This article was downloaded by: [Zhejiang University]
On: 05 May 2014, At: 05:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tjen20

Catalytic dechlorination of 2,4-dichlorophenol by Ni/Fe nanoparticles in the presence of humic acid: intermediate products and some experimental parameters

Zhen Zhang [a] [b] , Xiaoshu Lv [a] , Shams Ali Baig [a] & Xinhua Xu [a]
[a] Department of Environmental Engineering , Zhejiang University , Hangzhou 310058 , People's Republic of China
[b] School of Bioscience, Taizhou University , Linhai 317000 , People's Republic of China
Published online: 24 Jul 2012.

To cite this article: Zhen Zhang , Xiaoshu Lv , Shams Ali Baig & Xinhua Xu (2014) Catalytic dechlorination of 2,4-dichlorophenol by Ni/Fe nanoparticles in the presence of humic acid: intermediate products and some experimental parameters, Journal of Experimental Nanoscience, 9:6, 603-615, DOI: 10.1080/17458080.2012.680929

To link to this article: http://dx.doi.org/10.1080/17458080.2012.680929

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Experimental Nanoscience, 2014
Vol. 9, No. 6, 603–615, http://dx.doi.org/10.1080/17458080.2012.680929

Catalytic dechlorination of 2,4-dichlorophenol by Ni/Fe nanoparticles in the presence of humic acid: intermediate products and some experimental parameters

Zhen Zhang[ab], Xiaoshu Lv[a], Shams Ali Baig[a] and Xinhua Xu[a]*

[a]*Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China;* [b]*School of Bioscience, Taizhou University, Linhai 317000, People's Republic of China*

(*Received 29 September 2011; final version received 23 March 2012*)

The catalytic dechlorination of *2,4*-dichlorophenol (*2,4*-DCP) by Ni/Fe bimetallic nanoparticles in the presence of humic acid (HA) was investigated in order to understand their applicability for *in situ* remediation of groundwater. *2,4*-DCP was catalytically dechlorinated to form the final products – phenol (P) via two intermediates, *o*-chlorophenol (*o*-CP) and *p*-chlorophenol (*p*-CP). It was demonstrated that the carbon mass balances during the dechlorination were between 84% and 92%, and other carbons were adsorbed on the surface of Ni/Fe bimetallic nanoparticles. The experimental results suggest that HA competed for reaction sites on the Ni/Fe bimetallic nanoparticles with *2,4*-DCP, and thus reduced the efficiency and rate of the dechlorination of *2,4*-DCP. The catalytic degradation slowed down as the increase of HA in solution, and when HA's concentrations were 0, 10, 20 and 30 mg L^{-1}, the maximum concentrations of *o*-CP were 0.025, 0.041, 0.039 and 0.034 mM in 10, 30, 30 and 30 min, respectively. High Ni content, low initial pH value, high Ni/Fe nanoparticles' dosage and high temperature favoured the catalytic dechlorination of *2,4*-DCP. The experimental results show that no other intermediates were generated besides Cl^-, *o*-CP, *p*-CP and P during the catalytic dechlorination of *2,4*-DCP.

Keywords: Ni/Fe bimetallic nanoparticles; catalytic dechlorination; *2,4*-DCP; HA

1. Introduction

Chlorinated organic contaminants (COCs) constitute an important class of pollutants because of their wide use in the production of wood preservers, pesticides and biocides [1]. Because of their reactive nature, COCs are highly toxic, mutagenic and possibly carcinogenic compounds, which were established as a class of environmental priority pollutants by the United States Environment Protection Agency (US-EPA) in 1988. Once released into the environment, COCs will accumulate in the surrounding areas and pose a great health threat to humans and ecosystems over a long period of time [1,2], this raises an urgent need for efficient dechlorination methods to eliminate COCs from both concentrated industrial effluents and diluted polluted groundwater.

Although COCs have been reported to be degraded by bacteria or plants, longer actor residence times are often required to achieve treatment goals [3]. Some physical and chemical methods have also been used for the removal of COCs as well as, their derivatives from wastewater, such as adsorption with activated carbon, air stripping, chemical oxidation, solvent

---

*Corresponding author. Email: xuxinhua@zju.edu.cn

Table 1. Abbreviations in the text.

Sequence number	Full name	Index
1	*2,4*-dichlorophenol	*2,4*-DCP
2	Humic acid	HA
3	Phenol	P
4	*o*-chlorophenol	*o*-CP
5	*p*-chlorophenol	*p*-CP
6	Chlorinated organic contaminants	COCs
7	Chlorophenol	CP
8	Zero-valent iron	Fe^0
9	Permeable reactive barriers	PRBs

extraction, ultraviolet light and ozone, etc [1]. However, high cost and low efficiency of these processes limit their practical applicability.

