Electrochemical reduction characteristics and mechanism of nitrobenzene compounds in the catalyzed Fe-Cu process

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Abstract: The reduction of the nitrobenzene compounds (NBCs) by the catalyzed Fe-Cu process and the relationship between the electrochemical reduction characteristics of NBCs at copper electrode and reduction rate were studied in alkaline medium(pH=11). The catalyzed Fe-Cu process was found more effective on degradation of NBCs compared to Master Builder's iron. The reduction rate by the catalyzed Fe-Cu process decreased in the following order: nitrobenzene >4-chloro-nitrobenzene $\geq$ m-dinitrobenzene > 4-nitrophenol $\geq$ 2,4-dinitrotoluene >2-nitrophenol. The reduction rate by Master Builder's iron decreased in the following order: m-dinitrobenzene $\geq$ 4-chloro-nitrobenzene > 4-nitrophenol > 2,4-dinitrotoluene $\approx$ nitrobenzene > 2-nitrophenol. NBCs were reduced directly on the surface of copper rather than by the hydrogen produced at cathode in the catalyzed Fe-Cu process. The reduction was realized by the hydrogen produced at cathode and $Fe(OH)_2$ in Master Builder's iron. It is an essential difference in reaction mechanisms between these two technologies. For this reason, the reduction by the catalyzed Fe-Cu depended greatly on NBC's electron withdrawing ability.

Keywords: wastewater contaminated by NBCs; electrochemical reduction characteristics; catalyzed Fe-Cu process; reduction mechanism

Introduction

Nitrobenzene is a common environmental contaminant because of their use as munitions, insecticides, herbicides, pharmaceuticals, and industrial feed stock chemical for dyes, plastics, etc.(Hatter, 1985). It also may be formed in the environment from aromatic contaminants, as in the case with nitro-PAHs and nitrophenols found in atmospheric water(Mantha et al., 2001). The remediation of nitrobenzene is of interest because it is among the most characteristic of anthropogenic contaminants, being second in the organochlorine functional groups (Agrawal and Tratnyek, 1996). Nitrobenzene is resistant to chemical or biological oxidation and to hydrolysis due to the electro-withdrawing effect of the nitro group. It is outside the scope of peroxidase catalysis; the biodegradation of nitrobenzene is generally difficult to achieve; furthermore it usually inhibits the action of the microorganism. Among the processes contributing to the remediation of nitrobenzene, reduction of the nitro group is certainly the most characteristic. Master Builders' iron and the bimetallic systems with an iron base(Marquez and Pletcher, 1980; Devlin et al., 1998; Klausen et al., 2001; Bell et al., 2003; Hung et al., 2003; Keum and Li, 2004; Mu et al., 2004), which scientists have used extensively, have provided an economical approach to treat wastewater. However, the reduction mechanisms related to iron-base bimetallic system have not yet been fully understood.

Noble metal catalysts such as palladium had satisfactory results in reducing nitrobenzene in the laboratory, but it is too costly for waste treatment (Kralik et al., 1998); moreover, in certain instances,

the catalysts dissolve in the presence of nitroaromatic explosives(Rodgers and Bunce, 2001), so they cannot be applied in wastewater treatment. The reduction by Fe^0 usually requires a mass of acid to adjust pH of wastewater at 2—3. Copper was used as a catalyst to remediate nitrobenzene-containing water in this paper. Copper is cheap, and has a relatively high hydrogen overpotential (i.e. hydrogen is relatively difficult to evolve on its surface)(Li, 1999), so the reduction of nitrobenzene at the copper electrode is achieved rather through the direct pathway than through the hydrogen produced at cathode.

The redox couple formed by zero oxidation state metallic iron, Fe^0, and dissolved aqueous Fe^{2+}

$$Fe_0 - 2e^- \longrightarrow Fe^{2+} \qquad (1)$$

has a standard reduction potential of -0.441 V. This makes Fe^0 a reducing agent relative to many redox-labile substances, including hydrogen ions, carbonate, sulfate, nitrate and oxygen. The redox couple formed by zero oxidation state metallic copper, Cu^0, and dissolved aqueous Cu^{2+}

$$Cu^{2+} + 2e^- \longrightarrow Cu^0 \qquad (2)$$

has a standard reduction potential of +0.345 V. The graphite electrode is inert; it does not participate in electrode reactions. Hydrogen evolution($E_0(H^+/H_2)$=0 V) is the cathodic half-reaction in the absence of oxygen. Therefore, galvanic corrosion of iron and electrode reaction rate will be intensified and accelerated under the action of a cell of iron and copper in the absence of oxygen. Additionally, organics will be reduced directly on the surface of copper due to its electro-catalytic activity.

Fan *et al.*(2004) treated nitro-benzene containing water with zero-valent iron powder, Master Builder's iron and the catalyzed Fe-Cu process. The experiments indicated these 3 systems produced similar results under the acidic conditions. However, under the neutral and alkaline conditions the reduction efficiency by iron powder dropped drastically, while under neutral conditions the reduction efficiency by the catalyzed Fe-Cu process was found about 20% higher than by Master Builder's iron, under the weakly alkaline conditions (pH about 9.5) the former was found about 40% higher than the latter. Additionally, the reduction efficiency was comparable with that obtained under the strongly acidic conditions. Xu *et al.* (2005) investigated the electrochemical reduction characteristics of NBCs using cyclic voltammetry and came to the conclusion that NBCs were capable of reducing directly at the copper electrode. pH strongly influenced the electrochemical reduction characteristics of the NBCs at the copper electrode(Xu *et al.*, 2005), and it mainly depends on the properties of the substituent groups on the benzene ring, their configurations and numbers, and their location versus nitro-group on the benzene ring.

