



Rapid dechlorination of chlorophenols in aqueous solution by [Ni|Cu] microcell

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ABSTRACT

The [Ni|Cu] microcell was prepared by mixing the Ni⁰ and Cu⁰ particles. The composition and crystal form were characterized by X-ray diffraction (XRD) and scanning electron microscope. The results evidenced the zero-valence metals Ni and Cu were exposed on the surface of particles mixture. The [Ni|Cu] microcell was employed to decompose chlorophenols in aqueous solution by reductive dechlorination. The dechlorination rates of chlorophenols by [Ni|Cu] were >10 times faster than those by [Fe|Cu], [Zn|Cu], [Sn|Cu], and [Fe|Ni] mixtures under the same conditions. [Ni|Cu] is different from other zero valent metals (ZVMs) in that it performed the best at neutral pH. The main products of chlorophenol dechlorination were cyclohexanol and cyclohexanone. The reduction kinetics was between pseudo zero-order and first-order, depending on the pH, concentration, and temperature. These results, combined with electrochemical analysis, suggested that Ni⁰ acted as a reductant and catalyst in dechlorination reaction. The H⁺ corridor mechanism from Ni⁰ to Cu⁰ was also proposed based on hydrogen spillover. The inhibition on the release of Ni²⁺ by adding natural organic matters and adjusting pH was investigated.

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1. Introduction

Toxic chlorinated organic compounds including chlorinated methane, chlorobenzenes, and chlorophenols have become current environmental concerns [1–3]. Among various chlorinated pollutants, chlorophenols and their derivatives are carcinogenic, persistent, and bio-accumulative [4–6]. Under certain conditions, chlorophenols occurred in the aqueous environment can be transformed to more toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) [7]. Therefore, chlorophenols, even at the trace level, need to be removed from water.

The use of zero valent metals (ZVMs) to treat chlorinated hydrocarbons in wastewaters has been the focus of many studies [8–10]. Numerous feasibility studies, pilot tests, and field scale demonstration projects have been initiated using granular zero valent iron (ZVI) as the reactive medium in permeable reactive barriers [11–13]. Other ZVMs, such as Sn⁰ [14] and Zn⁰ [15], have been studied in the batch test and have been found to produce intermediates with low toxicity when they reacted with chlorophenols in aqueous solution. However, the transformation process tended to last for days or weeks, and the final removal rate was limited

(usually <30%) [16]. The passivation and inactivation of ZVM are still challenging problems.

Nickel (Ni) has been used as a catalyst to increase the rates of chloroethene reductive dechlorination by ZVI [17,18]. In laboratory and pilot studies, small amounts of nickel doped on iron filings increased the dechlorination rates by orders of magnitude. Although nickel is an effective catalyst for reduction by corroding iron media, few studies have involved environmental applications using Ni⁰ as reductant or anode in a primary cell. Some researchers have reported the hydro-dechlorination of chlorophenols over nickel catalysts in a gas-phase or aqueous solution [19,20]. However, reaction conditions of high pressure, high temperature, and hydrogen richness impose a restriction on the application for in situ remediation of natural water.

Ni⁰ is a feasible remediation alternative because of its low reduction potential of Ni²⁺/Ni⁰ ($E^\circ = -0.257 \text{ V vs SHE}$, from CRC Handbook of Chemistry & Physics, 2006 Edition). However, the potential might not be low enough to reduce chlorinated organics, such as chlorobenzenes and chlorophenols, in water at ambient temperatures and pressure. Oxidation products such as nickel oxide and nickel hydroxide cover the surface of Ni⁰ and stop further reductive reaction [21]. Although the activity of Ni⁰ could be recovered at low pH, problems of ion release and consumed cost of Ni⁰ and acid still arised.

Technically, Ni⁰ acts as a reductive anode and catalytic agent during dechlorination. If a suitable cathode was utilized, nickel-based bimetal could be used to reduce chlorophenols in aqueous solution, such as ZVI and other ZVMs. Hence, we explored dechlorination reaction by [Ni|Cu], [Fe|Cu], [Zn|Cu], [Sn|Cu], and [Fe|Ni] particle mixtures under moderate aqueous condition.

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Here $\text{Cu}^{2+}/\text{Cu}^0$ was selected as the anode for the microcell because copper is conventional metal and the redox potential of $\text{Cu}^{2+}/\text{Cu}^0$ is relatively high. The goal of this study was to investigate the possible reduction capacity of Ni^0 and inert metal mixture to remedy chlorophenol-contaminated water. We addressed the following questions: (i) Is the major role of Ni^0 in the dechlorination process used as reductant or as catalyst? (ii) How is the transformation process of chlorophenols controlled? (iii) How about the loss of chlorine substituents by this method and what are the major dechlorination products? Mass spectrometry, surface characteristics, and kinetics analyses were carried out to interpret the detailed dechlorination mechanism.