PRBs packed with zero-valent iron (Fe^0) have shown to be an effective technology for the remediation of contaminated groundwater because of its low cost and least environmental impact [4]. As reactive media, common Fe^0 was micron to sub-millimeter-sized with low reactivity. In addition, the reactivity of Fe^0 has recently been improved by the development of smaller-sized Fe^0 or zero-valent bimetallic nanoparticles (Ni/Fe, Pd/Fe, etc.). Compared with the common iron or bimetallic particles, Fe^0 or zero-valent bimetallic nanoparticles has higher specific surface area, surface reactivity and efficiency for dechlorination of COCs, as well as a much lower loading required in the hydro-dechlorination process [5–7]. Furthermore, the nanoparticles could remain suspended under gentle's agitation condition, so it may be possible to inject them into the contaminated soils, sediments and aquifers for *in situ* remediation of COCs [5].

Although bimetallic nanoparticles are quite effective in dechlorination of the contaminants, the reactivity of the zero-valent metals is highly controlled by the surface characteristics of metals and groundwater quality. In subsurface environments, natural humic matter is abundantly available and always plays an important role in both electron transfer and adsorption processes. The inhibition of chlorinated hydrocarbon's dechlorination by zero-valent metals in the presence of natural humic matter was reported by Tratnyek et al. [8]. They suggested that any nonreactive adsorbate, which without compete with the contaminants for reactive surface sites would result in a decrease in the degradation rate.

The general objective of this work is to prepare Ni/Fe bimetallic nanoparticles for the dechlorination of *2,4*-dichlorophenol (*2,4*-DCP) and evaluate the performance of the nanoscale bimetallic system in the remediation of contaminated groundwater. *2,4*-DCP was selected as a model compound due to its abundance in the contaminated groundwater. The specific objectives are to (1) investigate the role of humic acid (HA) in the dechlorination of chlorinated hydrocarbons by Ni/Fe bimetallic nanoparticles and (2) study the intermediate products and some experimental parameters, which may affect *2,4*-DCP reduction, such as HA concentration, Ni/Fe nanoparticles dosage, Ni content, initial pH value and temperature. The abbreviations were used in the manuscript are listed in Table 1.

2. Experimental section

2.1. Chemicals

Chemicals used in this dechlorination process such as nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$, $\geq 99.0\%$), iron sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), *2,4*-DCP, *o*-chlorophenol (*o*-CP), *p*-chlorophenol (*p*-CP) and other reagents were of analytical grade and used as received without further purification. *2,4*-DCP was dissolved in deionised water and stored at 4°C. HA was obtained from Sigma-Aldrich (ash ~20%, Switzerland). The HA stock solution (500 mg L^{-1}) was prepared by dissolving 0.25 g HA in 2 mL NaOH aqueous solution of 0.1 mol L^{-1}, followed by sonication and further dilution with deionised water up to 500 mL, and the pH was adjusted to 7.0. The final HA solution was then filtered through a 0.45 μm filter membrane, and HA solutions were stored at 4°C before use.

Earlier, both Fe^0 and Ni/Fe nanoparticles were synthesised, and the synthesis of Fe^0 and Ni/Fe nanoparticles was performed as described by Zhang et al. [9]. First, the iron nanoparticles were synthesised by drop-wise addition of stoichiometric amounts of $NaBH_4$ aqueous solution into a flask containing $FeSO_4 \cdot 7H_2O$ aqueous solution simultaneously with electrical stirring at 25°C. The ferrous iron was reduced to Fe^0 according to the following reaction:

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \qquad (1)$$

The Fe^0 nanoparticles were then rinsed several times with deoxygenated deionised water. Subsequently, the nanoparticles were prepared by the reaction of the wet Fe^0 nanoparticles with an aqueous solution of nickel sulphate hexahydrate (Ni content was 1.5(wt)%) under stirring according to the following equation:

$$Fe^0 + Ni^{2+} \rightarrow Fe^{2+} + Ni \qquad (2)$$

The reaction time was controlled in 120 min to ensure nearly 100% Ni was loaded on Fe^0 nanoparticles. Finally, the nanoparticles were rinsed with deoxygenated deionised water to remove excess SO_4^{2-} ions.

2.2. Batch experimental procedure

The batch experiments for *2,4*-DCP dechlorination in the presence of HA were performed in the same three-necked flask into which 3.0 g Ni/Fe nanoparticles slurry were added. The experimental benchmark conditions were as follows: 5 mL HA of 1.0 g L^{-1}, 10 mL *2,4*-DCP stock solution of 1.0 g L^{-1} and a certain amount of deoxygenated deionised water were added into the flask containing freshly prepared Ni/Fe nanoparticles, and the total volume of reaction solution was 500 mL. The reaction solution was stirred under nitrogen flow to simulate anaerobic environment in groundwater at 25°C, and the initial pH was 6.0 with the hydraulic retention time of 2 h. Samples were periodically collected at the time of 0, 10, 30, 60, 90, 120 min with glass syringes, and the reaction was stopped by filtrating the aliquots through 0.22 μm nylon membrane filters, and the reaction solution was then analysed in 4 h. Experiments were conducted under the experimental benchmark settings except that the corresponding conditions were changed.