Different NBCs will be unable to be reduced equally by Master Builder's iron and the catalyzed Fe-Cu process. However, these two technologies are both effective in treating NBCs contaminated water, and the catalyzed Fe-Cu process often produces more noticeable results. Additionally, wastewater could be contaminated by different NBCs simultaneously in practice. It is therefore helpful to study the electrochemical reduction characteristics at copper electrode and the reduction mechanism of NBCs by the catalyzed Fe-Cu process. The reduction mechanism by the catalyzed Fe-Cu process was discussed in this paper using cyclic voltammetry. The difference in reduction mechanisms between the Fe-Cu bimetallic process and Master Builders' iron was also discussed.

1 Experimental

1.1 Reagents and instruments

The waste scrap iron (scrap cast iron) with a surface area of 0.3—0.4 m^2/g was received in the Mechanical Factory of Tongji University and washed with soap to remove oil. The catalyst was the pure copper tinsel with a 0.12-mm thickness, readily available on the market, and was cut into thin pieces of the size 5 × 1 cm^2 before the experiments. The water for the experiments was obtained after distilling deionized water. In order to study the reduction of NBCs by the catalyzed Fe-Cu process and the relationship between NBCs' molecular structure and the reduction rate, 6 representative NBCs were selected for the experiments: nitrobenzene, *m*-dinitrobenzene, 4-chloro-nitrobenzene, 2-nitrophenol,

4-nitrophenol and 2,4-dinitrotoluene. The electrolyte for cyclic voltammetric scanning was prepared with the highly purified water twice distillated in the lab; anhydrous sodium sulfate (0.1 mol/L) was used as the supporting electrolyte. All reagents applied in the process of the experiments were analytical grade(AR) materials.

The shaker of model HYG-A made in Taicang Experimental Equipment Factory of China was used to conduct the batch experiments. All the measurements of cyclic voltammetry were done with a conventional three-electrode configuration. The graphite electrode and the homemade copper electrode, which have an area of 1.33 cm^2 and 1.44 cm^2 respectively, were used as working electrodes. A Pt electrode served as an auxiliary electrode and a saturated calomel electrode (SCE), model 232 manufactured by Shanghai Analytical Instrument Factory of China, was used as a reference electrode. Cyclic voltammetry scanning was conducted using a CHI600A electrochemical station made in the Shanghai Chenhua Instrument Company, as was the stochastic software applied to collecting data and plotting the cyclic voltammograms. Electrolysis was conducted using the Rex potentiostat, model DJS-292, made in Shanghai Rex Instrument Co. Ltd. UV spectrophotometers, models 721 and 756 MC made in Shanghai Precision Instrument Factory, were used to analyze the compositions of the water before and after the treatment.

1.2 Experimental conditions

Master Builders' iron is effective in treating nitrobenzene-containing water at low pH, which is to say acidity greatly favors the reduction. The superiority of the addition of copper to Master Builders' iron cannot be observed under such circumstances. At alkaline pH NBCs are basically reduced via the direct pathway(Section 2.2) and by the Fe(OH)$_2$ produced in the system. The relationship between the electrochemical reduction characteristics of NBCs at the copper electrode and the reduction rate by the catalyzed Fe-Cu process cannot be discerned under acidic conditions, so the experiments were conducted in the alkaline medium(pH=11.0).

1.3 Experimental methods
1.3.1 Batch experiments

Dried the above-mentioned iron scrap of a 100-g weight by heating, mixed it and the copper evenly in a certain proportion (10:1, w/w) and held them down so that the observed density reached about 0.5 kg/L. Then put these 2 fillings in 500 ml wide neck ground-glass stoppered flasks, mixed 300 ml of the prepared NBCs-containing solution with 250 mg/L nitrobenzene into them respectively and covered the flasks' lids. Afterwards, put the flasks with the fillings and water in the shaker of model HYG-A and shook at

140 r/min for a certain time (10, 20, 30, 40 and 60 min), then sampled about 50 ml water from each flask respectively with a close 10-ml injector and analyzed its composition.

1.3.2 Cyclic voltammetry scanning

Twenty milliliter aqueous organic solution was flushed with nitrogen gas continuously for about 1 min to drive away the oxygen dissolved in the water, then stabilized for 10—15 s. Cyclic voltammetry scanning rate was set at 4 V/s. In order to avoid oxidation of Cu, the highest scanning potential at the copper electrode was set at -0.2 V. The homemade copper electrode lay soaked in 10% (w/w, %) hydrochloric acid for about 2 h and acetone for 2 h separately to clean its surface.

1.3.3 Analysis of the reduction products by GC/ MS

Finnigan Voyager gas chromatographic and mass spectrographic instruments were applied to analyzing compositions of organic compounds in the water before and after the treatment. 10 ml water was extracted with 1 ml dichloromethane of analytical (AR) grade before injecting into the column, and 1 μl of extracted sample was injected for analysis. The carrier gas helium flow rate was set at 1 ml/min. The MS was operated in electron impact mode (70 eV). Injection port temperatures were 250℃ and the column temperature started at 50℃ for 2 min, was ramped to 250℃ at a rate of 20 ℃/min and finally held for 10 min. A non-polar capillary column of model DB/5(30 m in length, 0.25 mm in diameter, the thickness of the stationary liquid 5% phenylpoly-dimethylsiloxane is 0.25 μm) was used in the analytical process. Dodecane was used as the internal standard (IST) while determining the reactions corresponding to the reduction waves at the copper cathode.

