (0.25 wt %) and Ni/AC (0.25 wt %) were prepared at the same conditions.

Table 1 The actual contents of metal in Fe-Ni/AC

Components	**Theoretical lue (mg g^{-1})**	**Actual value (mg g^{-1})**	**Actual Fe-Ni/AC** (wt%)
Fe	1.875	1.627	0.22
Ni	0.625	0.557	

2.3 Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the samples were carried out using Cu Kα radiation in the 2θ ranges of 20°- 80° on a Rigaku D-MAX 2200 VPC X-ray diffractometer. The accelerating voltage and applied current were 40 kV and 30 mA, respectively. The surface morphology of the samples was visualized using SEM (ZEISS Ultra 55) with an accelerating voltage of 5.0 kV. The textural structure of samples was characterized by N_2 adsorption-desorption isotherms at 77 K on a Quantasorb surface area analyzer (Micromeritics, ASAP2020, USA). The surface area was estimated by the BET equation and the pore size distributions were determined by the BJH method.

Potentiometric titration method was used to determine the zero potential charge of the AC and Ni-Fe supported AC.

2.4 Experimental set-up and process

A 1.4 L glass tubular reactor (h = 500 mm, Φ_{in} = 60 mm) was set up and filled with 1.4 L 2,4-D solution (10 mg L^{-1}, pH = 4.18) and catalyst (0.5 g L^{-1}). The reaction temperature was controlled by circulation water from a thermostatic bath (SDC-6, Ningbo, China). Ozone was produced from pure oxygen (flow rate = 1.2 L min^{-1}) at a 50.0 mg h^{-1} ozone output rate by a DHX-SS-1G Ozone Generator (China). Ozonized oxygen was continuously bubbled into the solution through a porous plate. The excess ozone in the outlet gas was absorbed by a 5 % $Na_2S_2O_3$ solution. Water samples were taken at intervals to analyze 2,4-D and total organic carbon (TOC) concentrations. $Na_2S_2O_3$ solution was used to stop the continuous ozonation reaction in the sample.

2.5 Analytical methods

All water samples were filtered by a 0.45 μm prefilter. 2, 4-D concentration was determined by a high performance liquid chromatography (HPLC, LC-10A Shimadzu, Japan) with a UV detector (SPD-10AV) at 230 nm. A Discovery C18 column (250 mm × 4.6 mm, Dikma technologies) was used. The mobile phase was a mixture of methanol and water at 75:25 (v:v) with a 1.0 mL min^{-1} flow rate. TOC was analyzed by a Shimadzu TOC 5000 analyzer. The concentration of leaching Fe and Ni in Fe-Ni/AC/O_3 process was detected by an atomic absorption spectrometer (AAS, TAS-986, Pgeneral). The actual metal contents in Fe-Ni/AC samples were also detected by AAS. 0.10 g Fe-Ni/AC was put into 10 ml HNO_3 solution (v:v = 1:1), and dispersed by ultrasonication for 120 min at 333 K, followed by a 48 h quiescent time. The supernate was then filtered, diluted and analyzed by AAS.

3. Results and Discussion

3.1 Characterization of Fe-Ni/AC sample

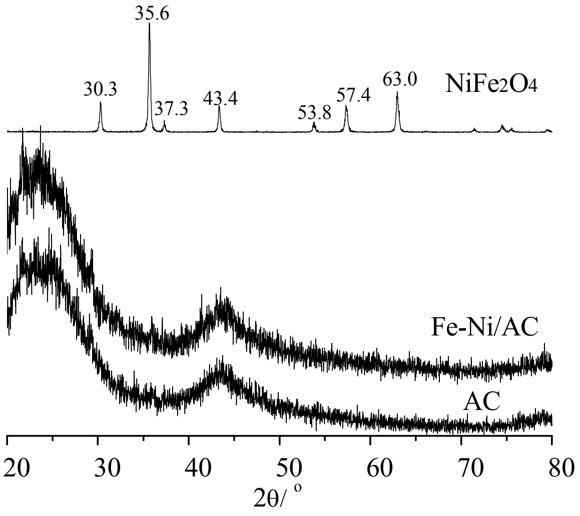
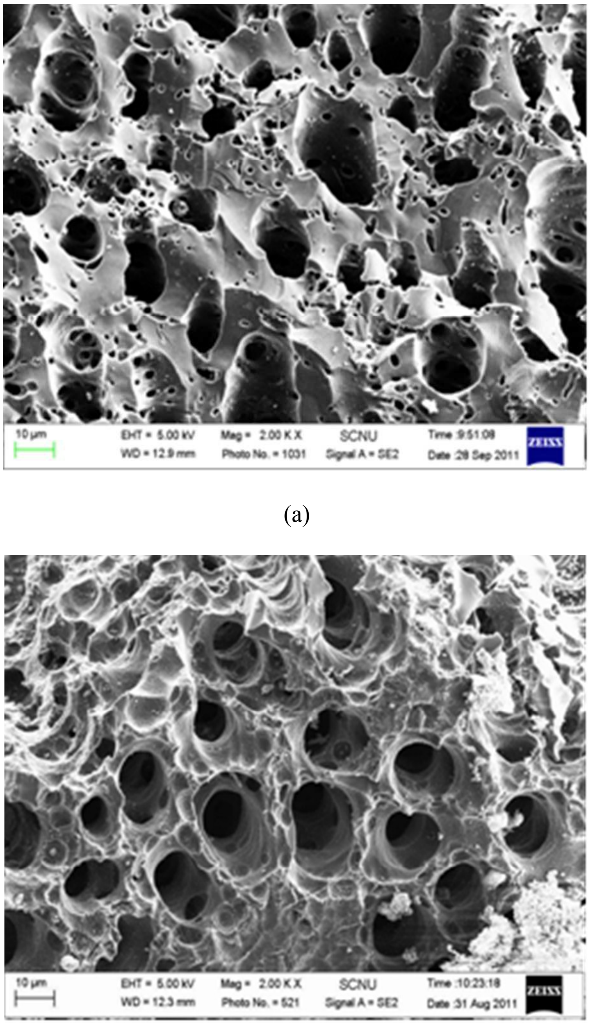