2. Experimental

2.1. Reagents and materials

The chemical reagents used in this study, sodium hydroxide, hydrochloric acid, particles of Ni^0 , Fe^0 , Zn^0 , Sn^0 , and Cu^0 (all particles are 50–70 μm in size), were reagent grade and were obtained from Sigma–Aldrich. Ni^0 , Fe^0 , and Cu^0 foils were from Sinopharm, CHN. The chlorophenols including 2-CP (2-chlorophenol, >98%), 4-CP (4-chlorophenol, >99.0%), 2,4-DCP (2,4-dichlorophenol, 98%), 2,4,6-TCP (2,4,6-trichlorophenol, 98%), and PCP (pentachlorophenol, 98%), were from J&K. All chemicals were used as received. Deionized water was from a Milli-Q water system (18 M Ω resistance). Water was deoxygenated as needed by purging with high-purity nitrogen and hydrogen for 30 min.

2.2. Microcell preparation

The bimetal microcell was prepared by mixing the commercial particles using mechanical mixing. Before the batch reaction, metal and bimetal particles used in the experiments, including Fe^0 , Ni^0 , [Fe|Ni], [Fe|Cu], [Ni|Cu], [Zn|Cu], and [Sn|Cu] (all 10 g L⁻¹ or 10:10 g L⁻¹), were pre-soaked in 0.05 mol L⁻¹ hydrochloric acid (or nitric acid for Cl^- detection only) with shaking for 5 min to remove the oxide layers. Then these particles were washed with deaerated water three times.

2.3. Batch experiments

All batch experiments were carried out in 200 mL conical flasks with Teflon-faced crimped-seal septa. The microcell particles and 200 mL of chlorophenol aqueous solution were added to the conical flasks on a thermostatic table. A metal-free control flask containing only the solution was prepared for each batch experiment. The initial concentration of the chlorophenol solution for these batch experiments was 10 mg L⁻¹. The chlorophenol solution was pre-adjusted to pH 3.0, 5.0, 7.0, 9.0, and 11.0 using hydrochloric acid and sodium hydroxide, depending on the pH experiments. To determine effects of temperature on the chlorophenol removal rate, temperature-controlled batch experiments were carried out at 5 °C, 20 °C, 40 °C, and 60 °C. Metal-free control flask containing only the solution was prepared for each batch experiment. All flasks were placed in water bath shakers and shaken at 240 rpm (to dismiss the limitation by external diffusion) [22].

To determine the transformation rate, the dosage of Cu^0 particle was doubled or tripled. In the experiments for inhabitation of released Ni^{2+} , 1.0 g L⁻¹ gum arabic or hydroxymethyl cellulose was added before shaking. Other conditions were the same as those of the batch experiments with [Ni|Cu] bimetal mixture. In addition, the effect of high pH on the inhabitation of Ni^{2+} was conducted in

the regular sampling solution by adjusting pH with sodium hydroxide. In the test for primary cell mechanism, Ni^0 , Fe^0 , and Cu^0 foils (20 mm \times 40 mm each) were pre-connected as [Ni|Cu] and Ni/Fe bipolar plates. The plates were then dipped into a phosphate buffer solution with 5 mg L⁻¹ 2,4,6-TCP at pH 4.5. The solution was sampled at specific intervals while stirring. All the experiments were conducted in triplicate.

2.4. Analysis

The concentrations of chlorophenols in all resulting samples were monitored by high-performance liquid chromatography (HPLC; Waters 600, USA). Quantitative analysis of Ni^{2+} was determined by the absorption method using dimethylglyoxime as the color-producing reagent on a Varian Cary-50 UV–vis spectrometer at λ 470 nm. Ion chromatography on a Shimadzu PIA-1000 was used for quantitative analysis of Cl^- .

A Finnigan LCQTM DUO ion trap mass spectrometer coupled to the LC equipped with Varian Pursuit 5-C₁₈ and Inertsil 5 ODS-3 columns was used to identify the intermediates. The electrospray ionization (ESI) source was operated in negative mode. On the C₁₈ column, a linear gradient of 0.15% acetic acid and methanol increased from a ratio of 100:0 to 50:50 within 35 min. The flow rate was 1.0 mL min⁻¹. On the ODS-3 column, the mixture of water and acetonitrile at a ratio of 30:70 was used to separate the intermediates that were not retained well [23].

