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Evaluation of microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides

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Abstract

Microwave-enhance catalytic degradation (MECD) of 4-chlorophenol (4-CP) using nickel oxide had been studied. A nickel hydroxide, $Ni(OH)_2$, was prepared by microwave-assisted heating technique from nickel nitrate aqueous solution and sodium hydroxide (assigned as PM). Then, the as-prepared PM was oxidized by liquid oxidation with sodium hypochlorite (assigned as PMO). Further, pure nanosized nickel oxide was obtained from the PMO by calcination at 300, 400 and 500 °C (labeled as C300, C400 and C500, respectively). They were characterized by X-ray (XRD), infrared spectroscopy (IR) and temperature programmed reduction (TPR). Their catalytic activities towards the degradation of 4-CP on the efficiency of the degradation were further investigated under continuous bubbling of air through the liquid phase and quantitative evaluated by high pressure liquid chromatography (HPLC). Also, the effects of initial concentration, pH, temperature and kinds of catalysts on the efficiency of the degradation have been investigated. The relative activity affected significantly with the oxidation state of nickel and decreased slightly with the particle size of nickel oxide, i.e., PMO (> +2) $\gg$ C300 (+2, $d = 4.1$ nm) > C400 (+2, $d = 9.4$ nm) > C500 (+2, $d = 12.0$ nm).

Keywords: Nickel oxide; Microwave; Degradation of 4-chlorophenol

1. Introduction

The content of the organic pollution is serious in industrial wastewater. Aromatic pollutants, in particular phenol, chlorophenol compounds and phenolic derivatives have been considered on the EPAs priority pollutants list since 1976 [1]. These compounds are considered as hazardous pollutants because of their potential to harm human health. Indeed, it is necessary to eliminate them from industrial wastewater before discharged. Sonochemical degradation [2–4], phtocatalytic degradation [5–9], advanced oxidation process with UV/H_2O_2 (AOP) [10], catalytic oxidation [11] and the microwave-enhanced advanced oxidation processes [12–15] have been given considerable attention in recent years for removal of these hazardous pollutants. One of the most promising technologies is to utilize microwave-enhanced photocatalysis method for the degradation of 4-chlorophenol [16]. Microwave radiation technology has already been applied to industry, family, medical science and environmental organic pollution for polycyclic aromatic hydrocarbons (PAHs) [17–19] and polychlorinated biphenyls (PCBs) [20], etc. The use of microwaves as a source of energy is rapidly growing economized and getting convenient advantage.

4-Chlorophenol (4-CP) is a toxic and non-biodegradable organic compound that is widely used for the production of fungicides, drugs and dyes [21]. It is commonly detected in soil, sediments, surface water and wastewater that cause severe environmental problems. Many efforts have been dedicated to minimize the deleterious effect. Using solid materials as catalysts is of great interest and important in purifying waste waters. Transition metal oxides have proved to be active in the catalytic reactions of the degradation of chlorophenol and its derivatives

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[22]. However, how to eliminate this compound at low concentrations in water is still a fundamental challenge.

In a previous work, we have succeeded performance of degradation of phenol with microwave-enhance catalytic degradation (MECD) method [23]. For this reason the present work has been devoted the MECD method on the degradation of 4-CP. Variable factors can influence the activity, such as initial concentration of 4-CP, pH, temperature and kinds of catalysts. Therefore, the major objective of this study adopts nickel oxide as active components and combining the microwave irradiation technology to promote the degradation of 4-CP.

2. Experimental

2.1. Preparation of nickel oxide

All the chemical reagents used in this study were analytical grade and used without further purification. A 5.0 ml of 0.6 M $Ni(NO_3)_2{\cdot}6H_2O$ solution was added to the 100 ml of 3.2 M NaOH solution. The reaction was carried out for 10 min in air in a microwave apparatus (100 W, 2450 MHz, CEM, USA). The obtained as-prepared nickel hydroxide, $Ni(OH)_2$, presents a green colloid solution and assigned as PM. Then, the as-prepared PM was oxidized by liquid oxidation with sodium hypochlorite drop by drop under a constant stirring at 0 °C for 2 h. Finally, a kind of black sediment was formed and assigned as PMO. The as-prepared PMO precipitate was thoroughly washed with distilled water six times, respectively, to remove the possible adsorbed ions. After dried at 110 °C for 20 h, the as-prepared PMO powder was calcined under air at 300, 400 and 500 °C, respectively, for 2 h to obtain nanosized nickel oxides (labeled as C300, C400 and C500).

