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Degradation of 2,4,6-trichlorophenol using magnetic nanoscaled Fe_3O_4/CeO_2 composite as a heterogeneous Fenton-like catalyst

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ABSTRACT

The degradation of 2,4,6-trichlorophenol (TCP) was investigated by using magnetic nanoscaled Fe_3O_4/CeO_2 composite as a heterogeneous Fenton-like catalyst. The individual and interactive effects of four process variables, i.e. solution pH, initial TCP concentration, Fe_3O_4/CeO_2 dosage and H_2O_2 concentration, on TCP removal, mineralization and dechlorination were investigated by response surface methodology (RSM) using the central composite design (CCD). The optimal regions of degradative conditions were pH 2.0–2.1, TCP 20–100 mg/L, Fe_3O_4/CeO_2 1.5–2.5 g/L, and H_2O_2 17–30 mM. The removal efficiency, mineralization and dechlorination rate of TCP was 99%, 65% and 95% after 90 min, respectively under the conditions of pH 2.0, TCP 100 mg/L, Fe_3O_4/CeO_2 2.5 g/L and H_2O_2 30 mM, which agreed well with the modeling prediction. Fe_3O_4/CeO_2 showed a high catalytic ability for the removal of TCP in comparison with other processes. The recyclability of Fe_3O_4/CeO_2 was also examined. According to the results of iron leaching, the effects of radical scavengers and intermediates determination, a possible pathway of TCP degradation was proposed based on ·OH mechanism (including free ·OH in the bulk liquid and surface-bounded ·OH).

1. Introduction

2,4,6-Trichlorophenol (TCP), widely employed in the manufacturing of fungicides, herbicides, pesticides, insecticides, antiseptics, pharmaceuticals, dyes and plastics, has been listed as a priority pollutant by the US Environmental Protection Agency and the European Union [1,2]. Adverse effects on human health caused by TCP, such as respiratory effects from cough to serious pulmonary defects, gastrointestinal effects, and cardiovascular effects, have been reported [1]. Due to its xenobiotic characteristics, carcinogenic and mutagenic properties, high toxicity and bioaccumulation, TCP must be removed before being discharged into the aquatic environment.

The toxicity and removal efficiency of cholorophenols are largely dependent on the number and position of chlorine atoms in the aromatic ring, which can be attributed to steric, inductive, and resonance effects [3]. As a result of high toxicity, carcinogenic properties and structural stabilization, traditional processes such as biological treatment are not very effective for removal of cholorophenols. In recent years, various technologies using novel materials have been studied to remove cholorophenols from aqueous solutions, such as adsorption technology [1,4,5], reductive treatment with zero-valent iron [6], electrochemical oxidation [7], catalytic wet oxidation [8,9], radiation-induced degradation [10,11]. Among the advanced oxidation processes, Fenton technology has become a favored process because of its high performance, cost-effectiveness, simplicity of technology, and low toxicity of the reagents [12]. Many researchers have investigated the decomposition of TCP by Fenton's reagent [13,14]. When combined with photolysis, the TCP degradation was faster than that by the Fenton process (dark reaction) [15,16]. Yuan and Lu [17] reported the removal of chlorophenols by electro-Fenton method, and they observed that the addition of small quantities of Fe^{2+} or Fe^{3+} significantly accelerated the degradation rate. However, the assistance of photolysis or electrochemical technology increases the energy requirements and the overall cost of treatment. Ferromagnetic nanoparticles have recently received more and more attention due to their large specific surface area and high surface reactivity as well as their stability and reusability [18–21]. In our previous study, a heterogeneous Fenton-like system using superparamagnetic nanoscaled Fe_3O_4/CeO_2 composite was successfully developed to oxidize 4-chlorophenol [20]. The component CeO_2 facilitated the dissolution of Fe_3O_4, and hydroxyl radicals (·OH)

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were generated by the reaction of Fe^{2+} and Ce^{3+} with H_2O_2, leading to the enhanced Fenton chemistry [20].

The efficiencies of heterogeneous Fenton-like systems depend on several operation parameters, mainly solution pH, initial pollutant concentration, catalyst dosage, H_2O_2 concentration, and reaction time. To optimize experimental conditions and to study the interactions of these variables, response surface methodology (RSM) has been found to be a very useful tool, as it is faster, more economical and effective. In the water treatment field, RSM has already been applied in many processes, such as adsorption [3], electrocoagulation [22], UV/H_2O_2 [23], O_3/UV [24], O_3/UV/H_2O_2 [24], Fenton and Fenton-like integrated process [25,26], and photo-Fenton process [27]. An experimental comparison between Box–Behnken design (BBD), central composite design (CCD), and Doehlert matrix design (DM) has been conducted by Zolgharnein et al. [28], which shows that CCD has a better prediction than the others. Nevertheless, few studies have been reported on the heterogeneous Fenton-like degradation of TCP, especially on the application of RSM to optimize the operating conditions.

