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Removal of *p*-nitrophenol (PNP) in aqueous solution by the micron-scale iron–copper (Fe/Cu) bimetallic particles

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ABSTRACT

In this study, in order to further investigate the degradation capacity and mechanism of Fe/Cu bimetallic system, the prepared Fe/Cu bimetallic particles with different theoretical copper mass loadings (0.05, 0.11, 0.24, 0.41, 0.62, 0.89, 1.26 and 1.81 g Cu/g Fe) were characterized by SEM, EDS, XRD and laser particle size analyzer. Also, the effect of theoretical Cu mass loading and five key operating parameters on the PNP removal efficiency was investigated thoroughly. Furthermore, the mineralization process of PNP was studied by using COD, TOC, UV–vis spectra, FTIR spectra and GC/MS. The results show that a large number of fine Cu particles were produced from the excessive theoretical Cu mass loading, and they facilitated the catalytic reactivity of the Fe/Cu bimetallic particles at Cu loading <0.89 g Cu/g Fe. Additionally, the heterogeneous Cu layer is also favor for the catalytic reactivity of the Fe/Cu bimetallic particles, while the uniform and dense Cu layer can decrease its reactivity severely. The degradation rates of PNP by the Fe/Cu particles with different theoretical Cu mass loadings are all in accordance with the pseudo-first-order kinetics model, and the optimal operating parameters were obtained by the batch experiments. In addition, both the indirect reduction by atomic hydrogen and the direct reduction on the catalytic activity sites play a leading role on the pollutants removal. Finally, the degradation pathway of PNP was proposed according to the detected intermediates by GC/MS. Collectively, these results suggest that the Fe/Cu bimetallic system should be proposed as a cost-effective pretreatment process for the toxic and refractory PNP wastewater.

1. Introduction

Nowadays, industrial wastewater containing aromatic pollutants represent a big challenge for the researchers. *p*-Nitrophenol (PNP) and its derivatives all are the typical aromatic pollutants discharged from dyes, explosives, pesticides, plasticizers and herbicides industries [1]. All these compounds in industrial wastewater are toxic and refractory organic pollutants, and most of them are considered as hazardous wastes and priority toxic pollutants by the US Environmental Protection Agency (EPA). However, these pollutants are usually hard to be treated directly by the traditional biological treatment process due to their high toxicity and low biodegradability [2]. Advanced oxidation processes (AOPs) including Fenton reagent [3], electro-Fenton [4], photocatalysis [5,6], catalytic wet air oxidation [7] and microwave assisted oxidation process [8] were usually used to degrade these toxic and refractory PNP. However, all of these AOPs suffer from the limitations of high costs.

Zero-valent iron (ZVI) and Fe/GAC micro-electrolysis have been used to treat the toxic and refractory wastewater including dye wastewater [9], atrazine [10], and ABS resin wastewater [11]. Despite the widespread studies on these treatment technologies, their practical applications are still suffering from many limitations. In particular, these systems will lose their reactivity over time resulted from the corrosion products or other precipitates on the surface of the Fe^0 and GAC [12]. One strategy that has proven effective in overcoming some shortcomings of ZVI and Fe/GAC micro-electrolysis involves the addition of Cu pieces into ZVI reactor. The Fe–Cu process is developed by the thorough mixture of iron scrap and Cu pieces in a desired proportion [13]. High reaction potential can improve reduction capacity of Fe^0, and a higher pollutant removal efficiency would be obtained even in neutral pH range [14,15]. However, the mixture of Fe^0 and Cu^0 shavings are put to form a fixed bed in the Fe–Cu process, and the fixed bed structure can limit the mass transport rates of intermediates, products and reactants between the solution phase and the Fe^0/Cu^0 surfaces.

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Recently, the micron-scale bimetallic reductants prepared by the deposition of a second transition metal on the iron surface can enhance rates of the pollutants reduction remarkably [16–20]. The previous studies suggest that the transition metal involving Ni, Pd, Cu, Co, Au and Ru can enhance the catalytic reactivity of Fe^0 [20–22]. Somehow, these transition metals have different reactivity enhancements for the prepared bimetallic reductants. Cwiertny et al. [22] found the following reactivity trend of the prepared bimetallic reductants towards 1,1,1-TAC: $Ni/Fe \approx Pd/Fe > Cu/Fe > Co/Fe > Au/Fe \approx Fe$. Lin et al. [20] also found that the catalytic activity of the noble metal followed the order of $Pd > Ru > Pt > Au$. Two types of catalytic mechanisms of the bimetallic reductants have been proposed by the previous researchers, (a) indirect reduction by the atomic hydrogen ($[H]_{abs}$) absorbed on the surface of bimetallic reductants, and the transition metal additives can facilitate the generation of surface-bond atomic hydrogen ($[H]_{abs}$) [20,21], (b) direct reduction on the catalytic activity site by accepting electrons from the oxidation of Fe^0, and the surface additives (i.e., transition metal) can increase the oxidation of Fe^0 through the formation of infinite galvanic cells [13,14,23]. At present, the prepared bimetallic reductants were mainly used to reduce the lower concentration organohalides (such as 1,1,1-trichloroethane) [22]. The experiment results of Bransfield et al. [21] show that surface-bond atomic hydrogen ($[H]_{abs}$) plays a leading role on the reduction of organohalide, while Xu et al. consider that the dechlorination is mainly resulted from the direct reduction on the surface of catalytic activity site (Cu) [13].