Fig. 1 X-ray powder diffraction patterns of Fe-Ni/AC catalyst.

Fig. 1 shows X-ray powder diffraction patterns of $NiFe_2O_4$, AC and Fe-Ni/AC sample. $NiFe_2O_4$ was the decomposed product from the mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ at the same conditions. The diffraction peaks of $NiFe_2O_4$ include 2θ = 30.3º, 35.6º, 37.3º, 43.4º, 53.8º, 57.4º, 63.0º. Activated carbon and Fe-Ni/AC sample were amorphous carbon, the crystalline phase unchanged. Compared with activated carbon, there were no $NiFe_2O_4$ diffraction peaks on Fe-Ni/AC sample. Previously studies reported that the reflections of lower metal loadings on relatively high surface area supports can hardly be observed because of their highly dispersed surface phase[21]. Therefore, it can be deduced that the metal was dispersed well over activated carbon surface.

The AC and the used Fe-Ni/AC (reused three times) samples were analyzed by SEM, as shown in Fig. 2. It reveals that some oxide particles were deposited on the surface of spent Fe-Ni/AC sample (Fig. 2b), comparing with that of activated carbon (Fig. 2a). As comparing between SEM images of AC and the spent Fe-Ni/AC, some differences can be observed in Fe-Ni/AC morphology after reused three times, which supposed that activated carbon surface was partly oxidized by ozone[10,22]. The metal leaching data obtained can also explain that some oxide particles on Fe-Ni/AC sample fell off (spalled) in the catalytic ozonation process of 2, 4-D.



(a)

(b)

Fig. 2 SEM micrographs obtained from AC and the spent Fe-Ni/AC catalyst: (a) AC, (b) the spent Fe-Ni/AC (reused three times).

Table 2 summarizes the results of the textural characterization of activated carbon and Fe-Ni/AC. The surface area of AC and Fe-Ni/AC are 550.84 m^2 g^{-1} and 519.68 m^2 g^{-1}, respectively. The result showed that the metal loaded activated carbon slightly decreased its surface area and pore volume, but its pore size slightly increased. The surface area and pore volume of the spent Fe-Ni/AC (reused three times) sharply decreased; its surface area, pore volume and pore size were only 401.54 m^2 g^{-1}, 0.196 cm^3 g^{-1} and 1.952 nm, respectively. These results illustrate that activated carbon was partly oxidized by ozone in the catalytic ozonation process of 2,4-D, which lead to the decrease of its catalytic activity, and can also be confirmed by Fig. 2.