1.4 Analysis of the reduction products by UV spectrophotometry

1.4.1 Setting up standard curve for the nitrobenzene solutions

Diluted the prepared nitrobenzene solution with 104.2 mg/L into the solutions of the different strengths (1.3, 3.26, 4.34, 6.51, 13.03 and 26.05 mg/L) and measured the obtained solutions' absorbance at λ = 268.5 nm where nitrobenzene has an adsorption peak respectively. As shown in Fig.1 the received solution absorbance characteristic $A = f_{(c)}$ conformed Beer's law, and the obtained standard curve can be expressed by the following straight-line equation:

$$A = 0.0591 C + 0.0041, \quad R^2 = 0.9995$$

where A is absorbance, C is nitrobenzene solutions concentration.

1.4.2 Influence of aniline on the measurement of nitrobenzene and its concealment
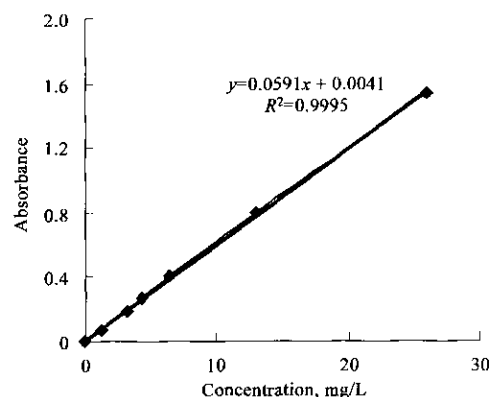

Fig.1 The standard curve of nitrobenzene solution

It has been reported that the final reduction product of nitrobenzene is aniline (Agrawal and Tratnyek, 1996). Formally this process consists of a series of two-electron additions, proceeding through nitroso and hydroxylamine intermediates. Hydroxy-lamine is labile as it can be oxidized to more stable nitroso-benzene fast at room temperature (Klausen et al., 2001). Nitroso-benzene will not accumulate as it can be reduced at a more positive potential compared to nitrobenzene (Agrawal and Tratnyek, 1996). There is not much difference in the UV spectrum between acidified product of aniline and benzene (Chen, 1985; Wang et al., 1997). Under this circumstance acidi-fication can be used to conceal the interference of aniline in UV spectrophotometry. The interference arisen at $\lambda > 220$ nm can be concealed after acidifying the analyzed solutions (Wang et al., 1997), and the absorption spectrum of nitrobenzene remains uninfluenced. In this case, two-component system can be treated like one-component system. The absorbance with and without concealment of aniline were measured respectively at λ = 268.5 nm.

Exactly measured 0, 2.0, 5.0, 8.0, 10.0, 16.0, 20.0 ml the prepared 128 mg/L aniline solution, added 2 ml the prepared 1042 mg/L nitrobenzene solution respectively, then diluted the obtained mixtures to 50 ml with distilled water.

The obtained solutions were divided into 2 groups of solutions of the same volume (25 ml). Diluted the solutions in the first group with distilled water to 50 ml and measured their absorbance at λ = 268.5 nm. Acidified the solutions in the second group with 2 drops 0.1 mol/L HCl and diluted to 50 ml, then measured absorbance of the mixtures at λ = 268.5 nm. The results are shown in Fig.2.

1.4.3 Reduction of nitrobenzene by the catalyzed Fe-Cu process

The UV absorption spectra of the solutions before and after the treatment are shown in Fig.3a. The adsorption peak at λ = 268.5 nm weakened in the reduction by the catalyzed Fe-Cu process. Additionally, it had a red shift. An adsorption peak at
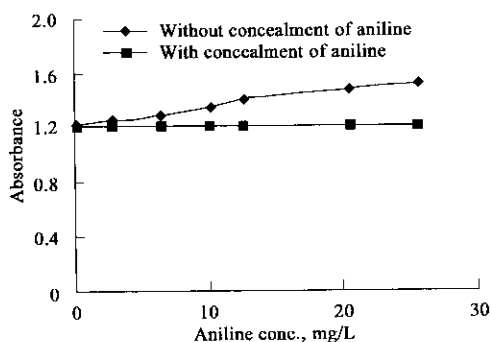
Fig.2　The influence of aniline on the measurement of nitrobenzene
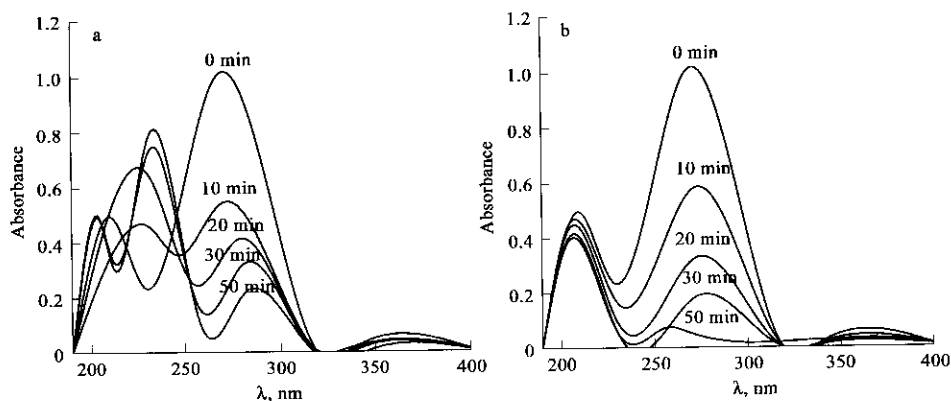
λ= 230 nm came into view in the reduction process, moreover it grew in strength. After the thorough reduction the absorption peak at λ=268.5 nm disappeared from sight, and the ultimate product had the absorption maximums at the wavelengths λ=230 and 280 nm, which is identical to aniline. After acidifying the reduced solutions the absorption peak at the wavelength λ=230 nm disappeared, and the shifted peaks went back to λ=267 nm. Additionally, its strength decreased. The experiments showed that nitrobenzene was reduced to aniline by the catalyzed Fe-Cu process. The B-adsorption band of aniline and nitrobenzene overlapped partly, that is the reason for