Analyses were performed on a 30 m \times 0.53 mm DB-5 column (J&W Scientific, Palo Alto, CA) in an Agilent Technologies Model 5890 gas chromatograph (GC) equipped with a flame ionization detector, or in a Varian Model 3900 GC fitted with a Model 8400 autosampler and a model 2100T ion trap detector. One micro liter aliquot of the sample was added to the head of the 30 m \times 0.25 mm DB-5 capillary column and eluted with helium at 1.0 mL min⁻¹. After an initial hold of 1 min at 50 °C, the column was ramped at 10 °C min⁻¹ to 300 °C, and was further held for 3 min prior to cooling down. The temperatures of the injector and detector were maintained at 250 °C and 150 °C, respectively. Eluting components were tentatively identified by comparing the experimental mass spectra with the spectra catalogued at the National Institute of Standards and Technology (NIST) or the Saturn spectral libraries, and corroborated by cochromatography and spectral matching with authentic standards.

2.5. Characteristics

X-ray particle diffraction (XRD) analysis was performed using a Phillips X'Pert MPD X-ray diffractometer, using Cu K α radiation at 40 kV and a step size of 0.03°, 2θ at 1.5 s step⁻¹. The infrared spectra (IR) were obtained with a PerkinElmer spectrum GX spectrometer in the range of 400–4000 cm⁻¹. Each particle sample (1 mg each) was diluted with 200 mg vacuum-dried IR-grade KBr and subjected to a pressure of 8 tons. Scanning electron micrograph (SEM) and energy dispersive X-ray spectrometer (EDXs) were generated using a Hitachi S-800 field emission secondary electron microscope and PGT (EDS) Imix/Imagist analyzer. Images were collected with a beam potential of 15 kV.

2.6. Electrochemical analysis

Electrochemical characterization of chlorophenol potentials was performed in sulfuric acid solution by Tafel scan method using a Model CHI 660D Potentiostat/Galvanostat controlled by CHI 660D software (CHI, USA). The working electrode was a polished Ni^0 foil (20 mm \times 20 mm, 0.1 mm thickness). A polished Cu^0 foil (20 mm \times 20 mm, 0.1 mm thickness) was used as the counter

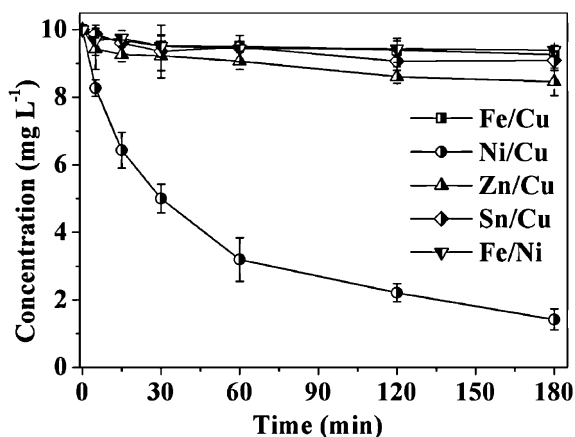


Fig. 1. The removal rates of 2,4,6-TCP by [Fe|Cu], [Ni|Cu], [Zn|Cu], [Sn|Cu], and [Fe|Ni] bimetal (10: 10 g L⁻¹) at pH 5.0, 20 °C.

electrode and a Hg/HgSO₄ saturated K₂SO₄ electrode was used as the reference electrode.

3. Results and discussion

3.1. Comparison of reductive activity

Zero valence nickel is not a good reductant for dechlorination. The redox potential of Ni²⁺/Ni is -0.257 V, higher than other active metals, such as Fe (Fe²⁺/Fe⁰ -0.44 V), Zn (Zn²⁺/Zn⁰ -0.7631 V), Sn (Sn⁴⁺/Sn⁰ -0.191 V), and Mn (Mn²⁺/Mn⁰ -1.029 V) [24,25]. However, the [Ni|Cu] bimetal microcell exhibited better reductive capacity than the microcells composed by other metals and copper. As shown in Fig. 1, by adding the same dose of metals, the elimination rate by [Ni|Cu] for 2,4,6-TCP was higher than those by [Fe|Cu], [Zn|Cu], [Sn|Cu], and [Mn|Cu] bimetals, although the redox potential of Ni²⁺/Ni⁰/Cu²⁺/Cu⁰ is lower than those of the other three bimetals theoretically.