3.2 Comparison of 2,4-D and TOC removal among different oxidation processes

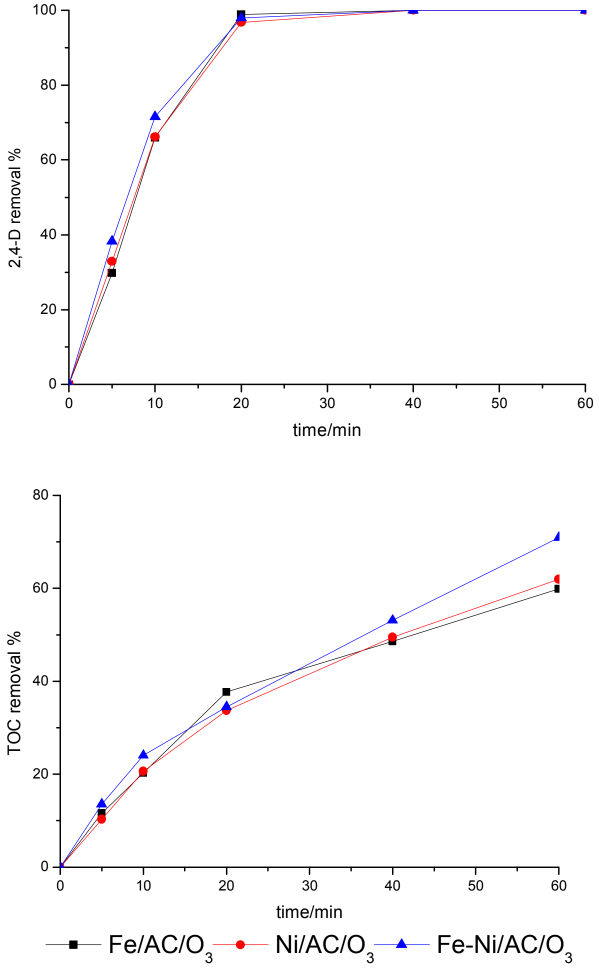


Fig. 3 Comparison of 2,4-D and TOC removal among different catalytic ozonation processes.

Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2,4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH= 4.18, flow rate of oxygen: 1.2 L min^{-1}.

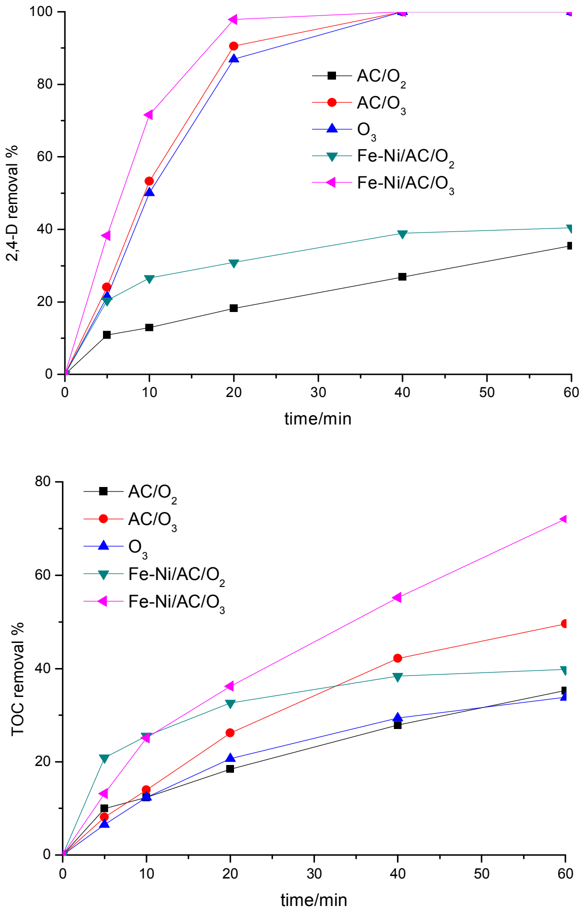


Fig. 4 Comparison of 2,4-D and TOC removal among different processes. Ozone dose(if have): 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2,4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH= 4.18, flow rate of oxygen: 1.2 L min^{-1}.(AC/O_2 and Fe-Ni/AC/O_2 : processes under oxygen flow without ozone dose)

Table 2 The specific surface area, pore volume and pore size of catalysts

Sample	Surface area(m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size （nm）	pH_{ZPC}
AC	550.84	0.289	2.102	4.6
Fe-Ni/AC	519.68	0.284	2.186	3.8
used Fe-Ni/AC	401.54	0.196	1.952	--

Fig. 3 shows the catalytic activity of Fe/AC, Ni/AC and Fe-Ni/AC in the process of ozonation. It was clearly seen that the presence of Fe-Ni/AC improved 2, 4-D and TOC removal efficiency. TOC removal rate reached 72 % at 60 min, 60 % with Fe/AC, and 62 % with Ni/AC.

Fig. 4 shows the comparison of 2, 4-D and TOC removal among O_3, AC/O_3, Fe-Ni/AC/O_3 processes and the adsorption processes. It was clearly illustrated that the presence of AC or Fe-Ni/AC improved 2,4-D and TOC removal, compared with the ozonation alone, in which Fe-Ni/AC/O_3 process was the most efficient for the 2,4-D and TOC removal. During the ozonation alone, the 2,4-D removal rate can reach 100 % at 40 min reaction time and be more mineralized in the presence of Fe-Ni/AC, while the TOC removal rate reached 72 % at 60 min, only 50 % with AC, only 34 % by the ozonation alone. It can be also seen from Fig. 4 that 35 % and 40 % 2,4-D was removed by AC and Fe-Ni/AC adsorption, respectively. The adsorption gap may be due to the metal electrostatic interactions. The results suggest that the composite oxides of iron-nickel was the better active component for the catalytic ozonation of 2,4-D. The TOC removal rate in the presence of Fe-Ni/AC was due to increasing ozone decomposition into highly oxidant species ($HO^{\bullet}$) in the system. Because the resonance structure of ozone molecule results in its high reactivity, the chemistry of ozone in aqueous solution is complex. It can react as a dipole, an electrophilic or nucleophilic agent. It is generally believed that molecular ozone can oxidize water impurities via direct, selective reactions or can undergo decomposition following chain reaction mechanism leading to the production of $HO^{\bullet}$ [23]. Activated carbon can act as a conventional initiator or promoter for the ozone transformation into $HO^{\bullet}$ radicals[24]. The active component Fe or Ni enhances ozone transformation into $HO^{\bullet}$ [6,25]. The reaction rate constant of $HO^{\bullet}$ radicals with 2,4-D is 6.6 ± 0.5 × 10^9 M^{-1} s^{-1} [26]. The increased TOC removal in Fe-Ni/AC catalytic ozonation of 2,4-D also suggest that Fe-Ni/AC promoted ozone transformation into $HO^{\bullet}$ in aqueous phase and started chain reactions that continue in aqueous phase.