2.3. Analytical methods

Organic compounds such as *2,4*-DCP, *p*-CP, *o*-CP and P were analysed by Shimadzu high performance liquid chromatography. Agilent TC-C18 Column, 150 × 4.6. Mobile phase: $MeOH/H_2O$ (60/40 v/v), flow rate: 1.0 mL min^{-1}, detector: UV at 280 nm and sample size: 20 μL.

Chloride ion analysis was performed by ion chromatography (792 Basic IC, Metrohm). Column: Metrosep A Supp 4, column size: 4 × 250 mm. Analysis condition: Eluent: 1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3 (with chemical suppression), sample size: 20 μL, flow rate: 1.0 mL min^{-1} and detector: suppressed conductivity detector. Before injection, samples were always filtered through a 0.45 μm membrane filter.

[redacted]The concentratio[redacted]HA was determined by Shimadzu UV1800PC ultraviolet spectro-[redacted]ometry at a wav[redacted]h of 254 nm.

[redacted]esults and discus[redacted]

[redacted]Dechlorination o[redacted]DCP

[redacted]ormal environm[redacted] condition, natural humic matter is abundantly available from [redacted]L^{-1} to over 100[redacted]$^{-1}$ concentration and it ranged from $0\,mg\,L^{-1}$ to $20\,mg\,L^{-1}$ in most [redacted]ns. To investiga[redacted] adsorption behaviour of HA on the Ni/Fe bimetallic nanoparticles, [redacted](20 $mg\,L^{-1}$) ads[redacted]n on Ni/Fe bimetallic nanoparticles was investigated with Ni/Fe [redacted]particles dosage[redacted] $g\,L^{-1}$ at an initial pH of 6.0. Approximately 60% HA was adsorbed [redacted]min, and more th[redacted]% HA was adsorbed after 60 min, and then approximately 96% HA [redacted]bserved to be a[redacted]d after 120 min.

[redacted]igure 1 illustr[redacted]he catalytic dechlorination of *2,4*-DCP with Ni/Fe bimetallic [redacted]particles. Duri[redacted] catalytic degradation process, most of the *2,4*-DCP was first [redacted]formed into *o*-C[redacted]d *p*-CP, and then they reduced rapidly to P. This was evident in the [redacted]ntration change[redacted]ring the reduction of *2,4*-DCP that while more and more P and [redacted]ide ion were p[redacted]d. However, the concentrations of *o*-CP and *p*-CP were initially [redacted]ased in the prop[redacted]reaction and then decreased slowly. Furthermore, P and chloride ion [redacted]detected as th[redacted]products of the dechlorination reaction. The results also demonstrate [redacted]although in th[redacted]r catalytic degradation process, *o*-CP was more easily reduced to P [redacted]*p*-CP, more *o*-C[redacted]generated the prophan

[redacted]

accounted for 20.7% of the original carbon. The production ra[illegible] of P, wh[illegible]n was expr[illegible]d as the ratio of the total amount of P produced to the theoretical [illegible]ount of [illegible]produc[illegible] du[illegible]ng the complete dechlorination of *2,4*-DCP, increased quickly from [illegible] in 0 mi[illegible]o 51% [illegible] 10[illegible]min and then to 77% in 30 min. Accordingly, the production rat[illegible]f chlori[illegible]ion, w[illegible]ich [illegible]was expressed as the ratio of the total amount of chloride ion produc[illegible]o the th[illegible]tical a[illegible]ou[illegible] of chloride ion produced during the complete dechlorination of *2,4*[illegible]CP, incr[illegible]d quic[illegible]ly f[illegible]om 0% in 0 min to 46% in 10 min, then to 61% in 30 min. It is no[illegible]fficult to [illegible] no m[illegible]tt[illegible] the production rate of chloride ion or that of P was smaller than [illegible]-DCP r[illegible]oval p[illegible]c[illegible]ag at the same time accordingly. During the experiment, the carb[illegible]mass ba[illegible]nces w[illegible] in the range of 84–92%, so approximately 8–16% carbon mass losses w[illegible]observ[illegible]d [illegible] caus[illegible]*4*-[illegible]CP or chlorophenol (CP, including *o*-CP and *p*-CP) was adsorbed on[illegible]surface [illegible]Ni/Fe b[illegible]m[illegible]llic nanoparticles during the dechlorination, some *2,4*-DCP w[illegible]r[illegible]duced d[illegible]o CP [illegible]r[illegible]h n n dechlorinated to P directly on the surface of Ni/Fe and did n[illegible]turn to [illegible] soluti[illegible]n. This indicates that a fraction of organic compounds were adsorbed [illegible]overed [illegible] surface [illegible]pa[illegible]sive layers due to the precipitation of metal hydroxides on t[illegible]face o[illegible]iron an[illegible]/Fe nanoparticles. This is also evidenced by Noubactep [11,12], [illegible]alidat[illegible]th ‘ads[illegible]on/co-precipitation concept’ for contaminant removal in $Fe^{0}/H_{2}O$[illegible]ns.

