Reduction of nitrobenzene by the catalyzed Fe–Cu process

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Abstract

The electrochemical reduction characteristics of nitrobenzene were investigated using cyclic voltammetry. In addition, the difference in reduction mechanisms between Master Builders' iron and the catalyzed Fe–Cu process was discussed in this paper. The results showed that nitrobenzene was reduced directly on the surface of copper rather than by the hydrogen evolved at cathode in the catalyzed Fe–Cu process. The reduction was realized largely by the hydrogen evolved at cathode in Master Builders' iron. Both acidity and basicity favored the direct reduction at the copper electrode. The catalyzed Fe–Cu process was superior to Master Builders' iron in treating nitrobenzene-containing water, withal. This advantage was particular noticeable under alkaline conditions. The reduction was investigated in the cathode and anode compartments, respectively, and the experimental results showed that the direct pathway had a large role in the reduction by the catalyzed Fe–Cu process. To reduce nitrobenzene directly at the copper electrode is easier than to reduce it by the hydrogen evolved at cathode, copper could be regarded as the electrocatalyst in this case. The influence of copper usage on the treatment efficiency by the catalyzed Fe–Cu process was also studied. The results indicated copper increased the reduction rate. The catalyzed Fe–Cu process is of practical value.
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Keywords: Nitrobenzene; The catalyzed Fe–Cu process; Electrochemical reduction characteristics; Reduction mechanism; Electrocatalyst

1. 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. [1]. It also may be formed in the environment from aromatic contaminants, as is the case with nitro-PAHs and nitrophenols found in atmospheric water [2]. The remediation of nitrobenzene is of interest because it is among the most characteristic of anthropogenic contaminants, being second in this regard only to organochlorine functional groups [3]. 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 [4–10], which scientists of the world over 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.

Under reducing conditions, nitrobenzene may react by a variety of pathways. Most of these reactions have been studied in great detail either as preparative methods in synthetic chemistry or as model reactions for electrochemical investigations [3,11,12]. In almost all cases the major process is reduction of the nitro functional group to the corresponding amine. Formally, this process consists of a series of two-electron additions, proceeding through nitroso and hydroxylamino intermediates. In general the dominant reaction pathway under anaerobic environmental conditions appears to be nitro reduction to the amine. There is however the evidence of coupling of the nitro reduction intermediates

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to form azo and azoxy compounds, and reactive cleavage of azo compounds to form amines [3].

The earliest detailed surveys involving degradation of halocarbons by zero-valent iron in laboratory batch systems [13,14] raised speculations that the dechlorination occurs through a surface reaction. There is enough evidence to suggest that adsorption of halogenated organic compounds to the Fe^0 surface does indeed occur [15–18]. For heterogeneous reactions to take place it is required that the reactant molecules reach the solid surface; they then combine with either "reactive" or "non-reactive" surface sites. According to Burris et al. [17] reactive sites are those where the breaking of bonds in the reactant molecule takes place, while on non-reactive sites only sorption interactions occur and the solute molecule remains intact. Burris et al. also speculated that the bulk of sorption was to the non-reactive sites. The role of surface bond Fe^{2+} has been studied, and it was found that Fe^{2+} adsorbed on the surface might play a role in the reduction of nitroaromatics. Agrawal and Tratnyek [3] studied the reduction of nitrobenzene by iron under anaerobic conditions in bicarbonate-buffered batch systems. They found that the nitrobenzene reduction rate increased linearly with the available iron surface area, and the effect of solution pH was minimal on the conversion. Mass transfer to the metal surface seemed to be the rate-controlling step in the zero-valent iron reduction of nitroaromatic compounds.

Bimetallic particles are extremely interesting in accelerating the decholorination of chlorinated organics [19]. Four noble metals (Pt, Pt, Ru and Au), separately deposited onto the iron surface through a spontaneous redox process, promoted the trichloroethylene (TCE) dechlorination rate, and the catalytic activity of the noble metal followed the order of $Pd \gg Ru > Pt > Au$. This order was found to be dependent on the concentrations of absorbed atomic hydrogen, indicating that the initial reaction was cathodically controlled. Perchloroehylene (PCE) dechlorination in the presence of nickel-plated iron, acid treated iron, and untreated iron surfaces displayed pseudo first-order kinetics [20]. The highest degradation rate of PCE occurred on the nickel-plated iron surface, followed by the acid treated iron, and the untreated iron. The degradation process is generally accepted to be electrochemical in nature including a simple dechlorination process, with Fe^0 serving as the source of electrons where oxidation of the iron and reductive chlorination of the organic compounds take place [21].