The data presented in Table 3 indicates that the TOC removal reached 34 % at 60 min by ozonation alone, the TOC removal reached 42 % when Fe-Ni/AC was added as adsorbent after 60 min ozonation alone, so 8% TOC was removed by Fe-Ni/AC adsorption. But it reached 72% at 60 min using Fe-Ni/AC catalytic ozonation. The result suggests that the TOC removal in Fe-Ni/AC catalytic ozonation of 2, 4-D was due to synergic action among ozone oxidation, adsorption and catalytic oxidation respectively.

Table 3 Contributions of three effects to the TOC removal rate

effect	TOC (%)	Contribution (%)
Ozonation	34	47
Fe-/Ni/AC adsorption	8	11
Catalytic oxidation	30	42
Total	72	100

3.3 Influence of 2,4-D initial concentration on catalytic ozonation process

Fig. 5 shows the effect of initial concentration on the 2,4-D and TOC removal in the Fe-Ni/AC catalytic ozonation process. It can be seen that the 2, 4-D and TOC removal followed similar trends at different initial concentrations. That is, 2,4-D or TOC removal decreased with increasing its initial concentration. Because the by-product concentration in the solution increases with 2,4-D initial concentration, at higher initial concentrations of 2,4-D more available ozone will be consumed for 2, 4-D further degradation and oxidation of intermediates[10].

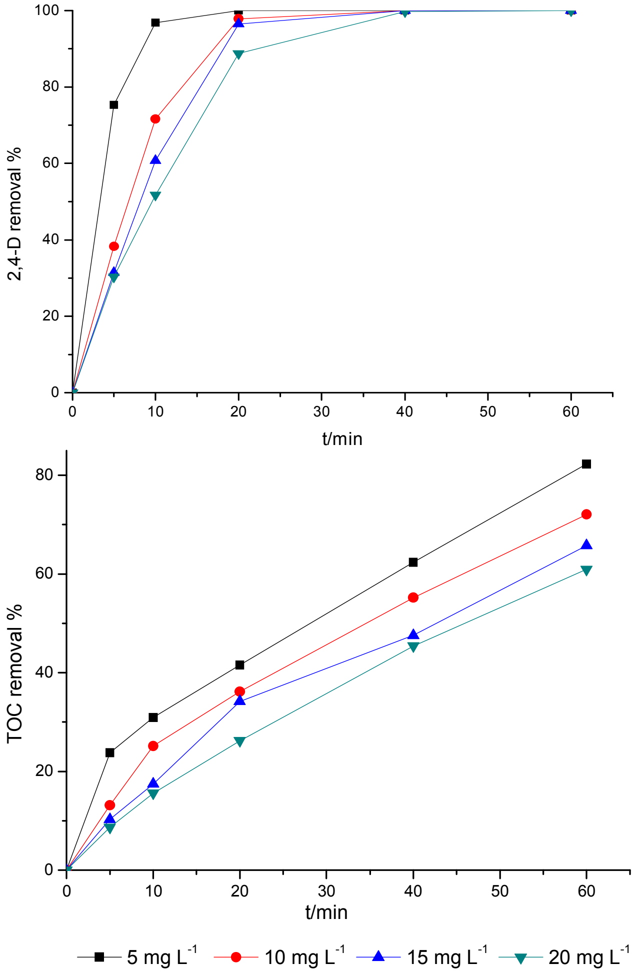


Fig. 5 Influence of initial concentration on degradation of 2,4-D and TOC removal. Ozone dose: 50 mg h-1, catalyst dose: 0.5 g L-1, initial concentration of 2,4-D solution: 5 mg L-1 - 20 mg L-1, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH = 4.18, flow rate of oxygen: 1.2 L min-1.