The objective of this research was to investigate the treatability of wastewater containing TCP with the heterogeneous Fenton-like system using magnetic nanoscaled Fe_3O_4/CeO_2 composite, and also to optimize the key operating conditions using RSM. A central composite design was selected to study simultaneously the individual and interactive effects of four variables (pH value, initial TCP concentration, Fe_3O_4/CeO_2 dosage and H_2O_2 concentration) on the three responses (TCP removal, mineralization and dechlorination). Quadratic models were proposed to describe the relationships between these responses and variables. Furthermore, iron leaching, H_2O_2 decomposition, reactive oxidizing species mediated in the system, the mechanism of TCP degradation as well as the reusability of the catalyst were evaluated.

Table 2
Range of different parameters investigated with CCD design.

Factors	Variables	Actual values for the coded levels				
		−2	−1	0	1	2
X_1 (A)	pH	2.0	2.5	3.0	3.5	4.0
X_2 (B)	Initial TCP concentration (mg/L)	20	40	60	80	100
X_3 (C)	Fe_3O_4/CeO_2 dosage (g/L)	0.5	1.0	1.5	2.0	2.5
X_4 (D)	H_2O_2 concentration (mM)	6	12	18	24	30

2. Materials and methods

2.1. Chemicals and materials

Ferrous sulfate ($FeSO_4·7H_2O$) and ferric sulfate ($Fe_2(SO_4)_3$) were supplied by Shenyang Reagent Factory and Tianjin Yongda Chemical Reagent Co., Ltd., respectively. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3·6H_2O$) and polyethylene glycol (PEG) 4000 were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium carbonate ($(NH_4)_2CO_3$) was purchased from Beijing Yili Fine Chemicals Co., Ltd. TCP was obtained from Alfa Aesar (USA). Analytical grade carboxylic acids, H_2O_2 (30%, v/v), sulfuric acid (H_2SO_4), *n*-butanol, and KI were supplied by the Beijing Chemical Factory. Double distilled water was used throughout this study.

The magnetic nanoparticles (MNPs) with the weight ratio of Fe_3O_4 and CeO_2 1:1 used in this study were synthesized and characterized as described previously [20]. First, CeO_2 NPs were precipitated from aqueous solution of 100 mL 0.1 M $Ce(NO_3)_3·6H_2O$ and 4 g/L PEG 4000 by the addition of 150 mL 0.1 M $(NH_4)_2CO_3$ solution under violently stirring for 10 min at 40 °C. After filtrated, dispersed by ultrasonic wave (frequency 99 kHz), and washed

Table 1
Central composite design and experimental results of heterogeneous Fenton-like degradation of TCP.

Run	Variables				Responses		
	A: pH	B: Initial TCP concentration (mg/L)	C: Fe_3O_4/CeO_2 dosage (g/L)	D: H_2O_2 concentration (mM)	R_1: TCP removal (%)	R_2: Mineralization (%)	R_3: Dechlorination (%)
1	3.0	60	1.5	18	32.5	16.62	27.25
2	3.0	60	1.5	18	29.66	16.5	27.18
3	2.5	80	2.0	24	69.23	37.91	64.63
4	3.0	60	1.5	18	30.24	17.39	29.45
5	3.0	60	1.5	18	29.18	15.36	29.38
6	3.5	40	1.0	12	18.5	11.33	16.8
7	2.5	80	1.0	12	41.01	26.76	41.12
8	3.0	60	1.5	30	24.74	9.01	23.48
9	3.5	80	2.0	24	17.65	7.37	15.79
10	3.5	40	2.0	24	20.13	8.71	16.21
11	2.5	40	2.0	12	72.89	43.3	69.02
12	3.5	40	2.0	12	18.38	9.4	16.07
13	3.5	40	1.0	24	18.34	3.7	14.32
14	2.5	80	2.0	12	57.2	29.66	54.28
15	4.0	60	1.5	18	7.38	0.08	2.86
16	3.0	60	1.5	18	31.48	18.5	28.23
17	3.5	80	2.0	12	12.32	6.66	1.95
18	2.0	60	1.5	18	87.8	59	85.76
19	2.5	40	1.0	12	47.5	24.35	48.87
20	3.5	80	1.0	24	10.04	4.52	3.26
21	2.5	80	1.0	24	43.96	26.58	41.06
22	3.0	60	1.5	6	10.25	4.94	9.6
23	3.5	80	1.0	12	16.07	2.12	3.07
24	3.0	60	2.5	18	20.85	7.09	18.04
25	3.0	60	1.5	18	29.51	16.61	28.82
26	3.0	60	0.5	18	15.96	9.59	14.99
27	3.0	100	1.5	18	8.8	1.94	8.42
28	2.5	40	1.0	24	54.73	19.43	54.87
29	3.0	20	1.5	18	30.15	9.7	29.41
30	2.5	40	2.0	24	78.81	40.44	78.47