2.2. Characterization of nickel oxide

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu Kα1 radiation ($\lambda = 1.5405$ Å) at 40 kV and 30 mA with a scanning speed in 2θ of $4^\circ\ \mathrm{min}^{-1}$. The crystallite size of nickel oxides was estimated using the Scherrer equation.

The infrared spectra were obtained by a Nicolet 5700 FT-IR spectrometer in the range of 500–4000 cm^{-1}. One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tonnes.

Reduction behavior of nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10% H_2/N_2 gas mixture at a flow rate of 10 ml min^{-1}. During TPR, the temperature was increased by 7 °C min^{-1} increment from room temperature to 600 °C.

2.3. Degradation of 4-chlorophenol

The MECD experiments for degradation of 4-CP were carried out in a thermostated static microwave apparatus (CEM. Discover, USA, 2450 MHz, 300 W, temperature was controlled with IR sensor) upon continuous stirring, likewise providing an equal level of all parameters describing the state of the system (temperature, pH, catalysts and initial concentration of 4-CP). A 60 ml of aqueous 4-CP solution was used for each experimental run. Air was bubbled in the solution for 30 min before adding the catalyst. Then, a fit amount of catalyst was suspended in the solution. The air was continuously bubbled during the runs. To draw 3–5 ml the upper layers of suspension after static 10 min and filtrated with syringe filters (Cellulose Acetate, 0.2 μm, Japan) for each experimental data for quantitative analysis with HPLC. The absorbance of 270 nm was used to measure the concentration of 4-CP.

The chromatographic experiment were performed using high pressure liquid chromatograph Agilent 1100 Series equipped with diode array detector and a column oven. A 125 mm × 4 mm reverse-phase C-18 column (chrompack) was used for separation. The injection volume was 20 μl, flow rate was 1.0 ml/min, UV detector wavelength was 270 nm and column oven temperature maintained 25 °C. The compounds were eluted with acetonitrile–water (v/v, 50/50). Calibration graphs at five concentration levels were prepared from working solutions containing the 4-CP in the range 0.1–200 mg/l ($R^2 = 0.9997$, S.D. = 2.15).

3. Results and discussion

3.1. Characterization of as-prepared materials (PM and PMO)

Fig. 1 shows the XRD patterns of the as-prepared materials, PM and PMO. It indicates that all the major peak positions and relative intensities of the as-prepared PM (Fig. 1(a)) matches the JCPDS 14-0117 file identifying β-$Ni(OH)_2$, with a hexagonal structure. The XRD pattern of the as-prepared PMO (Fig. 1(b)) has the peaks at ca. 19.0° and 38.4° and these locations are similar with the β-NiOOH with the peaks at (0 0 1) and (0 0 2) planes.

The infrared spectrum of the as-prepared materials is shown in Fig. 2. The broad absorption bands centered around 3450

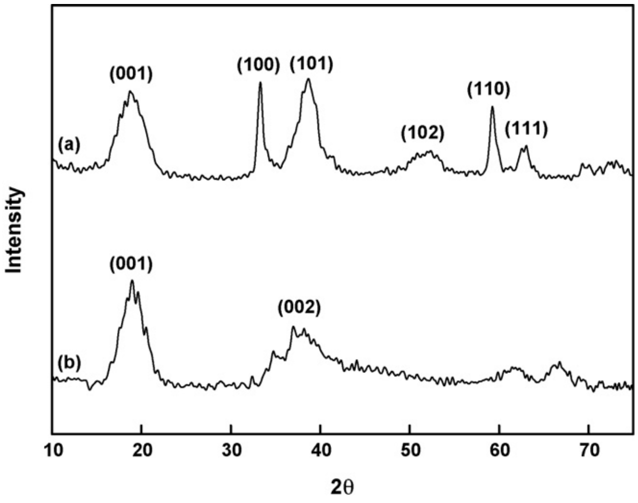

Fig. 1. XRD pattern of the as-prepared materials: (a) PM; (b) PMO.