3.4 Influence of initial pH on 2, 4-D and TOC removal

Fig. 6 depicts the influence of initial pH on catalytic ozonation of 2,4-D. 2,4-D and TOC removals were slightly increased with pH from 3.0 to 11.0 at 298 K. Compared with the acidic conditions, their removal was improved in the alkaline conditions. First of all, ozone is very unstable in aqueous solution due to its high active resonance structures of molecules. The half-life time of ozone molecules varies from a few seconds up to a few minutes, which depends on pH, water temperature and concentration of organic compounds in aqueous solution[27]. Secondly, the increase of pH will result in producing much more $HO^{\bullet}$ radicals, which are the major secondary oxidants formed from the ozone decomposition in aqueous solution[28]. The point of zero charge(pH_{PZC}) of AC was 4.6, which was higher than that of Ni-Fe/AC(3.8). It meant that the Ni-Fe/AC catalyst surface was negatively charged at pH=4.18, or higher, and it was favorable to the transformation of O_3 to $HO^{\bullet}$ radicals and to the adsorption of 2,4-D on the surface.

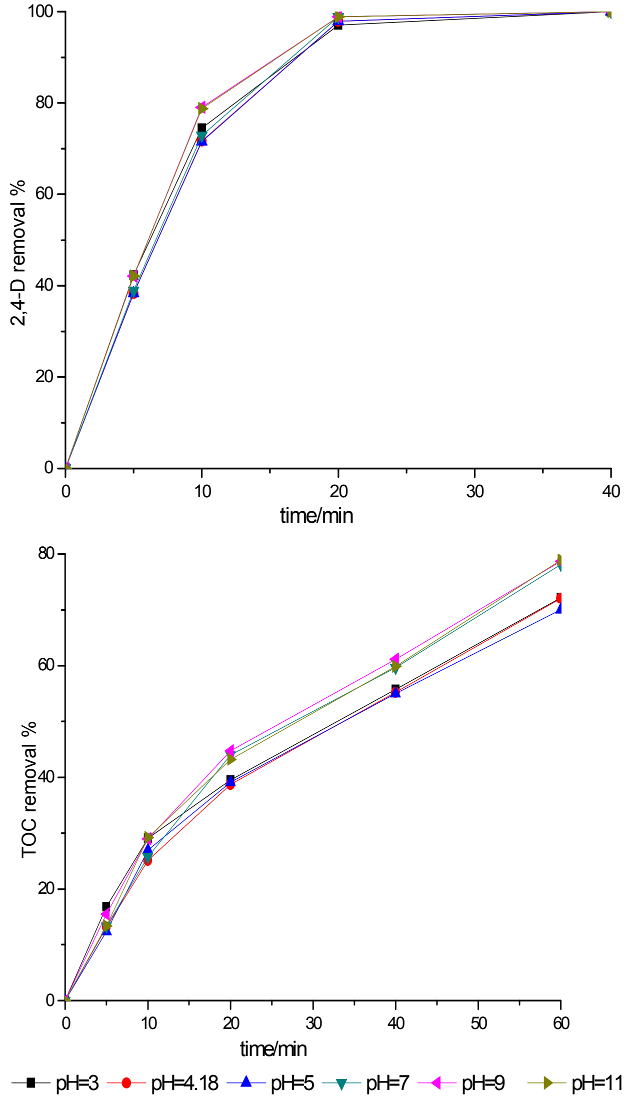


Fig. 6 Influence of pH on degradation of 2,4-D and TOC removal. Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2,4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature:298 K, pH= 3.0 – 11.0, flow rate of oxygen: 1.2 L min^{-1}.

As the pH value increases, 2,4-D was more easily ionized which facilitated the transmission of 2,4-D and ozone between the catalyst surface and the bulk solution. Therefore, the 2,4-D degradation and mineralization efficiencies were accelerated by $HO^{\bullet}$ at high pH levels.

Table 4 Influence of pH on the metal leaching contents in aqueous solution(298K)

pH	3.00	4.18	5.00	7.00	9.00	11.00
Ni(mg L^{-1})	0.047	0.059	0.057	0.065	0.064	0.062
Fe(mg L^{-1})	0.131	0.110	0.103	0.116	0.132	0.172

Table 4 indicates the metal leaching contents in aqueous solution at 298K. The metal Ni leaching content slightly increased in the pH range of 3 to 7, then to a nearly stable value with the pH value over 7. While the metal Fe leaching content slightly decreased in the acidic pH condition, then increased as the pH was over 5. The increase of metal leaching content with the pH value was consistent with the influence of pH value on 2,4-D and TOC removal.

3.5 Influence of reaction temperature on the 2,4-D and TOC removal

The reaction temperature was an important factor for 2,4-D degradation, whether in the ozonation alone or the Fe-Ni/AC catalytic ozonation process. As indicated in Fig. 7, the 2,4-D and TOC removal was remarkably increased with the reaction temperature (278 K - 308 K) in the processes of the ozonation alone and the catalytic ozonation, respectively. It can be concluded that the influence of reaction temperature was positive to the degradation efficiency in the range of 278 K -308 K. However, Fig. 7 suggests that its effect in the ozonation alone was better than that in the catalytic ozonation for 2,4-D removal when the reaction temperature was further increased up to 308 K. And compared with other reaction temperatures, the gap of the

TOC removal was smaller between the processes of the ozonation alone and the catalytic ozonation. The anomalous phenomenon was due to the balance of both the ozone solubility and the ozonation reaction rate. On the one hand, the ozone solubility in aqueous solution decreases with the increasing reaction temperature[16]. On the other hand, the oxidation rate constant increase with the reaction temperature[19]. The competition of the two opposite effects lead to the similar synergic result in the processes of ozonation alone and the catalytic ozonation of 2,4-D within the reaction temperature from 278 K to 308 K. The phenomena of Fig. 6 indicate that the effect of increasing reaction temperature on the degradation efficiency can be chiefly attributed to the ozone transformation[28].