The previous studies mainly show that Fe/Cu bimetallic reductant with low Cu loading (<10 μmol Cu/g Fe) was used to reduce the organohalide with low initial concentration (<100 μmol/L) [21,24]. Also, their results reveal a more modest rate of increase in the K_{obs} at Cu loading <10 μmol Cu/g Fe [24]. However, the Fe/Cu bimetallic reductant has not been used to treat the higher concentration organic pollutants, and the effect of Cu loading on the degradation of higher concentration organic pollutants might be completely different.

Therefore, it is important to further investigate the operating parameters and catalytic mechanism of the prepared Fe/Cu bimetallic system for the treatment of higher concentration pollutants. In the present investigation, we have setup experiments specifically to study the effect of theoretical copper mass loadings and operating parameters on the pollutant removal efficiency by Fe/Cu bimetallic system. The prepared Fe/Cu bimetallic particles with different theoretical copper mass loadings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and laser particle size analyzer. Furthermore, effect of theoretical Cu mass loading, Fe/Cu bimetallic dosage, initial PNP concentration, initial pH, electrolyte and stirring speed on the PNP removal efficiency was investigated, respectively. Additionally, the mineralization of PNP was studied by analyzing the variation of COD, TOC, UV–vis and FTIR spectra after treatment of Fe/Cu bimetallic system. Finally, the degradation products of PNP by the Fe/Cu bimetallic system were analyzed using a gas chromatography-mass spectrometry (GC/MS), and the degradation pathway was proposed according to the detected intermediates.

2. Experimental

2.1. Reagents

PNP (99%), $CuSO_4{\cdot}5H_2O$ (analytical reagent), Na_2SO_4 (analytical reagent) and zero valent iron (ZVI) powders from Chengdu Kelong chemical reagent factory were used in the experiment. The zero valent iron powders have mean particle size of approximately 120 μm, and their iron content reaches approximately 97%. Dichloromethane (HPLC grade) were obtained from J.T. Baker (Deventer, The Netherlands). Other chemicals used in the experiment were of analytical grade. Deionized water was used throughout the whole experiment process.

2.2. Preparation of the iron–copper (Fe/Cu) bimetallic particles

The micron-scale zero valent iron powder was used as the base material for the preparation of iron–copper (Fe/Cu) bimetallic particles. Prior to plating, iron particles were not needed acid washing by HCl, since there was no iron oxide to be detected on the surface of iron particles by SEM–EDS (Fig. 1(a)

). The iron–copper (Fe/Cu) bimetallic particles were prepared by the displacement plating, via adding 200 mL of $CuSO_4$ solution to the iron particles. After the $CuSO_4$ solution was added to the iron particles, the slurry was mixed by hand for 10 min. Then the prepared Fe/Cu bimetallic particles were separated from the supernatant after 5 min precipitation process. Finally, the separated Fe/Cu bimetallic particles were rinsed three times with deionized water, once with ethanol, and then were dried under N_2 protection at 80 °C for 40 min.

$CuSO_4$ was used to deposit Cu on the surface of iron particles by the iron–copper replacement reaction, and the Cu mass loading on the surface of iron particles (i.e., Fe/Cu ratio) could affect the catalytic activity of the prepared Fe/Cu bimetallic particles [21,22]. In addition, the copper mass loading of the prepared Fe/Cu bimetallic particles could be changed by adjusting the concentration of $CuSO_4$ solution. In order to prepare the Fe/Cu bimetallic particles with different theoretical copper mass loadings, 15 g iron particles were added in 200 mL $CuSO_4$ solution with different concentration (specifically, 9.38, 18.75, 37.50, 56.25, 75.00, 93.75, 112.50 and 131.25 g/L), respectively. Immersion plating with these solution

Table 1
The parameter of the prepared Fe/Cu bimetallic particles with different Fe/Cu ratio.

Fe/Cu[a]	M_{Fe} (g)	M_{Cu} (g)	C_{CuSO_4} (g/L)	V_{CuSO_4} (mL)	R_{Fe}	TML_{Cu} (g Cu/g Fe)	Fe/Cu[b]
20:1	15.00	0.75	9.38	200.00	14.34	0.05	10:0.5
10:1	15.00	1.50	18.75	200.00	13.69	0.11	10:1.1
10:2	15.00	3.00	37.50	200.00	12.38	0.24	10:2.4
10:3	15.00	4.50	56.25	200.00	11.06	0.41	10:4.1
10:4	15.00	6.00	75.00	200.00	9.75	0.62	10:6.2
10:5	15.00	7.50	93.75	200.00	8.44	0.89	10:8.9
10:6	15.00	9.00	112.50	200.00	7.13	1.26	10:12.6
10:7	15.00	10.50	131.25	200.00	5.81	1.81	10:18.1

[a] Mass ratio of zero iron particles with Cu in $CuSO_4$ solution before replacement reaction.
[b] Mass ratio of Fe with Cu in the prepared Fe/Cu bimetallic particles after replacement reaction.
M_{Fe}: The mass of zero iron particles which added in the $CuSO_4$ solution.
: The mass concentration of $CuSO_4$ solution.
R_{Fe}: The mass of Fe in the prepared Fe/Cu bimetallic particles after replacement reaction.
TML_{Cu}: Theoretical Cu mass loading on the surface of iron particles.