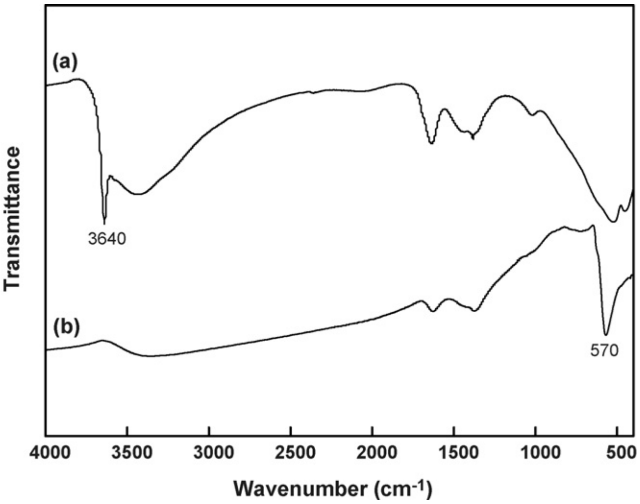

Fig. 2. IR spectrum of the as-prepared materials: (a) PM; (b) PMO.

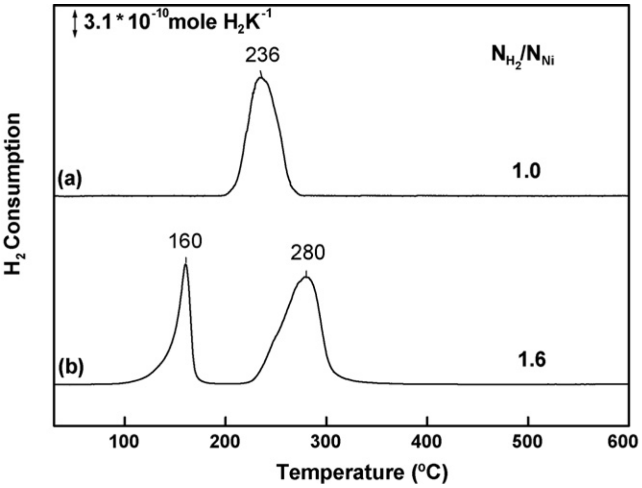

Fig. 4. TPR profile of the as-prepared materials: (a) PM; (b) PMO.

and 1630 cm^{-1} are assigned to the existence of water. From the strength of absorption, we know that the as-prepared PM (Fig. 2(a)) has stronger absorption ability than the as-prepared PMO (Fig. 2(b)) for moisture. The absorption band at 1530–1320 cm^{-1} indicates the existence of carbonates. The spectrum (Fig. 2(a)) displays a sharp ν_{OH} (–OH group stretching vibration) peak around 3640 cm^{-1} and this confirms that the as-prepared PM is β-Ni(OH)$_2$ [24]. The absorption band at 570 cm^{-1} (Fig. 2(b)) indicates that the as-prepared PMO possesses the in-plane vibration of hydrogen-bonded hydroxyl group.

Fig. 3 shows the TG/DTG curves of the as-prepared PMO under a dynamic nitrogen (100 ml min^{-1}) environment. The TG curve shows three weight loss steps (assigned as D$_1$, D$_2$ and D$_3$) and the DTG curve shows the maximum loss rate of a D$_2$ step at 227 °C, while the D$_3$ step is not obvious. Prior to 100 °C, the rapid weight loss (D$_1$ step) should be came from the desorbed of water on PMO surface in heating process. The weight loss of 18% in D$_2$ and D$_3$ steps is accompanied by the dehydration and desorbed of oxygen from β-NiOOH that transfers into NiO according to Eq. (1).

$$2\text{NiOOH} \rightarrow 2\text{NiO} + \text{H}_2\text{O}+\tfrac{1}{2}\text{O}_2 \qquad (1)$$

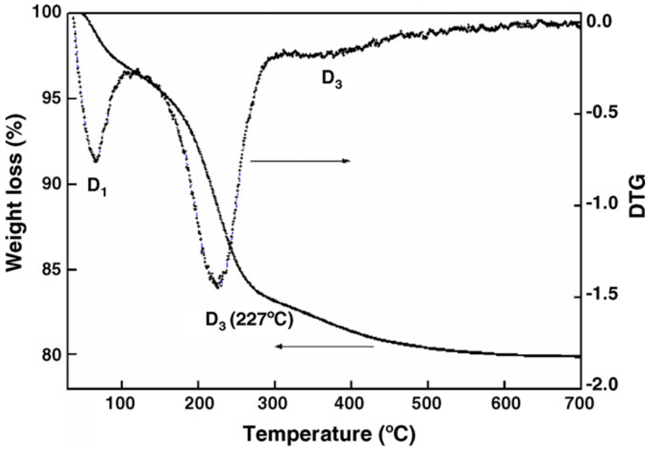

Fig. 3. TG/DTG profiles of the fabricated PMO in a dynamic nitrogen environment.