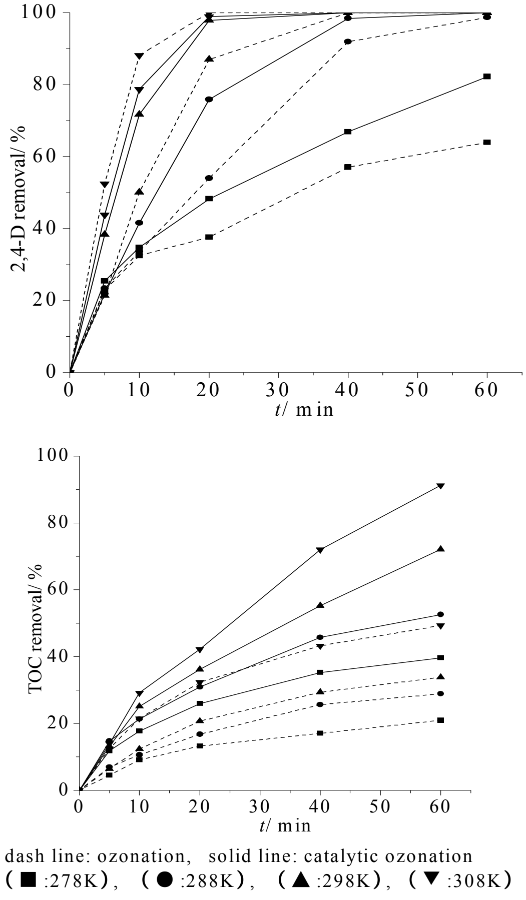


Fig. 7 Influence of reaction temperature on degradation of 2,4-D and TOC removal. Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2,4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 278 K - 308 K, pH = 4.18, flow rate of oxygen: 1.2 L min^{-1}.

Table 5 Influence of reaction temperature on the metal leaching contents in aqueous solution

Reaction temperature (K)	**278**	**288**	**298**	**308**
Ni (mg L^{-1})	0.055	0.069	0.064	0.077

In addition, Table 5 lists the result of metal leaching contents at different reaction temperatures. The metal leaching contents in aqueous solution slightly increased as the reaction temperature increased from 278 K to 308 K, which also illuminated that the 2,4-D and TOC removal efficiencies were increased with the reaction temperatures.

3.6 Influence of TBA on catalytic ozonation process

Fig.8 shows the influence of TBA on catalytic ozonation. 2,4-D degradation was remarkably depressed with the presence of increasing TBA (2.5 - 10 mg L^{-1}) in aqueous solution. The result presents that the addition of TBA at different concentrations had a negative influence on the degradation efficiency of 2,4-D in the catalytic ozonation process, indicating that TBA competitively traps and consumes $HO^{\bullet}$ rapidly in aqueous solution.

Fig. 9 shows that the presence of 7.5 mg L^{-1} TBA in aqueous solution had a remarkable influence on 2,4-D degradation efficiency in the processes of ozonation alone and catalytic ozonation, and its degradation efficiency was obviously depressed. 2,4-D degradation efficiency (reaction for 20 min) decreased by 69 %, 56 % and 62 % in the processes of O_3, AC/O_3 and Fe-Ni/AC/O_3, respectively. Fig.7b also describes that TBA also affected the adsorption of 2,4-D on Fe-Ni/AC, its removal (37%) with the presence of TBA was lower than that (40%) with its absence.

Being a stronger radical scavenger, TBA has the reaction rate constant of 5.0×10^{8} M^{-1} s^{-1} with $HO^{\bullet}$ and 3.0×10^{-3} M^{-1} s^{-1} with ozone molecules. TBA reacts with $HO^{\bullet}$ and generates intermediates, which do not predominantly produce the radicals, thus causing the termination of the radical chain reaction[28, 30]. Based on the effects of scavenger and pH_{PZC} on catalytic ozonation, the result also suggests that 2,4-D was primarily oxidized by $HO^{\bullet}$ in the processes of O_3, AC/O_3 and Fe-Ni/AC/O_3. However, in the presence of TBA, the adsorption of 2,4-D on the Fe-Ni/AC had slightly decreased, meanwhile the adsorption of TBA on Fe-Ni/AC reached 10 %. As far as catalytic ozonation was concerned, it may be assumed that the initiation of $HO^{\bullet}$ was enhanced by the introduction of composite oxides of iron-nickel.