Fig.3　UV spectra of the reduction products in the system(a) and after acidification(b)

the red shift in the degradation. Neither azoxybenzene nor azobenzene were observed as the reduction products of nitrobenzene after the treatment indicating that condensation reactions were insignificant during the reductions in this study.

Measured the solutions absorbance before and after the treatment respectively, then according to the standard curve calculated residual concentration of nitro-group and its corresponding conversion(%):

$$\text{Conversion of nitro group (\%)} = \frac{A_b - A_a}{A_b} \quad (3)$$

where: A_b is the absorbance before the treatment; A_a is the absorbance after the treatment.

The interference of aniline in UV spectro-photometry was concealed before each single measurement by acidification. The existence of different substituting groups in molecules of NBCs caused the red shift of the characteristic peak of nitro group at λ=268.5 nm, the absorption peaks of 2-nitro-phenol, 4-chloro-nitrobenzene and 4-nitro-phenol are located at λ=278, 286 and 310 nm respectively, and the corresponding standard curves can be expressed by the following straight-line equations: $A = 0.0436\ C$; $0.0287\ C$; $0.0618\ C$. The NBCs concentration data obtained by UV spectro-photometry was accurate to ±5% compared to the

results obtained by GC/MS analysis. This work only has a calculation of the relative value conversion rate of nitro group (%), therefore, the experimental data is accurate to ±2% compared to the latter.

2　Results and discussion

2.1　Reductions of NBCs by Master Builder's iron and the catalyzed Fe-Cu process

The results of NBCs reduction by Master Builder's iron and catalyzed Fe-Cu process are shown in Fig.4.

As shown in Fig.4a, the reduction rate of NBCs by Master Builders' iron ranges in following rows: *m*-dinitrobenzene ≥4-chloro-nitrobenzene >4-nitro-phenol >2,4-dinitrotoluene ≈nitrobenzene >2-nitro-phenol. The reduction rate of NBCs by the catalyzed Fe-Cu process ranges in the following rows: nitro-benzene >4-chloro-nitrobenzene ≈>*m*-dinitroben-zene >4-nitrophenol ≥2,4-dinitrotoluene >2-nitro-phenol(Fig.4b).

From Fig.4 we found that the catalyzed Fe-Cu process is superior to Master Builders' iron in treating the majority of the NBCs-containing solutions. This advantage was noticeable under alkaline conditions. 2-nitro-phenol was the only exception because these 2 technologies produced almost identical results. This phenomenon was basically caused by the difference in
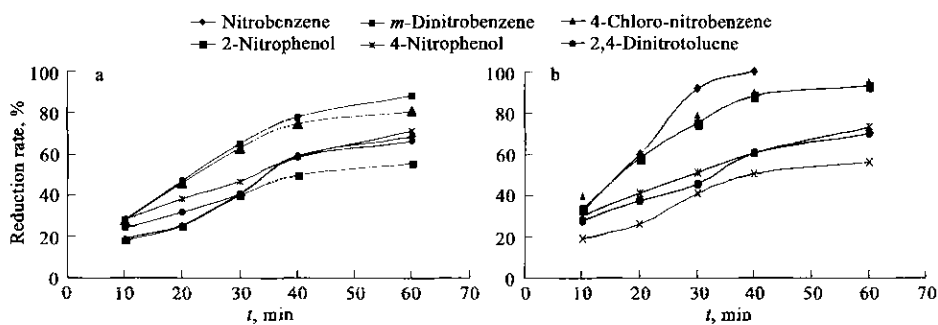
Fig.4 The reduction of NBCs by Master Builder's iron(a) and catalyzed Fe-Cu process(b)

eduction mechanisms between these 2 technologies. The pH of alkaline NBCs wastewater does not need to be adjusted to 2—3 before it is treated by the catalyzed Fe-Cu process. This process can even be applied to treating alkaline wastewater (pH about 11). Moreover it will not give rise to a hydrogen ion shortage as seen with Master Builder's iron, which further slowing the reduction is one of the weak points of the latter.

The reduction of NBCs by the catalyzed Fe-Cu process approximately followed pseudo-first order kinetics (Table 1), and the kinetics of the reduction of NBCs by Master Builder's iron also conformed to pseudo-first order (Table 2). The catalyzed Fe-Cu process is much better suited for treating nitro-benzene, 4-chloro-nitrobenzene and m-dinitrobenzene containing water(Table 3).