As shown in Table 1, the removal rate of 2,4,6-TCP by the Ni⁰/Cu⁰ particles mixture was higher than those of other bimetal mixtures by at least 15 times, no matter calculated on the basis of zero-order or first-order kinetics. The unexpected rapid transformation might be attributed to complicated reaction mechanisms, suggesting that not only Ni⁰ reduction but also other process (adsorption or catalysis) interrupt the apparent reaction kinetics.

The comparison experiments verified that the dechlorination rate for 2,4,6-TCP by the primary battery consisting of [Ni|Cu] plates

Table 1
Different bimetal mixtures on the kinetics parameters on the zero-order and first-order rules.

Bimetal	Zero-order		First-order	
	k (min ⁻¹)	R^2	k (min ⁻¹)	R^2
Fe/Cu	3.15×10^{-3}	0.50	5.64×10^{-3}	0.80
Ni/Cu	6.27×10^{-2}	0.75	6.86×10^{-2}	0.93
Zn/Cu	4.09×10^{-3}	0.74	1.11×10^{-3}	0.36
Sn/Cu	3.27×10^{-3}	0.68	1.94×10^{-3}	0.65
Fe/Ni	9.26×10^{-4}	0.72	4.14×10^{-4}	0.51

was slower than that by the [Fe|Cu] foil primary battery (see Fig. S1). At the end of the reaction, nearly 37% of 2,4,6-TCP was removed by the [Fe|Cu] metal plate primary battery, whereas little detectable removal was measured on the [Ni|Cu] plate pair. Aside from the difference between metal foils and particles on specific surface area and rate of diffusion, the only difference was the collision contact between Ni⁰ and Cu⁰ particles. Therefore, we inferred that the reaction process might be limited by metal reduction and hydrogen catalysis.

3.2. Transformation and intermediate product analyses

As shown in Fig. 2, the transformation rates of chlorophenols, especially for highly chlorinated phenols, slowed down when Ni⁰ was used alone. Low removal rate was detected for the concentration of chlorophenols during the reaction period. The transformation of chlorophenols was dramatically accelerated when nickel particle was mixed with equivalent weight copper particles. All chlorophenols, including 2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP, and PCP, were transformed nearly completely, faster than that by [Fe|Cu] mixture.

In the case of 2,4,6-TCP, the 82% concentration was reduced within 2 h. The transformation process followed pseudo-first-order reaction kinetics. Moreover, the transformation rate of PCP was 92.1%, much higher than that of 2,4,6-TCP. It might be that the more chlorine substituents on the ring facilitated the dechlorination reaction. On the other hand, some reactions took on the characteristics of zero-order kinetics under certain pH, [Ni|Cu] concentration, and reaction temperature. The optimal conditions including pH, concentration, and temperature for chlorophenol transformation were then obtained (Fig. 3). Detailed results and analyses are described in Supporting Information (SI).

The reduction rate by [Ni|Cu] particle mixture was improved by decreasing the pH value or increasing the amount of [Ni|Cu]. Generally, in an internal electrolysis electrode pair, anode corrosion can

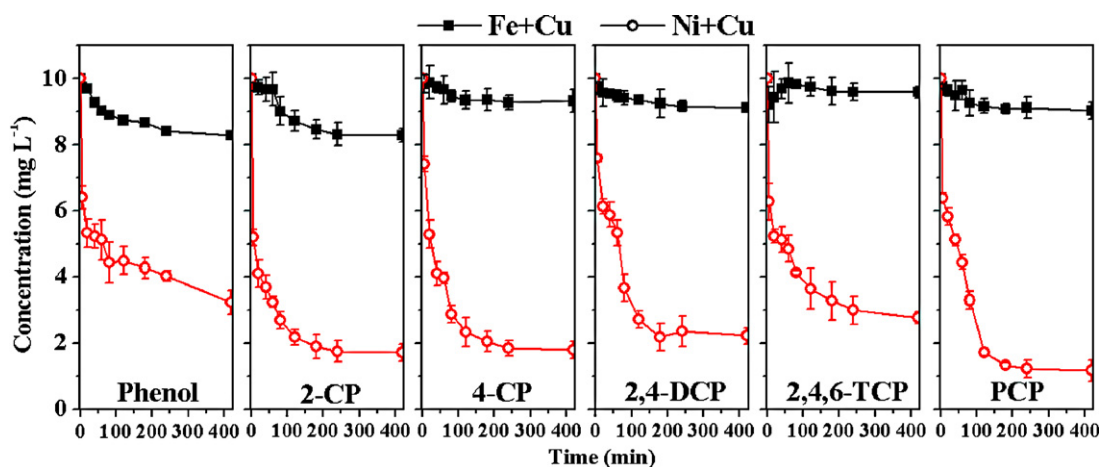


Fig. 2. The concentration change of chlorophenols transformed by [Ni|Cu] and [Fe|Cu] particle mixtures at pH 5.0, 20 °C. The dose of each metal particle was 10 g L⁻¹.