3.2. Effect of HA on the subsequent catalytic degradation of C[illegible]i/Fe na[illegible]particles

The effect of HA on the dechlorination of CP with Ni/Fe was [illegible]d. Figu[illegible] 2 illustr[illegible]s the dechlorination of *p*-CP and *o*-CP with Ni/Fe nanoparticles at v[illegible]concent[illegible]ations of [illegible]and HA concentrations were selected as 0, 10, 20 and 30 mg L$^{-1.0247}$(69Tf99.9626006.,[illegible])-28tiohich9[illegible]c na5.9(coct dclos

Figure 2 indicates that HA not only had an inhibition effect on the removal of CP to P but also remitted the creation of CP. The results also demonstrate that more *o*-CP was generated than *p*-CP, although in the further catalytic degradation, *o*-CP was more easily reduced to P than *p*-CP. The maximum concentrations of *o*-CP were 0.025, 0.042, 0.039 and 0.035 mM with HA of 0, 10, 20 and 30 mg L^{-1} in 10, 30, 30 and 30 min, respectively, and the maximum concentrations of *o*-CP seemed to be delayed, as the increase of HA in solution. But for *p*-CP, the maximum concentrations under the same conditions were just 0.001, 0.003, 0.003 and 0.002 mM in 10, 10, 10 and 60 min, respectively, much less than those of *o*-CP. Obviously, the catalytic degradation slowed down as the increase of HA concentration in solution, and the maximum concentrations of *o*-CP and *p*-CP appear delayed, leading to *o*-CP concentration increasing from 0.001, 0.003, 0.010 to 0.014 mM in 120 min when the reaction was terminated, and with the degradation going on, *o*-CP would be reduced to P. Several hypotheses were tested to identify the mechanisms behind the phenomenon. On the one hand, the accumulation of adsorbed HA on the nanoscale Ni/Fe surface may reduce the CP reduction rate. The complexation between HA and the generated Fe(II) may inhibit CP reduction or occupy the active surface sites and inhibit iron corrosion. On the other hand, release of active surface sites by dissolution of passive iron oxides may accelerate the CP reduction. The redox-active moieties in HA or in Ni/Fe-HA complexes may act as reductants to reduce CP to P or serve as electron-transfer mediators between Ni/Fe and CP [13].

3.3. The dechlorination mechanisms of 2,4-DCP with Ni/Fe nanoparticles in the presence of HA

It is hypothesised that the reduction and dechlorination of *2,4*-DCP occurred when it adsorbed on the surface of Ni/Fe particles [14,15]. This is also consistent with Noubactep's [11,12] report about 'the adsorption/co-precipitation concept' for conta643h reaction under the experimental condition of this study. Therefore, the elevation of solution pH during the reaction from 6 to more than 8.0 could support our assumption.

The overall dechlorination reaction on bimetallic catalyst surface can be represented as follows:

$$Fe + \mathit{2,4}\text{-DCP} + H^{+} \xrightarrow{Ni} CP + Cl^{-1} + Fe^{2+} \tag{8}$$

$$Fe + CP + H^{+} \xrightarrow{Ni} P + Cl^{-1} + Fe^{2+} \tag{9}$$

At lower pH, more atomic hydrogen on the catalyst surface attacked *2,4*-DCP to replace the chlorine and to form CP, P and chlorine ion (Equations (8 and 9)). Meanwhile, surface passive layers due to the precipitation of metal hydroxides and metal carbonates, which were developed at higher pH values, might not be easily formed at lower pH, would block the corrosion of iron and finally led to the reduction of the *2,4*-DCP dechlorination efficiency [19].

Under the current study, approximately 12% of mass loss was observed. It was most likely that of some the organic compounds, including P, CP and HA, could be adsorbed or covered by the surface passive layers [19]. The nondetected fraction of intermediates may be attributed to the fact that the Ni/Fe nanoparticles seem to serve as nonreactive sorption sites for intermediates [19].

The effect of HA on the mechanisms of *2,4*-DCP dechlorination by Ni/Fe nanoparticles could be described as follows: on one hand, HA was adsorbed on the surface of Ni/Fe nanoparticles, which would occupy the active surface sites for *2,4*-DCP reduction, and the accumulation of adsorbed HA on the nanoparticles surface may reduce the *2,4*-DCP reduction rate. On the other hand, the function groups in HA may act as electron shuttle promoting electron transfer, and this would accelerate the rate and efficiency of *2,4*-DCP dechlorination by Ni/Fe [20]. In this study, inhibition effect was dominated in the reaction. It is hypothesised that the existence of specific active surface sites were designated for *2,4*-DCP reduction, not for organic compound adsorption. But in the presence of HA, it would compete for active surface sites with *2,4*-DCP. During the reaction proceeding to exhaust those specific sites, the common active sites available for both *2,4*-DCP reduction and HA adsorption became limited. The adsorption of HA, together with the precipitation of metal hydroxides and metal carbonates on the nanoparticles, occupied the active surface sites and inhibited iron corrosion, leading to the further decrease of the *2,4*-DCP dechlorination efficiency.