Table 1 Reduction kinetics by the catalyzed Fe–Cu process

Organics appellation	Equation of reduction kinetics	R^2	K_{cu}, min^{-1}
2-Nitrophenol	$\ln(C/C_0) = -0.0151\,t$	0.9496	0.0151
Nitrobenzene	$\ln(C/C_0) = -0.0684\,t$	0.8625	0.0684
2,4-Dinitrotoluene	$\ln(C/C_0) = -0.0210\,t$	0.9736	0.0210
4-Nitrophenol	$\ln(C/C_0) = -0.0229\,t$	0.9761	0.0229
4-Chloro-nitrobenzene	$\ln(C/C_0) = -0.0517\,t$	0.9910	0.0517
m-Dinitrobenzene	$\ln(C/C_0) = -0.0465\,t$	0.9848	0.0465

Table 2 Reduction kinetics by Master Builder's iron

Organics appellation	Equation of reduction kinetics	R^2	K_{Mas}, min^{-1}
2-Nitrophenol	$\ln(C/C_0) = -0.0151\,t$	0.9496	0.0151
Nitrobenzene	$\ln(C/C_0) = -0.0188\,t$	0.9677	0.0188
2,4-Dinitrotoluene	$\ln(C/C_0) = -0.0199\,t$	0.9737	0.0199
4-Nitrophenol	$\ln(C/C_0) = -0.0216\,t$	0.9798	0.0216
4-Chloro-nitrobenzene	$\ln(C/C_0) = -0.0302\,t$	0.9669	0.0302
m-Dinitrobenzene	$\ln(C/C_0) = -0.0360\,t$	0.9959	0.0360

Table 3 Parallels of the reduction kinetics between these 2 technologies

Organics appellation	K_{cu}, min^{-1}	K_{Mas}, min^{-1}	$\Delta K = K_{cu} - K_{Mas}$, min^{-1}	$\Delta K/K_{Mas}$, %
2-Nitrophenol	0.0151	0.0151	0	0
Nitrobenzene	0.0684	0.0188	0.0496	263.83
2,4-Dinitrotoluene	0.0210	0.0199	0.0011	5.53
4-Nitrophenol	0.0229	0.0216	0.0013	6.02
4-Chloro-nitrobenzene	0.0517	0.0302	0.0215	71.19
m-Dinitrobenzene	0.0465	0.0360	0.0105	29.17

2.2 Reduction mechanism study
2.2.1 Electro-reductive characteristics of NBCs

Fig.5 represents the cyclic voltammetric response obtained in 100 mg/L nitrobenzene in 0.1 mol/L Na_2SO_4 aqueous solution for (a) the graphite and (b) the copper electrodes at a scan rate of 4 V/s in the alkaline medium(pH =11).
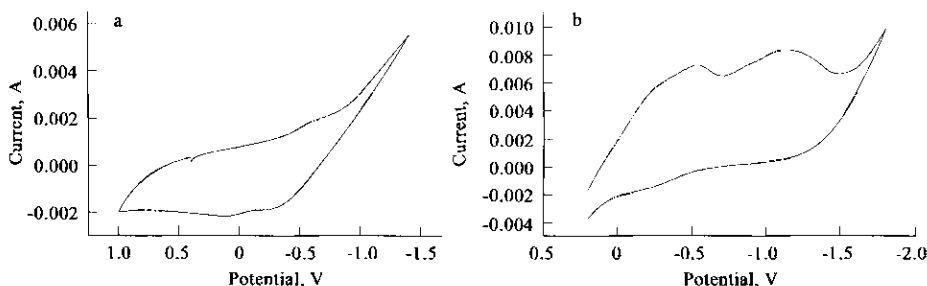

Fig.5 Cyclic voltammograms of 100 mg/L nitrobenzene in 0.1 mol/L Na_2SO_4 aqueous solution
a. at the graphite electrode; b. at the Cu electrode at pH = 11

As shown in Fig.5a, no other than hydrogen evolution peak can be found at the graphite electrode for nitrobenzene, which indicates that nitrobenzene is not capable of reducing at the graphite electrode directly. The nitro-group is therefore primarily reduced by the nascent state hydrogen formed after the reduction of water at the cathode. Its overall reaction can be expressed as:

$$ArNO_2 + 4H_2O + 6e \longrightarrow ArNH_2 + 6OH^- \qquad (4)$$
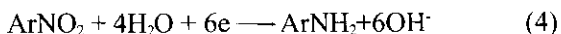
Cast iron is an alloy of pure iron, carbon and some other impurities. Carbon and impurities are dispersed evenly as very small granules in cast iron. Numerous corrosion cells are formed when the cast iron is immersed in an electrolyte solution. In this case the pure iron comes as an anode, and the carbon comes as a cathode(Li *et al.*, 2002).

The half reaction at the iron anode can be represented by Eq.(5).

$$\text{Cathode} \quad 2H^+ + 2e \longrightarrow 2[H] \longrightarrow H_2 \qquad (5)$$
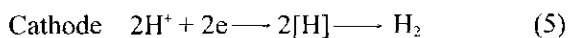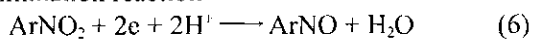
Nitrobenzene is reduced indirectly at the cathode in Master Builder's iron; specifically it is reduced by the hydrogen produced at cathode.
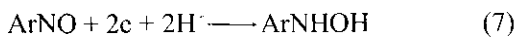
Nitrobenzene gives two reduction peaks corresponding to the irreversible electrochemical reduction at the copper electrode (Fig.5b), one at about -0.58 V, another at about -1.32 V. In order to determine the reactions corresponding to the reduction waves at the copper cathode, electrolysis was conducted for about 16 h having the cathodic potential under control at -1.32 V (vs. SCE) and using the copper electrode as cathode. The experimental results showed that aniline was by far the dominating reduction product corresponding to the wave at -1.32 V, indicating reduction of the intermediate product to aniline at -1.32 V or thereabout at the copper electrode.