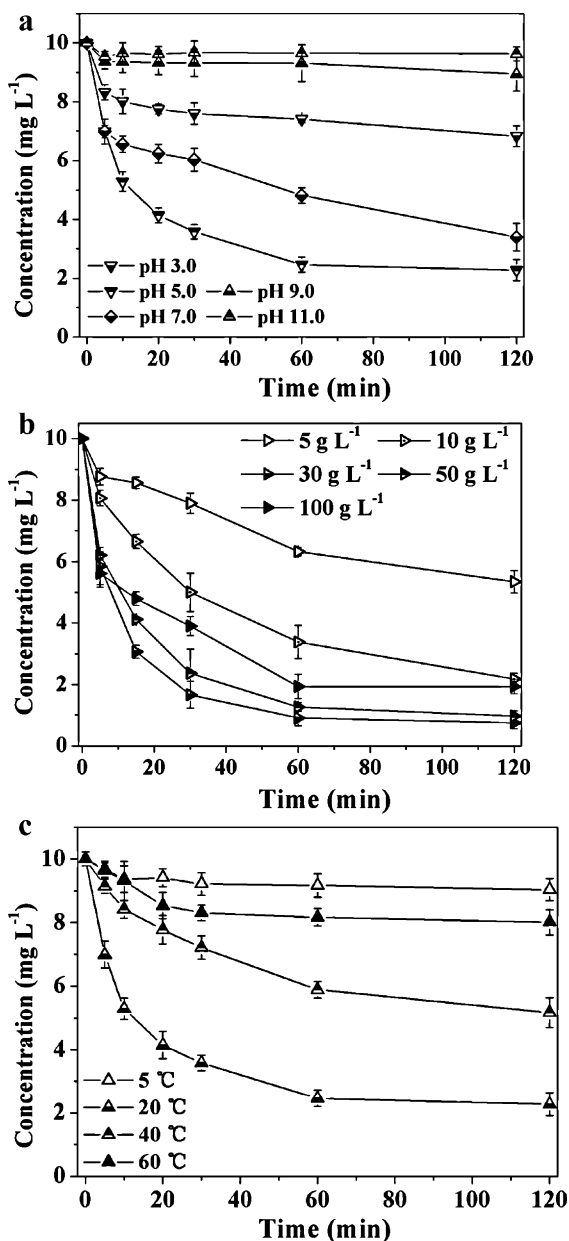


Fig. 3. The pH 3.0–11.0 (a: at 20 °C, 10 g L⁻¹), metal amount 5–100 g L⁻¹ (b: at 20 °C, pH 5.0), and temperature 5–60 °C (c: at pH 5.0, 10 g L⁻¹) effects on the removal rate of 2,4,6-TCP by [Ni/Cu].

be accelerated at lower pH by feeding more H⁺, whereas increasing the amount of metal could shift reaction equilibrium to products and then improve the conversion rate of chlorophenols [26]. However, the optimal pH for [Ni/Cu] internal electrolysis system was 5–7, and the optimal dosage of Ni⁰ was 30 g L⁻¹. A higher or lower value will bring down reductive activity. A detailed analysis will be provided in succeeding sections.

Chlorophenols could be reduced and transformed into dechlorinated chlorophenols, phenol, cyclohexanone, and cyclohexanol in the presence of [Ni/Cu] mixture. The concentration changes in the transformation products are shown in Fig. 4.

The dechlorination from chlorophenols to phenol, and then to cyclohexanone and cyclohexanol [27], are shown by Eqs. (1)–(3).

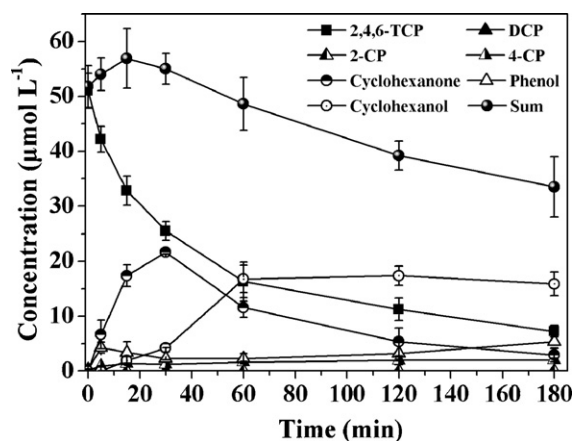
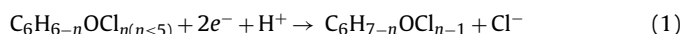
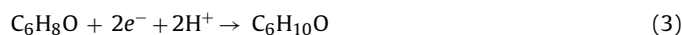


Fig. 4. The concentration change in the intermediate products during the dechlorination process at pH 5.0, 20 °C ([Ni/Cu] 10: 10 g L⁻¹, initial concentration of 2,4,6-TCP was 50.6 μmol L⁻¹).