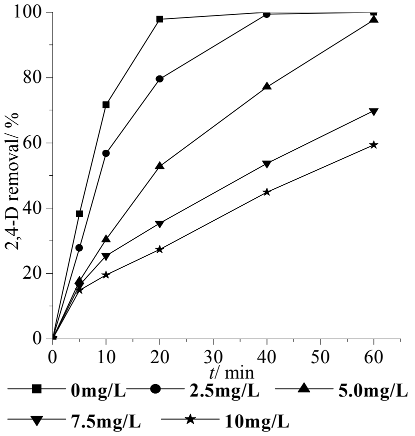


Fig. 8 Influence of TBA addition amount on catalytic ozonation of 2,4-D. Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2, 4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH = 4.18, flow rate of oxygen: 1.2 L min^{-1}.

Table 6 First-order kinetic parameters of the 2,4-D removal in O_3 alone, AC/O_3 and Fe-Ni/AC/O_3 processes

	k (min^{-1})	R^2
O_3	0.0930	0.9452
AC/O_3	0.1071	0.9366
Fe-Ni/AC/O_3	0.1762	0.9401

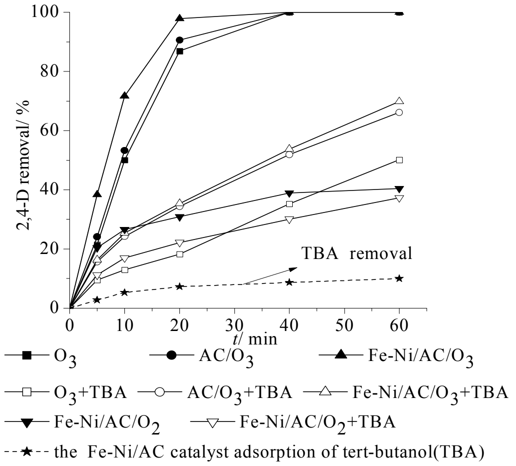


Fig.9 Influence of TBA on catalytic ozonation and absorption of 2,4-D. Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2, 4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH = 4.18, TBA: 7.5 mg L^{-1}.

3.7 Kinetic of the 2,4-D removal in O_3 alone, AC/O_3 and Fe-Ni/AC/O_3 processes

The kinetic data of semi-batch experiments with various different oxidation processes are listed in Table 6. The 2,4-D degradation rates by O_3 alone, AC/O_3 and Fe-Ni/AC/O_3 followed the pseudo-first-order kinetic model (see Table 6). The reaction rate constants were 0.0930 min^{-1} for O_3 alone, 0.1071 min^{-1} for AC/O_3 and 0.1762 min^{-1} for Fe-Ni/AC/O_3. The 2,4-D degradation rate constant with Fe-Ni/AC/O_3 was 1.6 times higher than that of AC/O_3, and 1.9 times higher than that of O_3 alone. The results indicate that Fe-Ni/AC has enhanced catalytic activity in the ozonation of 2,4-D.

The calculated pseudo-first-order kinetic constants of the Fe-Ni/AC/O_3 process were enhanced from 0.0291 min^{-1} to 0.2075 min^{-1} with the reaction temperature increased from 278 K to 308 K. Simultaneously, the 2,4-D degradation rate constants by ozone alone were also increased from 0.0192 min^{-1} to 0.2006 min^{-1} with the temperature from 278 K to 308 K. There was a positive relationship between the reaction rate constants and the reaction temperature in both the ozonation and the catalytic ozonation processes. Furthermore, according to the Arrhenius formula ($k = k_0 e^{-E_a/RT}$), the activation energy can be calculated depending on the reaction rate constants at different temperatures[31]. It can be seen from Table 7 that the activation energy of 2,4-D degradation by Fe-Ni/AC/O_3 was 46.88 kJ mol^{-1}, much lower than that of O_3 alone (52.72 kJ mol^{-1}) at the same reaction conditions, which supposes that Fe-Ni/AC offers the better catalytic activity in the ozonation of 2,4-D.

Table 7 Reaction activation energy of O_3 alone and Fe-Ni/AC/O_3 processes

T (K)	O_3		Fe-Ni/AC/O_3	
	k (min^{-1})	ln[k]	k (min^{-1})	ln[k]
278	0.0192	-3.95	0.0291	-3.54
288	0.0663	-2.71	0.0940	-2.36
298	0.0930	-2.38	0.1762	-1.74
308	0.2006	-1.61	0.2075	-1.57
	ln[k]= -6.3409/T + 19.011 R^2 = 0.9574		ln[k]=-5.6391/T + 16.972 R^2 = 0.9111	