As remarked, the reduction process proceeds through nitroso and hydroxylamino intermediates(Eq. (6)—(8)), when nitrobenzene is reduced to aniline at electrodes (Yu, 1981; Klausen *et al.*, 2001; Scherer *et al.*, 2001).

Elimination reaction
$$ArNO_2 + 2e + 2H^+ \longrightarrow ArNO + H_2O \qquad (6)$$
Addition reaction
$$ArNO + 2e + 2H^- \longrightarrow ArNHOH \qquad (7)$$
Substitution reaction
$$ArNHOH + 2e + 2H^- \longrightarrow \cdot ArNH_2 + H_2O \qquad (8)$$

The reduction potentials for Eq.(6) and Eq.(7) are very similar, so that polarography performed on acid to neutral aqueous solutions gives only 2 waves: the first corresponding to a four-electron reduction for formation of the hydroxylamine, and the second corresponding to a two-electron reduction of the hydroxylamine to the amine. As remarked earlier, nitroso will not accumulate as it is capable of being reduced at the more positive potential compared to nitrobenzene. So the peak at -0.58 V corresponds to a four-electron reduction for formation of hydroxylamine, and the peak at -1.32 V corresponds to a two-electron reduction of hydroxylamine to aniline.

Furthermore, the reduction happens prior to the reduction of water at the cathode, which indicates that nitrobenzene is capable of reducing directly at the copper electrode, and is not just reduced by the nascent state H formed after reduction of water at the cathode. This is an essential difference in reaction mechanism between the two processes. The overall reaction at the copper electrode can be expressed figuratively by the following equation:

$$C_6H_5NO_2 + 6e + 6H^+ \longrightarrow C_6H_5NH_2 + 2H_2O \qquad (9)$$
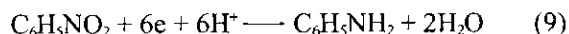
Nitrobenzene is reduced directly on the surface of copper rather than by the hydrogen produced at cathode in the catalyzed Fe-Cu process. The reduction was realized largely by the hydrogen produced at cathode in Master Builders' iron. The elimination reaction for the formation of nitroso-group (Eq. (6)) occurs easily under alkaline conditions since the structure of the nitrogen atom conjoined with both a hydroxyl and a hydrogen bond is relatively labile. In the general, the reduction of nitrobenzene by the catalyzed Fe-Cu process is due to the net effect of the following pathways:

(a) $2H_2O+2e \rightarrow 2[H]+2OH^- \rightarrow H_2+2OH^-$
$Fe+2H_2O \rightarrow Fe^{2+}+2[H]+2OH^- \longrightarrow Fe^{2+}+H_2+2OH^-$
$\cdot 6[H]+ArNO_2 \quad \cdot ArNH_2+2H_2O$
or $3H_2+ArNO_2 \rightarrow ArNH_2+2H_2O$

(b) $ArNO_2+6H^++3Fe \rightarrow ArNH_2+2H_2O+3Fe^{2+}$

(c) $ArNO_2+6e+6H^+ \rightarrow \cdot ArNH_2+2H_2O$

(d) $6Fe^{2+}+ArNO_2+6H^+ \rightarrow 6Fe^{3+}+ArNH_2+2H_2O$

2.2.2 Contribution of Fe^{2+} and Fe(OH)$_2$ to the reduction of nitrobenzene by the catalyzed Fe-Cu process

The contribution of the pathway(d) was estimated by the experiment with two aqueous solutions of 250 mg/L nitrobenzene of the same volume, one was added 1% iron(II) sulfate(w/w, %); another was added iron(II) and a certain amount(2 g) of copper powder. The reactions were conducted for 20 min under acidic conditions (pH was about 2) and stirring. The results showed that nitrobenzene did not diminish with time in the first solution, even 1 d later; in the second solution the quantity of nitrobenzene decreased slowly with time, the conversion rate of nitro-group reached 42.9% 1 d later. The results led up to the fact that the contribution of the pathway (d) was negligible throughout the whole reduction of nitrobenzene and the direct pathway(c) performed an important function in the reduction by the catalyzed Fe-Cu process.