3.4. Effect of Ni content on the subsequent catalytic degradation of CP by Ni/Fe nanoparticles in the presence of HA

It has been assumed that Fe^{0} can promote a hydrogenolysis reaction in which a Cl atom in the organic chlorinated compounds would be replaced by a hydrogen atom. Ni is a well-known catalyst for hydrogenolysis [19]. The co-existence of Ni and Fe in the particles has been proved to be very effective to accelerate the dechlorination process. Therefore, the content of Ni loading in the Ni/Fe nanoparticles may be one of the important factors in influencing dechlorination. The generation and further catalytic degradation of *p*-CP and *o*-CP during the reaction with different Ni contents in the presence of HA are presented in Figure 3. The results also demonstrate that more *o*-CP was generated than *p*-CP, although in the further catalytic degradation, *o*-CP was more easily reduced to P than *p*-CP. As shown in Figure 3, with Ni contents increased from 0.5, 1.0, 1.5 to 2.0(wt)%, the maximum concentrations of *o*-CP during the reaction were 0.029, 0.024, 0.027 and 0.037 mM, and these data were obtained in 120, 60, 30, 30 min, accordingly. But for *p*-CP, the maximum concentrations under the same conditions were

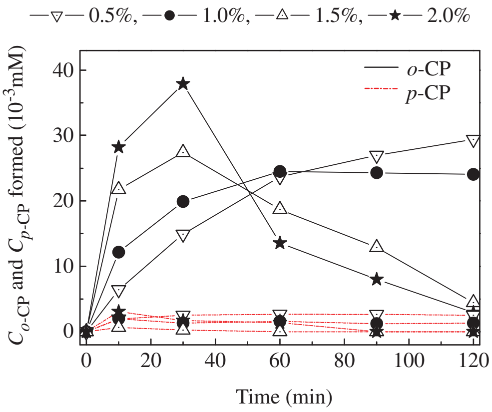


Figure 3. Effect of Ni content on the subsequent catalytic degradation process of *p*-CP and *o*-CP by Ni/Fe nanoparticles in the presence of HA ($T = 25$°C; pH$_{\mathrm{in}} = 6.0$; $C_{2,4\text{-DCP}} = 20\,\mathrm{mg\,L^{-1}}$; $C_{\mathrm{HA}} = 10\,\mathrm{mg\,L^{-1}}$; $C_{\mathrm{Ni/Fe}} = 6\,\mathrm{g\,L^{-1}}$ and stirring at $400\,\mathrm{r\,min^{-1}}$).

just 0.003, 0.002, 0.001 and 0.003 mM in 60, 10, 10 and 10 min, respectively, much less than those of *o*-CP. Because sampling time interval was long, it is impossible to decide the real moment at which the maximum concentrations of *o*-CP and *p*-CP appeared, and Figure 3 still shows that with the Ni contents increasing, the maximum concentrations of *o*-CP and *p*-CP appeared ahead, and the *o*-CP concentration decreased from 0.029, 0.024, 0.004 to 0.003 mM in 120 min when the reactions were terminated. Though increasing Ni content could accelerate the dechlorination reaction, excess Ni would cover the surface of Fe and hinder the contact between targeted pollutants and metal particles, further reduce the reduction rate of *2,4*-DCP. The optimal nickel content was selected as about 1.5(wt)% for efficient dechlorination and yet minimal nickel usage.

3.5. Effect of initial pH values on the subsequent catalytic degradation of CP by nanoscale Ni/Fe in the presence of HA

The solution pH value is important for reductive dechlorination of COCs using Fe^0 nanoparticles. Low pH favours the availability of more iron surface for reaction with the chlorinated molecules or at least promotes the corrosion rate, leading to the release of chloride ions. At higher pH values, carbonate and hydroxide coatings would undoubtedly develop, which could inhibit further decomposition of iron surface and hinder access to the Fe^0 surface [21,22]. As a result, the catalyst activity decreases. Figure 4 shows the effect of different initial pH values on the generation and subsequent catalytic degradation of *p*-CP and *o*-CP by Ni/Fe nanoparticles in the presence of HA. The results also demonstrate that more *o*-CP was formed than *p*-CP during this procedure, and in the subsequent catalytic degradation process, although *o*-CP was more easily reduced to P than *p*-CP. The maximum concentrations of *o*-CP were 0.038, 0.043, 0.019 and 0.033 mM in 10, 30, 120 and 120 min at initial pH values of 3, 6, 8 and 11, but for *p*-CP, the maximum concentrations under the same conditions were just 0.000, 0.003, 0.002 and 0.002 mM, respectively. Obviously, the catalytic degradation slowed down as the increase of initial pH in solution, and the maximum concentrations of *o*-CP and *p*-CP appeared delayed, leading to *o*-CP concentration increasing from 0.003, 0.005, 0.019 to 0.033 mM in 120 min when the reactions were terminated, and with the degradation going on, *o*-CP would be reduced to P gradually. Figure 4 also shows that with the initial pH values of the reaction solutions increasing from 6 to 8, which means that the reaction solution change from acidic to