3.8 Stability of Fe-Ni/AC

In order to investigate the stability of Fe-Ni/AC, the same test process (Fe-Ni/AC catalytic ozonation of 2,4-D) was repeated for seven times, as shown in Fig. 10. It shows that the TOC removal efficiency slightly decreased with the increase of the catalyst reused times, which suggests that the catalytic capacity of Fe-Ni/AC was slightly decreased with its reused times. The result also corresponds to Fig. 2 and Table 2. It can be seen from Fig. 2 that the spent catalyst had a different morphology after reused three times in catalytic ozonation of 2,4-D, compared with new Fe-Ni/AC. As illustrated in Table 2, the surface area of the spent Fe-Ni/AC catalyst sample was 401.54 m^2 g^{-1} after it was reused for three times, which was lower than that of the new Fe-Ni/AC sample (519.68 m^2 g^{-1}). It supposes that the activated carbon surface was partly oxidized by ozone, and some composite oxides of iron-nickel particles were spalled in the catalytic ozonation process of 2,4-D[22]. However, the TOC removal in catalytic ozonation of 2,4-D by Fe-Ni/AC was 61 % after repetition of three times and basically reached stable, while it only reached 34 % by ozonation alone and 50 % by AC/O_3, respectively. The above results demonstrate that the Fe-Ni/AC was an effective catalyst in the ozonation of 2,4-D.

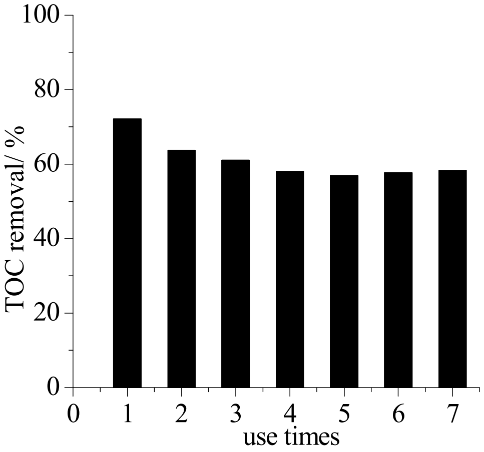


Fig. 10 Influence of Fe-Ni/AC catalyst use times on TOC removal in repeated reaction. Ozone dose: 50 mg h^{-1}, catalyst dose: 0.5 g L^{-1}, initial concentration of 2, 4-D solution: 10 mg L^{-1}, volume of 2,4-D solution: 1.4 L, temperature: 298 K, pH = 4.18, flow rate of oxygen: 1.2 L min^{-1}.

4 Conclusions

The composite oxides of iron-nickel supported on activated carbon (Fe-Ni/AC) was prepared and characterized by XRD, SEM, BET and AAS. Afterwards, it was investigated as ozonation catalyst in the mineralization of 2,4-D, and compared with the results in the absence of catalyst and in the presence of activated carbon. Compared to the ozonation alone, the presence of Fe-Ni/AC obviously improved the degradation and mineralization efficiency of 2,4-D. In the Fe-Ni/AC catalytic ozonation process, the TOC removal rate reached 72 % at 60min, while it was 50 % with AC, only 34 % by ozonation alone. On the other hand, the 2, 4-D and TOC removal followed similar trends in the range of 5 to 20 mg L^{-1}, but their removal rate reduced with the increase of 2,4-D concentration reasonably. Moreover, 2,4-D and TOC removal in aqueous solution both increased with the initial pH ranging from 3.00 to 11.00 in Fe-Ni/AC catalytic ozonation. Similarly, the 2,4-D and TOC removal was remarkably increased with the reaction temperature from 278 K to 308 K in the processes of ozonation alone and catalytic ozonation, respectively. In addition, the metal leaching contents in aqueous solution slightly increased with reaction temperature and pH, which was consistent with the 2,4-D and TOC removal efficiency in the process of catalytic ozonation.

Furthermore, it was demonstrated that the addition of TBA confirmed that 2,4-D was primarily oxidized by $HO^{\bullet}$ in O_3 alone, AC/O_3 and $Fe-Ni/AC/O_3$ processes. In the presence of TBA, the adsorption of 2, 4-D on Fe-Ni/AC slightly decreased, but the adsorption of TBA on Fe-Ni/AC reached 10%. Thus it may be assumed that the initiation of $HO^{\bullet}$ was enhanced by the introduction of composite oxides of iron-nickel, and the mechanism of Fe-Ni/AC catalytic ozonation is a synergic effect among ozone oxidation, adsorption and catalytic oxidation. The 2,4-D degradation rate followed pseudo first order reaction model well. Its degradation rate constant by $Fe-Ni/AC/O_3$ was 1.6 times higher than that of AC/O_3 and 1.9 times higher than that of O_3 alone at the same ozone concentration. While using Fe-Ni/AC as catalyst, the reaction activation energy could cut down 5.91 kJ mol^{-1} compared with O_3 alone at the same reaction conditions, which supposes that Fe-Ni/AC has better catalytic activity in the ozonation of 2,4-D. After the catalyst was reused for three times, the TOC removal was 61% and basically reached stable, better than O_3 alone or AC/O_3, which suggests that Fe-Ni/AC was an effective catalyst in the ozonation of 2,4-D.

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Notes and references

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