Fig. 4 shows the TPR profile of the as-prepared materials, PM and PMO. The reductive signal of the as-prepared PM (Fig. 4(a)) in TPR proceeded by one step at 236 °C according to Eq. (2).

$$\text{Ni(OH)}_2 + \text{H}_2 \rightarrow \text{Ni} + 2\text{H}_2\text{O} \qquad (2)$$

The ratio of nickel hydroxide species is quantitatively determined from the consumption of hydrogen in TPR traces. The $N_{\text{H}_2}/N_{\text{Ni}}$ ratio is 1.0.

Reduction profiles of the as-prepared PMO (Fig. 4(b)) shows two reduction peaks, which are similar to those observed in supported nickel catalysts [25,26]. These profiles point to a two-step reduction process: the first step is low intensity at 160 °C and the more intense second step whose maximum occurs at 280 °C according to the following equations:

$$\text{NiO}_x + x\text{H}_2 \rightarrow \text{NiO} + x\text{H}_2\text{O} \qquad (3)$$

$$\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \qquad (4)$$

The $N_{\text{H}_2}/N_{\text{Ni}}$ ratio is determined to be 1.6. This shows that the as-prepared PMO is confirmed to be a high valence nickel oxide with a non-stoichiometric chemical formula of $(\text{NiO})_{0.4}(\text{NiO}_2)_{0.6}$. The content of Ni^{4+} may be the factor to affect the activity for the degradation of 4-CP.

3.2. Characterization of nanosized nickel oxides

In order to obtain pure nanosized nickel oxide (NiO) particles and understand the thermal characterizations, the high valence nickel oxide (PMO) is further calcined at 300, 400 and 500 °C, respectively (the calcined temperature assigned as T_C).

Fig. 5 presents XRD patterns of nanosized nickel oxides. The effects of the calcination temperature on the crystallite size of NiO particles can be demonstrated. Traces of NiO crystallite phases (1 1 1), (2 0 0) and (2 2 0) are detected in the XRD pattern for all samples and their intensities increase with T_C. In general, the sharpness of the XRD peak (i.e., high crystallinity)

Table 1
Characterization and rate constant of the 4-CP degradation over nickel oxides

Catalyst	XRD		TPR		Degradation of 4-CP	
	Structure	*d* (nm)	T_{red} (°C)	N_{H_2}/N_{Ni}	α_{25}[a] (%)	k (min^{-1})
PMO	–	–	157, 277	1.58	100	0.132
C300	Cubic	4.1	361	1.09	23	0.005
C400	Cubic	9.4	385	1.11	23	0.005
C500	Cubic	12.0	391	1.11	17	0.002

[a] Degree of phenol conversion is determined at 25 min.

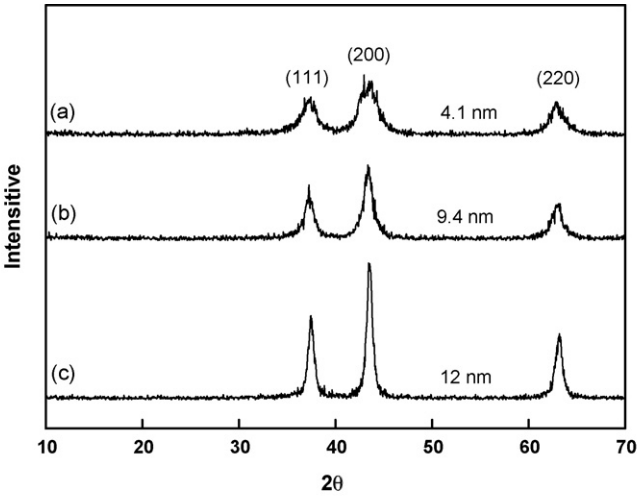

Fig. 5. XRD spectra of nickel oxides: (a) C300; (b) C400; (c) C500.

is increased as the T_C increases. According to the (2 0 0) diffraction pattern of NiO crystalline, the particle size of NiO can be calculated from the full width at half-maximum using the Scherrer equation. Obviously, the particle size (d) grows from 4.1 to 12 nm (given in the third column of Table 1) with the T_C.