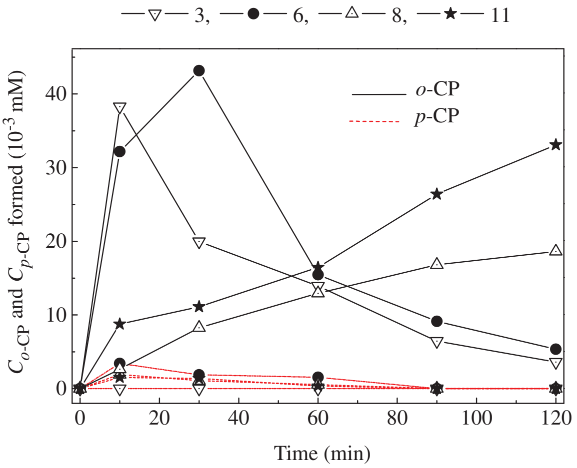


Figure 4. Effect of initial pH values on the subsequent catalytic degradation process of *p*-CP and *o*-CP by Ni/Fe nanoparticles in the presence of HA (T=25°C; $C_{\mathrm{HA}} = 10\,\mathrm{mg\,L^{-1}}$; $C_{2,4\text{-DCP}} = 20\,\mathrm{mg\,L^{-1}}$; $C_{\mathrm{Ni/Fe}} = 6\,\mathrm{g\,L^{-1}}$; stirring at 400 r min^{-1} and Ni content = 1.5(wt)%).

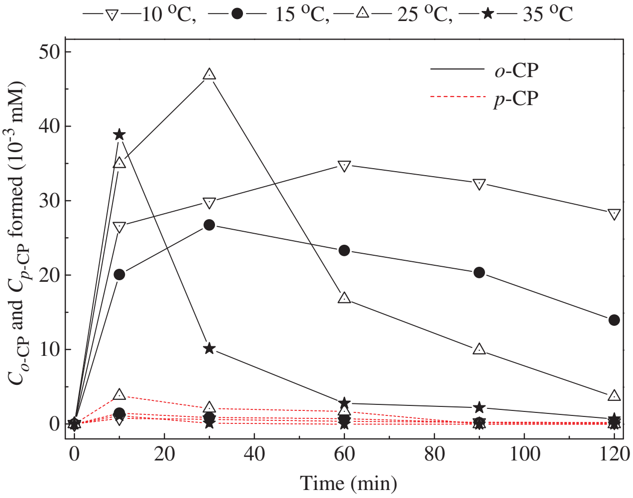
alkaline, the generation of *o*-CP and subsequent catalytic degradation of it dropped obviously. It indicates that the presence of H^+ largely enhanced the catalytic degradation of *2,4*-DCP and CP even though in the presence of HA. The possible reasons may be that (1) at lower pH values, the iron corrosion could be accelerated, producing enough hydrogen (or hydrogen atoms), which are in favour of hydrogenation reaction and (2) iron corrosion in solution of pH higher than 7 tend to lead to passive film formation of iron oxides and hydroxide on the iron surface, which inhibits further reaction [19].

3.6. Effect of Ni/Fe dosage on the subsequent catalytic degradation of CP by Ni/Fe nanoparticles in the presence of HA

Because the catalytic reductive dechlorination by Ni/Fe nanoparticles takes place on the surface of the particles, the Ni/Fe-to-*2,4*-DCP ratio (g Ni-Fe/mg *2,4*-DCP) is also a significant variable parameter. The quantity of available surface area is among the most significant experimental variables affecting contaminant reduction. Increasing Ni/Fe nanoparticles dosage will accelerate the initial reaction rate and provide more active sites of Ni/Fe nanoparticles for collision with CP during the reduction. Different Ni/Fe nanoparticles dosages of 2, 4, 6 and 8 g L^{-1} were evaluated as shown in Figure 5. With the elevation of the Ni/Fe nanoparticles dosage from 2, 4, 6 to 8 g L^{-1}, the maximum concentrations of *o*-CP were 0.029, 0.031, 0.042 and 0.023 mM in 90, 60, 30 and 10 min, but for *p*-CP, the maximum concentrations under the same conditions were just 0.002, 0.001, 0.003 and 0.002 mM, respectively. The catalytic degradation process was enhanced as the increase of Ni/Fe dosage, and the maximum concentrations of *o*-CP and *p*-CP appeared higher, leading to *o*-CP concentration decreasing from 0.028, 0.026, 0.003 to 0.002 mM in 120 min when the reactions were terminated, and with the ongoing degradation, CP would be reduced to P gradually.