In a review paper, Wu and Jin(1993) pointed out

that the dark green ferrous hydroxide $Fe(OH)_2$ formed by $Fe(II)$ at about pH 8.5 has a strong and selective disoxidation for nitro and nitroso groups and is able to reduce them to corresponding amines. Take the case of nitrobenzene, the reaction can be expressed figuratively as:

$$C_6H_5NO_2+6Fe(OH)_2+4H_2O$$

$$\longrightarrow C_6H_5NH_2+6Fe(OH)_3 \qquad (10)$$
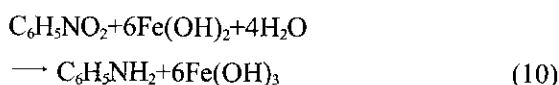
In order to study the effect of this reaction in the catalyzed Fe-Cu process, a similar experiment was conducted at about pH 8 (adjusted with NaOH). The dark green $Fe(OH)_2$ produced was able to reduce nitrobenzene in the solution in 5 min, afterwards Fe $(OH)_2$ was oxidized into brownish-yellow ferric hydroxide $Fe(OH)_3$. The reaction lasted 25 min in the presence of the copper powder. However, the conversion rate was a little higher in the latter case. The results showed that the addition of copper powder raised the utilization ratio of $Fe(OH)_2$ as a reductant while reducing the reduction rate. It is probably because the oxidation of $Fe(OH)_2$ into $Fe(OH)_3$ provided the electrons necessary to dominate in the catalyzed system direct pathway (c). In the system without catalyst copper, nitrobenzene was reduced by $Fe(OH)_2$ upon undergoing the chemical reaction represented by Eq.(10).

An additional experiment was conducted to study the influence of $Fe(II)$ usage on the treatment efficiency of nitrobenzene. It is observed from Fig.6 that the conversion rate increased along with the growth of Fe (II) usage. According to the reaction (Eq.(10)) 6 mol $Fe(OH)_2$ is required to reduce 1 mol nitrobenzene, which is to say 3340 mg/L is needed to reduce 250 mg/L nitrobenzene to aniline completely, but 2% of $FeSO_4 \cdot 7H_2O$ was consumed during the reduction. This showed that the majority of $Fe(II)$ transformed into Fe $(OH)_3$ immediately and did not take part in the reduction of nitrobenzene, although Fe $(OH)_2$ is apt to reduce nitrobenzene.

The pathways (a) and (c) made a practical contribution to the reduction of nitrobenzene in the cathode compartment. However, hydrogen is relatively difficult to evolve on the surface of copper, primarily nitrobenzene is not reduced by hydrogen because it is a less facile reductant in the system. Reducing nitrobenzene directly at the copper electrode is easier than reducing it with hydrogen, this pathway

(c) is therefore dominant in the system, and in this case copper could be regarded as electrocatalyst.

2.2.3 Contribution of hydrogen gas to the reduction of nitrobenzene by the catalyzed Fe-Cu process

An experiment was conducted to evaluate the contribution of the reduction by hydrogen gas: dried two portions of the above-mentioned iron scrap of a 100 g weight by heating. No copper was added to the first portion, while copper was added to the second portion in a certain proportion (10:1, w/w), then followed the steps described in 1.3.1. Regulated the hydrogen gas flow from a Kipp generator and purged an amount of hydrogen gas into these two solutions, then sampled 20 ml solution from each flask respectively and analyzed their compositions. The results showed that the contents of nitrobenzene in the solutions did not change in time, and they remained the same even one day later. In other words, hydrogen gas was incapable of reducing nitrobenzene without reference to the existence of copper catalyst, no other than the nascent atomic hydrogen [H] took part in the reduction pathway (a), and it lost the capacity to reduce nitrobenzene after its conversion into molecule of hydrogen.

2.2.4 Reduction of NBCs by the catalyzed Fe-Cu process

As discussed above, nitro-group is reduced directly on the surface of copper rather than by the hydrogen produced at cathode in the catalyzed Fe-Cu process, the reduction therefore depends primarily on the molecules' electron withdrawing ability.

Electronegativity is a measure of an atom's tendency to attract a bonding pair of electrons. An inductive effect is the electronic effect that occurs due only to differences in electronegativity. Conjugative effect (+C effect) (Yu, 1981) exists in conjugated systems, like inductive effect difference of electronegativity of atoms is at the bottom of uneven distribution of electron clouds and its deviation to a certain atom or atom group in a molecule. The existence of the substituent group Cl decreases the density of electron clouds of the benzene ring, especially in its p-position (Yu, 1981), the density of the electron clouds of the nitrogen and its conjoined oxygen atoms therefore decreases. Consequently, they are more electropositive than in nitrobenzene, which favors withdrawing electrons and the direct reduction. Fig.7a is the cyclic voltammigram of 50 mg/L 4-chloro-nitrobenzene in 0.1 mol/L Na_2SO_4 aqueous solution at the copper electrode. 4-Chloro-nitrobenzene gives two peaks corresponding to the irreversible electrochemical reduction at the copper electrode, one was at about -0.49 V, another one was at about -1.2 V. Nitro-group is a group with -I and -C effects (Yu, 1981), which causes transfer of electron clouds in the
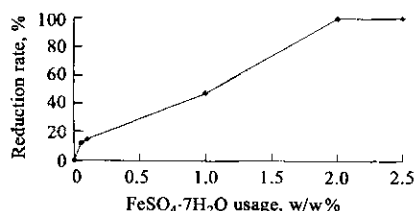