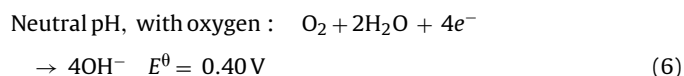
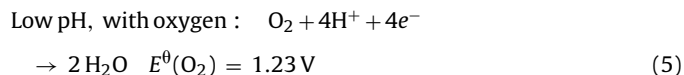
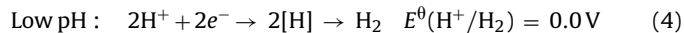


Cyclohexanone was the primary product during the major reaction. Only cyclohexanone and cyclohexanol accumulated in the reacting solution, suggesting that the reaction from cyclohexanone to cyclohexanol was the rate-controlling step. The dechlorination rate was fast, and only a minimal amount of low-chlorinated phenols accumulated in the solution. For PCP transformation, all of low-chlorinated phenols were emerged as the intermediate products during the reaction. However, exhaustive dechlorination could also be attained through this method. The yielding rate of Cl⁻ coincided with the dechlorination rate of chlorophenols (Fig. S2).

3.3. Surface characteristics

The Cl⁻ ion was not the only ion dissolved during the reaction process. Some Ni²⁺ ions dissolved from Ni⁰ due to anode corrosion. Such anodization might result in corrosion and oxidation on the surface of metals. Therefore, characterization on the surface of [Ni/Cu] mixture before and after the reaction was carried out. No erosional mark was observed on the metallic particle after the reaction based on the SEM pattern (Fig. S3). EDS (Fig. S4) and IR (Fig. S5) results proved that no obvious redox product was measured on the surface. However, some Cu₂O particles were found on the metal surface after the reaction by XRD, indicating that the oxidizing reaction mostly occurred on the surface of Cu⁰ rather than that of Ni⁰.

In a catalytic internal electrolysis system, Ni²⁺ dissolves from Ni⁰ and transfers electron onto Cu⁰. A part of the electron reacts with the chlorophenols adsorbed on the surface of Cu⁰ (Eq. (4)), while others react with H₂O and then produce OH⁻, in neutral or basic solution (Eq. (6)) [28].



The reaction system was close to neutral pH, thus oxygen-consumption corrosion might easily occur. Much of the OH⁻ near

Cu^0 might react with trace Cu^{2+} , resulting in it dissolving from Cu^0 and the production of cupric hydroxide.

Due to oxygen-consumption corrosion, Ni^0 could remain exposed on the surface of Ni^0 particles and prevent the inhibiting effect by oxidization. However, the problem of Ni^{2+} being released in the water arises along with it.

3.4. The role of Ni^0 : reductant or catalyst?

Friedrich et al. [29] investigated the role of Ni^0 in the N-nitrosodimethylamine (NDMA) reduction experiments. They believed that the NDMA transformation was catalyzed in the presence of hydrogen, whereas the reductive reaction by Ni^0 failed to occur without hydrogen [30,31]. Analogously, Wang et al. [19] investigated the reduction of CT (carbon tetrachloride) and stated that Ni^0 acted as a reductant. Some studies proved that loading Ni^0 on reductive metals, such as Fe^0 and Zn^0 , might accelerate the reduction process [15,32]. However, the role of Ni^0 in certain reactions remains unknown. In our case, analogous experiments were carried out to verify the dilemma. We switched pumping nitrogen and hydrogen into the [Ni/Cu] dechlorination reaction system. However, no detectable change on the transformation rate was observed. Furthermore, although the reduction experiments were conducted in the hydrogen-saturated solution, no observable change resulted from the acceleration by hydrogen catalysis was found. The quantitative relation between released Ni^{2+} and conversion rate of chlorophenols was measured based on the experimental results. On the assumption that those reduction reactions were single reactions without byproducts (Eqs. (1)–(3)), the exchange ratio between released nickel and chlorophenols, taking 2,4,6-TCP as an example, was (3–5):1. The cost of 3–5 mol nickel ions will dechlorinate 1 mol 2,4,6-TCP into cyclohexanol. This seems to be a simple Ni^0 direct reduction reaction. However, it is difficult to explain why the dechlorination of chlorophenols by the [Ni/Cu] mixture was more efficient than those by other bimetal mixtures.