Fig. 6 presents IR spectrum of nanosized nickel oxides. The absorption band at 1530–1320 cm^{-1} indicates the existence of carbonates. Comparison with the as-prepared PMO, the 570 cm^{-1} absorption band disappears for the refined nickel oxides. Combination with the analysis of XRD, we confirm that the purity of nickel oxide. For the bulk form of NiO, the main IR absorption maximum corresponds to the long wavelength transverse optical mode and the optical photon frequency lie between 390 and 403 cm^{-1} [27].

Fig. 7 displays the TPR profiles of the calcined product, NiO, at different temperatures. All the samples show a similar TPR profile. A qualitative analysis of the TPR profile shows that the reduction peak (T_{red}) appears shifted to higher temperatures as the T_C increased (as can be seen in the fourth column of Table 1) i.e., the T_{red} of sample C300 is 361 °C (Fig. 7(a)). While, the T_{red} of sample C500 is 391 °C (Fig. 7(c)). According to the calculated particle sizes of nickel oxide from XRD, we know that the shift in the T_{red} toward higher temperature is marked more as the particle size increases. The more reducible nickel oxide is located mainly in the small pores with a mean diameter of ∼4 nm and the less reducible oxide is located in the larger pores with a mean diameter larger than 10 nm. Also, the ratio of nickel oxide species for the calcined product, NiO, at different temperature is quantitatively determined from the consumption of hydrogen in TPR traces (given in the fifth column of Table 1). This shows that the dominant species upon calcination at 300–500 °C is NiO, where *x* approaches 1.0.

The TEM images of both C300 and C500 nickel oxide powers show in Fig. 8. From this image it is clearly seen that the C300 particle has nearly uniform size and well dispersion in the bulk state with diameter around 3–8 nm (Fig. 8(a)). As the thermal

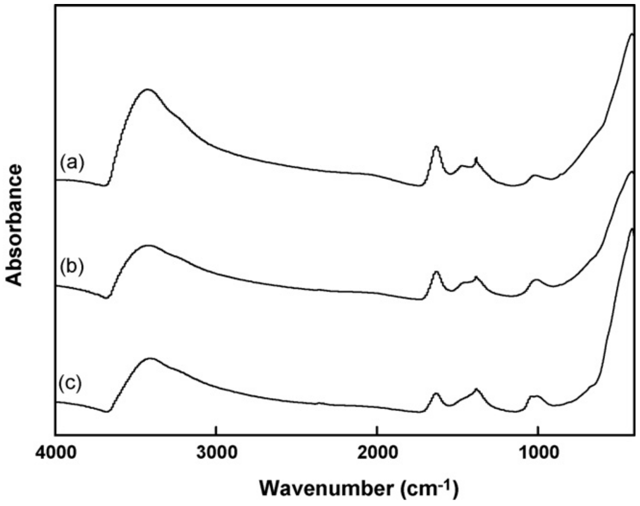

Fig. 6. IR profiles of nickel oxides: (a) C300; (b) C400; (c) C500.

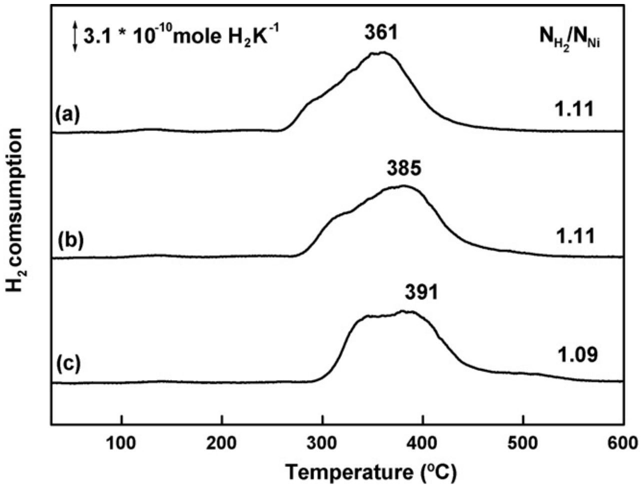

Fig. 7. TPR profiles of nickel oxides: (a) C300; (b) C400; (c) C500.