3.7. Effect of temperature on the subsequent catalytic degradation of CP by Ni/Fe nanoparticles in the presence of HA

The effect of reaction temperature on the subsequent catalytic degradation process of *p*-CP and *o*-CP by Ni/Fe nanoparticles in the presence of HA was investigated by varying the temperature



from 10 to 35°C (Figure 6). Figure 6 also demonstrates that more *o*-CP was formed than *p*-CP during this procedure, and in the subsequent catalytic degradation process, although *o*-CP was more easily reduced to P than *p*-CP. The maximum concentrations of *o*-CP were 0.035, 0.027, 0.047 and 0.039 mM in 60, 30, 30 and 10 min when the reaction temperatures were 10, 15, 25 and 35°C. However for *p*-CP, the maximum concentrations under the same conditions were just 0.001, 0.001, 0.004 and 0.001 mM, respectively. Obviously, the catalytic degradation was enhanced with the increase of reaction temperature, and the maximum concentrations of *o*-CP and *p*-CP appeared higher, leading to *o*-CP concentrations decreasing from 0.028, 0.014, 0.004

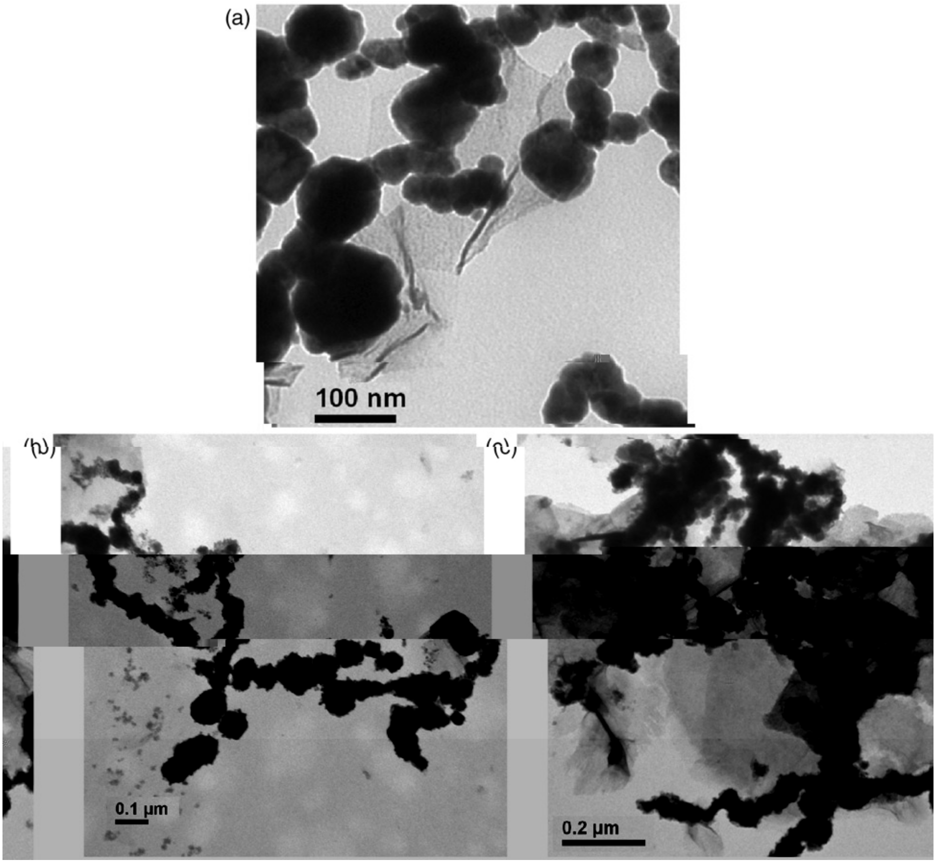


Figure 7. TEM images of Ni/Fe nanoparticles (a) fresh synthesised, (b) in HA solution for 2 h and (c) after 2 h of reaction.

to 0.001 mM in 120 min when the reactions were terminated, and with the degradation going on, CP would be reduced to P gradually. It is not difficult to see high temperature favours the catalytic dechlorination reaction, and the higher the reaction solution's temperature is, the faster the catalytic degradation would be. The possible reasons are that the mobility of CP from solution to nanoparticles increased at higher temperature, or the activation energy for electron transfer or formation of a reactive surface complex increased.