3.5. Proposed hypothesis

No single explanation (as reductant or catalyst) has been proven sufficient for the dechlorination by [Ni/Cu] mixture based on hydrogen adsorption trial. Therefore, this study aims to determine the differences in primary cell internal electrolysis, as well as the nature of [Ni/Cu] and other bimetals on primary cell reactions. To answer these questions, further electrochemical analysis was conducted for the process. Tafel curves were used to analyze the redox behaviors of the reducing metals. They yielded definite corrosion potential and corrosion current.

As shown in Fig. S6, the corrosion potential of Ni^0 increased when 10 mg L^{-1} of chlorophenols was added into the control solutions. The change in the electrode potential remained in the hydrogen-saturated, deoxidized, and oxygen-enriched chlorophenol solution.

In theory, internal electrolytic catalysis could be interpreted as Butler–Volmer equation [33,34]:

$$\ln(I_{\text{corr}}) = \frac{(E_{e,c} - E_{e,a})}{(\beta_a + \beta_c)} + \ln \frac{(A_1 I_{0,a}) \beta_a}{(\beta_a + \beta_c)} + \ln \frac{(A_2 I_{0,c}) \beta_c}{(\beta_a + \beta_c)} \quad (7)$$

where I_{corr} is the corrosion current; $E_{e,a}$ is the equilibrium potential of the oxidizing substance on the anode; $E_{e,c}$ is the equilibrium potential of reducing substances on the cathode; β_a is the Tafel slope from the oxidizing reaction; β_c is the Tafel slope of the cathode reaction; $I_{0,a}$ is the exchange current density of the anode reaction; $I_{0,c}$ is the exchange current density of the cathode reaction; and A_1 , A_2 are the relative coefficients of the exchange current density. The thermodynamic parameter is $E_{e,c} - E_{e,a}$, while

$E_{e,c}$ is the equilibrium potential of the depolarizer on the cathode (chlorophenols, in our case). The larger the $E_{e,c}$ is, the larger the corrosion current I_{corr} increase will be, and the more depolarizer is reduced. Kinetic parameters are exchange current density I_0 and Tafel slope of curve b or β . The I_0 reflects the difficulty level of the electrode reaction, and the Tafel slope suggests the influence on the reaction rate by the strength of the electric field between electric double layers.

It could be inferred that hydrogen-evolution corrosion was not a principal electrode reaction. In the dechlorination reaction, chlorophenols may act as a depolarizer or an inhibitor. Due to the Cl substituent and π structure, chlorophenols can be easily adsorbed on the Cu^0 anode. Thus, oxygen uptake corrosion reaction is translated into reduction reaction of chlorophenols (Eqs. (1)–(3)).

Adding chlorophenols increases the corrosion potential of Ni^0 , reduces the corrosion current, and inhibits the release of Ni^{2+} . Electronic transmission speed and chlorophenol reduction are restrained rather than activated. Therefore, the electrode course should not be the control step for internal electrolysis reduction dechlorination.

Accordingly, we deduced that mass transfer during particle collision enhanced dechlorination of chlorophenols. Although the rate of reduction was not improved in the hydrogen-saturated solution, hydrogen evolution should not be neglected. Hydrogen evolution might be controlled by the factors including the redox potential of $\text{Ni}^{2+}/\text{Ni}^0$, the adsorption and diffusion of chlorophenols on the surface of metal particles, the passivation of metal, and the release rate of metallic ions. Since metallic Ni^0 is chemically inert, the rate of hydrogen evolution could be seriously restrained. Hence, overloaded hydrogen or lower pH (more H^+) might result in excess hydrogen rather than an accelerated reaction. For example, bubbles of hydrogen could cover the surface of Ni^0 and prohibit further reaction [26,35].

On the other hand, the produced hydrogen could be easily adsorbed on the surface of Ni^0 and be dissociated into H^* . Hydrogen spillover could occur on the [Ni/Cu] mixture [36]. Adsorbed H^* might transport from Ni^0 to Cu^0 . The adsorption intensity on Cu^0 is not as strong as that on Ni^0 , thus H^* might get more chances to relinquish its hold on the metal or directly react with the chlorophenols adsorbed on the Cu^0 surface (Fig. 5).