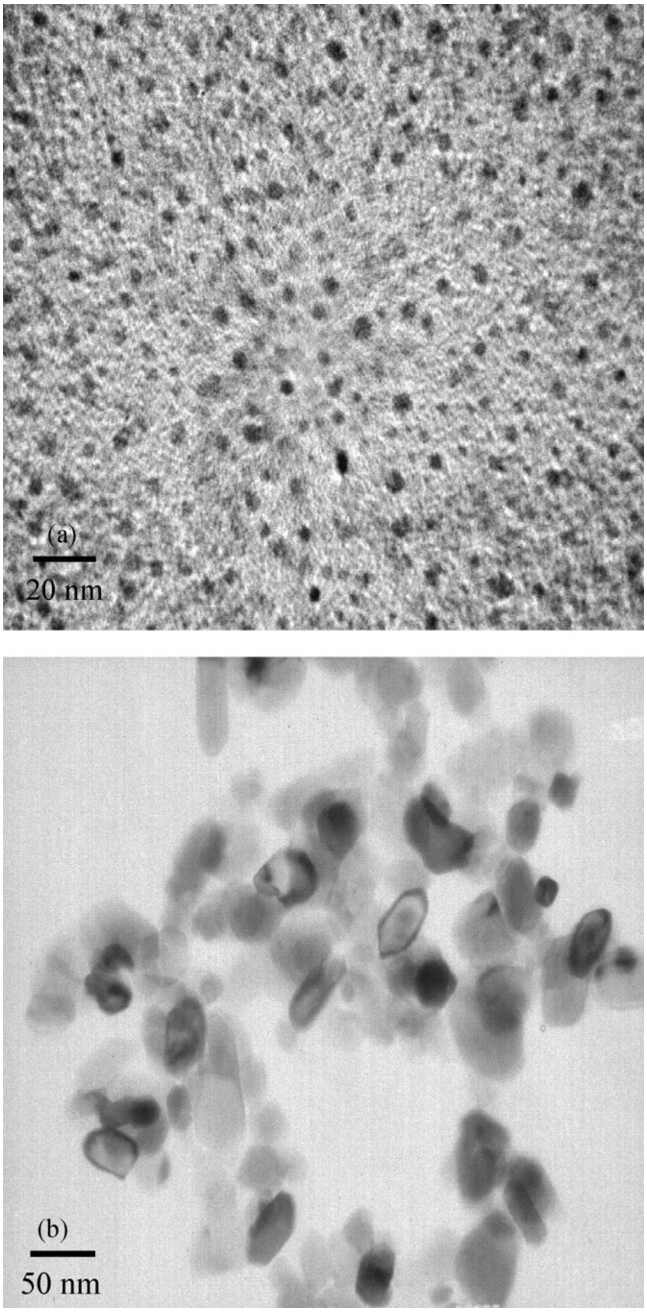

Fig. 8. TEM images of nickel oxides: (a) C300; (b) C500.

treatment temperature increasing, the agglomeration of particles is present (Fig. 8(b)). The irregular morphology of C500 particle shows larger diameter around 15–35 nm. Generally, it can be considered that the agglomeration of nanoparticles comes from the interfacial reaction.

3.3. Degradation of 4-chlorophenol

Since oxidation is carried out under constant bubbling of air in the mixture, we postulate that the reaction is of zero order against oxygen. Experimental conditions provide stationary concentration of oxygen on the surface of the catalyst. This means hat the reaction rate is independent of the concentration of dissolved oxygen. It should be noted that all experiments are carried out with the same concentration of dissolved oxygen [22].

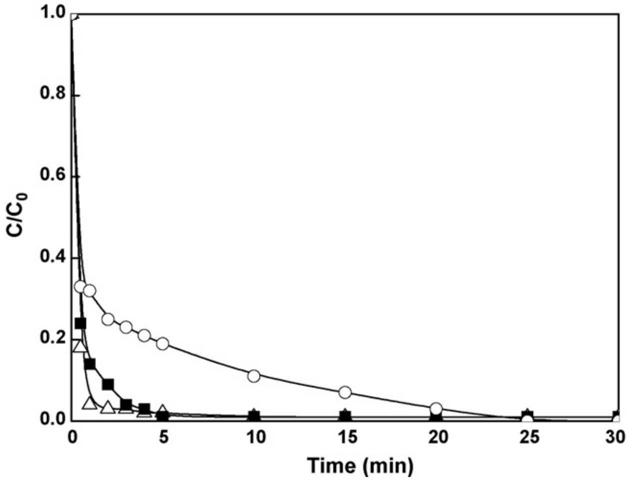

Fig. 9. The effect of the initial concentration on the degradation of 4-CP by MECD method over as-prepared PMO (0.12 g) catalyst at pH 7 and $T = 40\,^\circ$C: (△) 25 ppm; (■) 50 ppm; (○) 100 ppm.