3.8. Characterisation of nanoscale Ni/Fe particles

Newly prepared Ni/Fe nanoparticles show black agglomerates state. Because the size of nanoscale particles is smaller than the wavelength of visible light, they act as perfect black body for light absorbance. Figure 7 shows the transmission electron microscopy images of nanoscale Ni/Fe particles (a) fresh synthesised, (b) in HA solution for 2 h and (c) after 2 h reaction. The particles are spherical with the sizes arranging from 20 to 100 nm in diameter. Spherical particles connected together to form dendrites because of geomagnetic forces between nanoparticles and small particles and their surface tension interactions. Figure 7(a) shows without the addition of HA and *2,4*-DCP, the surface areas of the Ni/Fe nanoparticles are smoother, showing single spherical state. Because of a certain agglomeration, they are connected together forming a dendritic state. Figure 7(b) shows a mucous layer was adhered onto the surface of Ni/Fe in HA solution for 2 h. The speculated flocs are the results of adsorption of HA on the surface areas of Ni/Fe nanoparticles. That shows that when HA exists in the solution, there is a competition between HA, CP and *2,4*-DCP to occupying the active surface areas of Ni/Fe leading to the decrease of the remediation efficiency of nanoparticles. It illustrated the inhibition role of the HA. A more thick mucus layer was shown on the surface of the Ni/Fe nanoparticles after 2 h of reaction (Figure 7c). More organic components such as HA, CP and *2,4*-DCP, as well as metal hydroxides and carbonate passive layers on the nanoparticles' surface inhibited the particles' active sites, likely leading to lower dechlorination efficiency.

4. Conclusion

The experimental results suggest that HA has an inhibitory effect on the *2,4*-DCP catalytic dechlorination, and this inhibitory effect was remarkable at low HA concentrations. High Ni content, low initial pH value, high Ni/Fe nanoparticles dosage and high temperature favoured the catalytic dechlorination of *2,4*-DCP. During the dechlorination of chlorinated hydrocarbons, HA could act as an adsorbate to compete for reactive sites on the surface of Ni/Fe nanoparticles to decrease the dechlorination rate. The HA concentration increased from 0 to 30 mg L^{-1} led to the decrease in

[10] Y.H. Liu, F.L. Yang, P.L. Yue, and G.H. Chen, *Catalytic dechlorination of chlorophenols in water by palladium/iron*, Water Res. 35 (2001), pp. 1887–1890.

[11] C. Noubactep, *A critical review on the process of contaminant removal in Fe^0–H_2O systems*, Environ. Technol. 29 (2008), pp. 909–920.

[12] Noubactep, *An analysis of the evolution of reactive species in Fe^0/H_2O systems*, J. Hazard. Mater. 168 (2009), pp. 1626–1631.

[13] L. Xie and C. Shang, *Role of humic acid and quinone model compounds in bromate reduction by zerovalent iron*, Environ. Sci. Technol. 39 (2005), pp. 1092–1100.

[14] S.F. Niu, H.Y. Zhou, X.P. Ao, X.H. Xu, and Z.H. Lou, *Structure relationship of nitrochlorobenzene catalytic degradation process in water over palladium-iron bimetallic catalyst*, J. Zhejiang Univ. Sci. B 7 (2006), pp. 548–552.

[15] X.H. Xu, H.Y. Zhou, and M. Zhou, *Catalytic amination and dechlorination of para-nitrochlorobenzene (p-NCB) in water over palladium-iron bimetallic catalyst*, Chemosphere 62 (2006), pp. 847–852.

[16] B. Schrick, J.L. Blough, A.D. Jones, and T.E. Mallouk, *Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles*, Chem. Mater. 14 (2002), pp. 5140–5147.

[17] Y. Han, W. Li, M.H. Zhang, and K.Y. Tao, *Catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant*, Chemosphere 72 (2008), pp. 53–58.

[18] R. Cheng, W. Zhou, J.L. Wang, D.D. Qi, L. Guo, W.X. Zhang, and Y. Qian, *Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: Role of nano-Ni and its size effect*, J. Hazard. Mater. 180 (2010), pp. 79–85.

[19] Z. Zhang, N.M. Cissoko, J.J. Wo, and X.H. Xu, *Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid*, J. Hazard. Mater. 165 (2009), pp. 78–86.

[20] R.A. Doong and Y.J. Lai, *Dechlorination of tetrachloroethylene by palladized iron in the presence of humic acid*, Water Res. 39 (2005), pp. 2309–2318.

[21] Y. Fang and S.R. Al-Abed, *Dechlorination kinetics of monochlorobiphenyls by Fe/Pd: Effects of solvent, temperature, and PCB concentration*, Appl. Catal. B 78 (2008), pp. 371–380.

[22] G.N. Jovanovic, P. Plazl, P. Sakrittichai, and K. Al-Khald, *Dechlorination of p-chlorophenol in a microreactor with bimetallic Pb/Fe catalyst*, Ind. Eng. Chem. Res. 44 (2005), pp. 5099–5106.