The reaction rates were controlled by the transport of H^* . To verify the hypothesis, diffusion control experiments were conducted to test the role of mass transfer in the reduction of chlorophenols. As shown in Fig. S7, the removal rate of chlorophenols increased with the increasing Cu^0 addition in the reaction. Hence, the mass transfer rate is the rate-determining step. It can be assumed that a H^* transport channel exists between Ni^0 and Cu^0 . It can be assumed that the width of the channel is determined by the hydrogen spillover

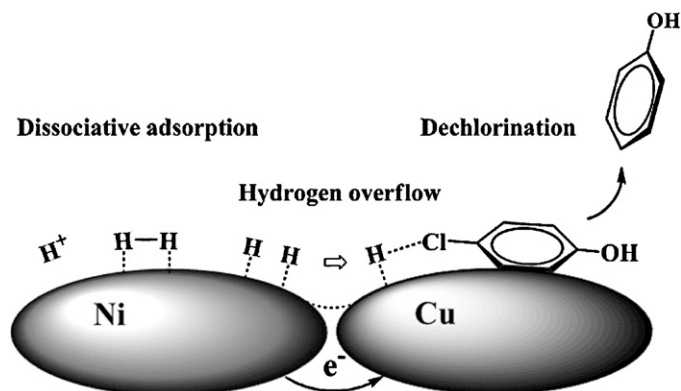


Fig. 5. Catalytic dechlorination mechanism (in the case of 4-CP) and hydrogen spillover transport of H^* from particle to particle.

speed. The hypothesis needs to be further tested and verified based on characterizations and detections. We will continue on the investigation for more proof of H^* and hydrogen spillover.

Friedrich et al. [29] demonstrated that the viability of metallic nickel catalytic reduction for wastewater treatment might actually make economic sense. Our findings proved the technical superiority of [Ni|Cu] mixture for chlorophenol transformation, including dechlorination rate and loss of chlorine substituents. Compared with other ZVMs or nanometals [30–32], [Ni|Cu] has the advantage of low cost, corrosion resistance, easy recyclability and reuse due to its ferromagnetism. Benefitting from the magnetism and chemical inertness of Ni^0 and Cu^0 , the particles tend to deposit in the gravity or magnetic field (Fig. S8), which prevents the secondary pollution of the metal particles. [Ni|Cu] mixture is a considerable technology alternative due to its high activity, persistence, and simplicity.

However, the release of Ni^{2+} is the prime technical hurdle for this application. Even at the ideal exchange ratio between Ni^{2+} and chlorophenols under laboratory conditions, the concentration of Ni^{2+} remains a problem. After a batch experiment of 2 h, the concentration of Ni^{2+} could reach 20–160 $\mu\text{mol L}^{-1}$ (Fig. S1). Although Ni^0 is a necessary microelement used in dentures, electroplates, and hardware, concentrated Ni^{2+} in water remains a potential threat for human health (Ni^{2+} , LD_{50} : 180–470 $\mu\text{mol L}^{-1}$, for amphibians, from Registry of Toxic Effects of Chemical Substances, RTECS). There is a need to develop an efficient method to inhibit the release of Ni^{2+} . For instance, adding natural organic matter, such as gum arabic and hydroxyethyl cellulose, will sorb Ni^{2+} from the solution. As shown in Fig. S9, the concentration of Ni^{2+} was reduced by about 90% by adding 1.0 g L^{-1} gum arabic, while the transformation rate of 2,4,6-TCP increased slightly. Ni^{2+} could be transformed into nickel hydroxide at $\text{pH} > 6.7$. Hence, it is reliable to deposit most Ni^{2+} in the form of hydroxide by adjusting the pH of the solution (Fig. S9). We would continue to explore technology development and improve the recyclability, feasibility, and activities (for example, Ni^0 -doped Cu^0 bimetal particle, nanosized metal particle, etc.) of these substances, and then incorporate them into the application attempt.

4. Conclusion

Conventionally, the Ni^0 dechlorination has been reported by many practical researches. However, most of them were related to the catalytic dechlorination in the presence of hydrogen under high temperature and pressure. However, the dechlorination of chlorophenols in aqueous solution by [Ni|Cu] particle mixture, to our knowledge, has been rarely reported. Chlorophenols could be reductively dechlorinated by [Ni|Cu] mixture microcell with a high transformation rate, yielding low-substituted chlorophenols, phenol, cyclohexanone, and cyclohexanol as intermediate products. Ni^0 was determined as the reductant and the spillover of H^* from Ni^0 to Cu^0 was responsible for the enhancement of chlorophenol reduction. The finding is highly favorable for the application of bimetal microcell and for addressing concerns regarding possible application of new ZVMs for wastewater treatment. Further experiments to improve the reduction efficiency and to inhibit the release of Ni^{2+} have been undertaken.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.044.

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