The effect of initial concentration on the degradation of 4-CP by MECD method over as-prepared PMO catalyst is investigated in the ranges from 25 to 100 ppm under pH 7 and $T = 40\,^\circ$C. The results (see Fig. 9) show that the increase of initial concentration causes a decrease in the degradation efficiency. We suggest that the reaction only proceeds on the catalyst surface, and not homogeneously. An additional evidence for this conclusion is the fact that, after removing the catalyst from the reaction mixture, the degradation process is ceased [28].

The effect of temperatures on the activity by MECD method over as-prepared PMO catalyst is investigated in the temperature ranges from 40 to 70 °C under pH 7 and $C = 100$ ppm. It can be seen from Fig. 10 that the fastest rate of 4-CP degraded also occurred within 1 min under different temperatures. Whereas, the decrease of residual 4-CP concentration inverses with temperature. The residual rapidly decreases under 40 °C but less

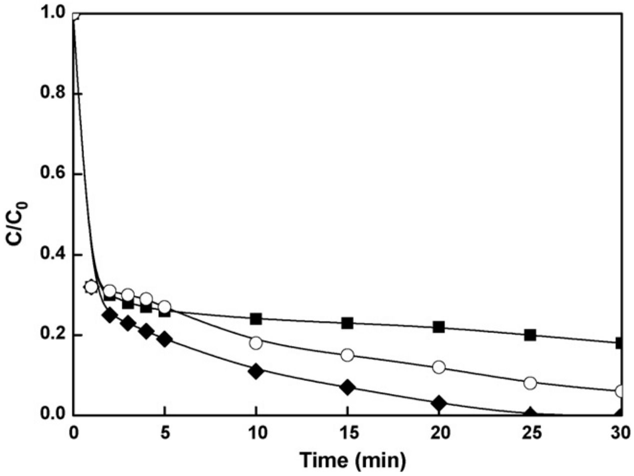

Fig. 10. The effect of the temperature on the degradation of 4-CP by MECD method over as-prepared PMO (0.12 g) catalyst at pH 7 and $C = 100$ ppm: (◆) 40 °C; (○) 55 °C; (■) 70 °C.

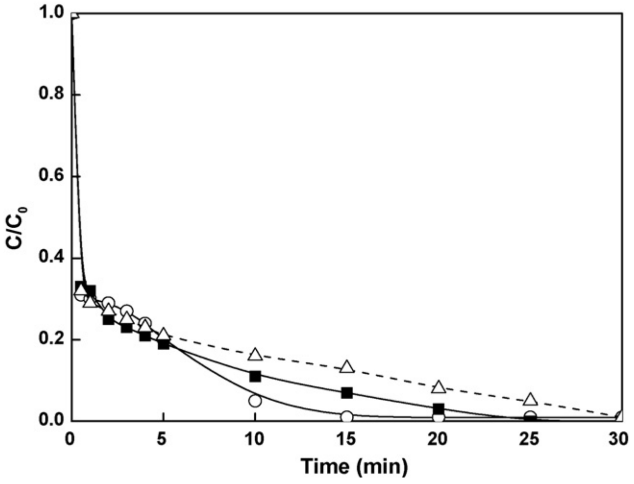

Fig. 11. The effect of the pH on the degradation of 4-CP by MECD method over as-prepared PMO (0.12 g) catalyst at $T=40$ °C and $C=100$ ppm: (○) pH 4; (■) pH 7; (△) pH 10.