Fig.6 Influence of Fe(II) usage on the treatment of nitrobenzene

direction of substituent groups, that is why the density of π electron clouds of the benzene ring decreases. The density of electron clouds of the benzene ring decreases greatly in a molecule of *m*-dinitrobenzene. However, nitro-group is a meta-orientating group(Yu, 1981). In other words, the two nitro-groups do not have a big effect on one another, so both of them are capable of capturing electrons. Fig.7b is the cyclic voltammigram of 30 mg/L *m*-dinitrobenzene in 0.1 mol/L Na₂SO₄ aqueous solution at the copper electrode. The intermediate hydroxylamine can hardly be reduced further due to lack of hydrogen ions needed for the substitution reaction in the system, so that although alkaline condition favors the elimination reaction for the formation of nitroso-group, the second peak almost vanishes from sight. The methyl in 2,4-dinitrotoluene increases the density of electron clouds of the benzene ring(Yu, 1981), the reactivity of the nitrogen and their conjoined oxygen atoms in the 2 nitro-groups decreases; consequently, the molecule is stabilized. Fig.7c is the cyclic voltammigram of 20 mg/L 2,4-dinitrotolune in 0.1 mol/L Na₂SO₄ aqueous solution at the copper electrode. 2,4-dinitrotolune gives only one peak corresponding to the irreversible electrochemical reduction at the copper electrode,

moreover, this peak is nearly "flat", which indicates that 2,4-dinitrotolune is difficult to capture electrons and reduce directly. 2-Nitrophenol and 4-nitrophenol are weak acids (Xu, 1991), so both of them existed in the state of phenoxy ions in the solutions in the alkaline medium. The negative charges are more scattered when the nitro-group is in *p*-position of hydroxyl (Xu, 1991). This favors capturing electronegative electrons, which is essential to direct reduction. 4-Nitrophenol is therefore reduced faster than 2-nitrophenol. Fig.7d is the cyclic voltammigram of 125 mg/L 2-nitrophenol in 0.1 mol/L Na₂SO₄ aqueous solution at the copper electrode. Like nitrobenzene, 2-nitrophenol gives two peaks corresponding to the irreversible electrochemical reduction at the copper electrode, but the first peak corresponding to the formation of hydroxylamine is nearly "flat". Under the alkaline conditions the first reduction peak in Fig.7e can be seen clearly, that is to say 4-nitrophenol is easier to reduce. There is no group in the molecule of nitrobenzene that hinders the direct reduction of nitro-group in space. This may be why nitrobenzene is easier than other NBCs to reduce in the catalyzed Fe-Cu process.
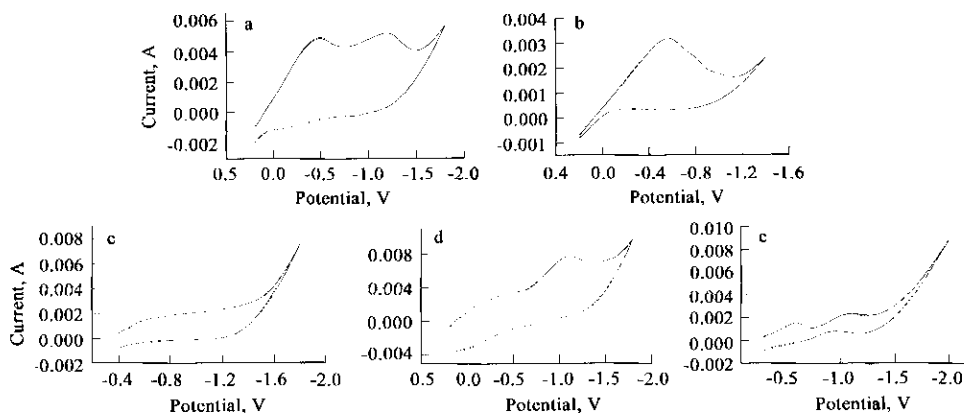

Fig.7 Cyclic voltammograms of different NBCs in 0.1 mol/L Na₂SO₄ aqueous solution under the alkaline conditions(pH -11)
a. 50 mg/L 4-chloro-nitrobenzene; b. 30 mg/L *m*-dinitrobenzene; c. 20 mg/L 2,4-dinitrotolune; d. 125 mg/L 2-nitrophenol; e. 300 mg/L 4-nitrophenol; experimental conditions: ph–11, scanning rate=4 V/s

3 Conclusions

In an alkaline medium (pH=11) NBCs were reduced directly on the surface of copper rather than by the hydrogen produced at the cathode in the catalyzed Fe-Cu process. The reduction was realized by the hydrogen produced at the cathode and Fe(OH)₂ in Master Builder's iron. The reduction rate by Master Builder's iron drops in the following order: *m*-dinitrobenzene ≥4-chloro-nitrobenzene >4-nitrophenol >2,4-dinitrotoluene ≈nitrobenzene >2-nitrophenol. The catalyzed Fe-Cu process was noticeably superior to Master Builder's iron in treating NBCs contaminated water under alkaline conditions.

Accordingly, this process can be used to treat alkaline NBCs wastewater. Moreover, it will not give rise to a hydrogen ion shortage as seen in Master Builders' iron and further slowing up the reduction with time. Thus one of the weak points of the latter is eliminated. The catalyzed Fe-Cu process is much better suited for treating nitro-benzene, 4-chloro-nitrobenzene and *m*-dinitrobenzene contaminated water. The majority of Fe(II) transformed into Fe(OH)₃ immediately and did not take part in the reduction of nitrobenzene, although Fe(OH)₂ is apt to reduce nitrobenzene.

In the catalyzed Fe-Cu process the nitro-group in NBCs captures electrons and is reduced directly at the copper electrode. Besides the influence of charge

distribution, the reduction depends on the sterically hindered effect of substituent groups. Accordingly, the degradation efficiency decreases in the following order:nitrobenzene > 4-chloro-nitrobenzene $\geq m$-dinitrobenzene >4-nitrophenol $\geq$ 2,4-dinitrotoluene > 2-nitrophenol.

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