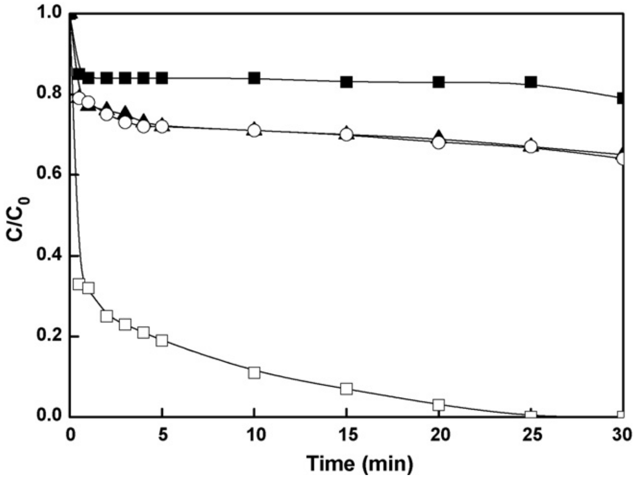

Fig. 12. Comparison of the degradation of 4-CP by MECD method over nickel oxides (0.12 g) under pH 7, $C=100$ ppm and $T=40$ °C: (□) as-prepared PMO; (▲) C300; (○) C400; (■) C500.

changed at 70 °C. A complete degradation is achieved after 25 min under 40 °C. The result is different from Christoskova and Stoyanova [28]. They found that the degradation of phenol without microwave irradiate is dependant on the temperature. In order to understand the effect of microwave, the dielectric loss tangent (tan δ) of 4-CP aqueous solution were measured at certain temperature using an Agilent 8714 ET Vector Network in the frequency range 300 kHz to 3 GHz. The measured tan δ in the 2450 MHz frequency is 0.099, 0.087 and 0.072 under 40, 55 and 70 °C, respectively. The larger of the tan δ can promote rapid heating of the system [29,30]. Obviously, it is suitable for microwave absorbance under low temperature to generate more microwave enhance catalysis the degradation of 4-CP.

Fig. 11 demonstrates the 4-CP can be totally eliminated in the pH range of 4–10 in 30 min by MECD method over as-prepared PMO catalyst under 40 °C and $C=100$ ppm. Obviously, the fastest rate of 4-CP degraded occurred within 1 min (degree of conversion attains 70%) under different pH conditions. The MECD method is likely to give a large effect on the removal of 4-CP. It means that microwave combined with catalysis can effectively degrade several kinds of intermediates produced in the course of 4-CP degradation, eventually driving the intermediates into CO_2, H_2O and HCl. A complete degradation is achieved after 20 min under pH 4 whereas at 40 °C and $C=100$ ppm.

Fig. 12 compares the degradation of 4-CP over PMO with the refined pure nickel oxides (C300, C400 and C500) under 40 °C, pH 7 and $C=100$ ppm. The degradation of 4-CP over each fresh catalyst generally increased with the reaction time. Clearly, the activity of the as-prepared PMO (high valence nickel oxide, NiO_x, $x>1$) is better than NiO. Within 25 min, the 4-CP can be degraded completely over PMO catalyst. However, even within 30 min, the 4-CP only approached 20–30% degradation over NiO (C300, C400 and C500). To compare the relative activity of the catalysts, kinetic parameters of the degree of conversion (α_{25}, determined at the 25 min) and rate constant (k) are listed in the sixth and last columns of Table 1. The rate constant on PMO catalyst is two orders of magnitude higher than C300, C400 and C500 catalysts. The driving force for PMO is probably the existence of Ni^{4+} that reaches rapidly the high conversion. According to the TPR result (Fig. 4(b)), the lower temperature reduction (R_1) reveals that the bond strength of Ni–O on NiO_x is weak and provides easily oxygen to oxidize the 4-CP. Apparently, the relative activity is strongly dependent on the oxidation state of nickel and decreases slightly with the particle size of nickel oxide, i.e., PMO (> +2) ≫ C300 (+2, $d=4.1$ nm) > C400 (+2, $d=9.4$ nm) > C500 (+2, $d=12.0$ nm).

4. Conclusion

A novel and environmentally friendly process for the degradation of 4-CP has been succeeded development. The following conclusions have been made as follows:

(1). The as-prepared PMO is confirmed to be a high valence nickel oxide with a non-stoichiometric chemical formula of $(NiO)_{0.4}(NiO_2)_{0.6}$.
(2). 4-CP is degraded completely by MECD method within 25 min under pH 7, $T=40$ °C and $C=100$ ppm over PMO catalyst.
(3). Activity of 4-CP degraded is strongly dependent on the oxidation state of nickel and decreases slightly with the particle size of nickel oxide.

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