The surface normalized reaction rate constants (K_{sa}) of trichloroethylene (TCE) and zero-valent iron (ZVI) were quantified in batch reactors at pH values between 1.7 and 10. The optimal TCE degradation rate was achieved at a pH of 4.9 [22]. This suggests that lowering solution pH might not expedite the degradation rate of TCE by ZVI as it also caused faster deisappearance of ZVI, and hence decreased the ZVI surface concentration.

Noble metal catalysts such as palladium had satisfactory results in reducing nitrobenzene in the laboratory, are too costly for waste treatment [23]; moreover, in certain instances, the catalysts dissolve in the presence of nitroaromatic explosives [24], so they cannot be put into the practice of wastewater treatment. The reduction by Fe^0 usually requires a mass of acid to adjust pH of wastewater to 2–3. Copper was used as a catalyst to remediate nitrobenzene-containing water in this paper. Copper is cheap relative to palladium, and it has a relatively high hydrogen overpotential (i.e. hydrogen is relatively difficult to evolve on its surface) [25], so the reduction of nitrobenzene at the copper electrode is achieved rather through the direct pathway than through the hydrogen evolved at cathode.

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

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \tag{1}$$

has a standard reduction potential of -0.441 V [26]. 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+}

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \tag{2}$$

has a standard reduction potential of $+0.345$ V [26]. Carbon 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. [27] treated nitro-benzene containing water with zero-valent iron powder, Master Builder's iron and the catalyzed Fe–Cu process. The experiments indicated these three 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 ~20% higher than by Master Builders' iron, under the slight alkaline conditions (pH ~ 9.5) the former was found ~40% higher than the latter. Additionally, the reduction efficiency was comparable with that obtained under the strongly acidic conditions. The electrochemical reduction characteristics of the nitro-benzene compounds were investigated using cyclic voltammetry technique [28], and the direct reduction pathway at the copper electrode was proposed in the paper.

The reduction mechanism by the catalyzed Fe–Cu process was discussed in this paper using cyclic voltammetry, and the role of copper in this process was also investigated. The difference in reduction mechanisms between the Fe–Cu bimetallic process and Master Builders' iron was put forward. The practicality of the technology was also discussed.

2. Experimental

2.1. 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 offered for sale in the market, and was cut into thin pieces sized $5\,cm \times 1\,cm$ before the experiments. Water for the batch experiments was prepared using the ordinary distilled water. The electrolyte for cyclic voltammetry scanning was prepared with the highly purified water twice distillated in the lab, anhydrous sodium sulfate (0.1 M) was used as the supporting electrolyte; water for investigating the role of copper in the reduction was prepared using the ordinary distilled water, anhydrous sodium sulfate (0.5 M) 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 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 and $1.44\,cm^2$, respectively, were used as working electrodes. A Pt electrode served as an auxiliary electrode and a saturated calomel electrode (S.C.E) of model 232 manufactured by Shanghai Analytical Instrument Factory was used as a reference electrode. Cyclic voltammetry scanning was conducted using CHI600A electrochemical station made in the Shanghai Chenhua Instrument Company, as was the stochastic software was applied to collecting data and plotting the cyclic voltammograms. Electrolysis was conducted using the Rex potentiostat of model DJS - 292 made in Shanghai Rex Instrument Co. Ltd. and the stabilized current supply of model LW3J3 (30 V, 3 A) made in Shanghia Liyou Electric Company. The digital conductivity detector of model DDS-11C made in Shanghai Tianda Instrument Co. Ltd. was applied to measuring electric conductance. The portable pH/ISE meter of model sensION2 made in HACH COMPANY was applied to measuring solutions pH.

2.2. Experimental methods

2.2.1. Batch experiments

Dried the above-mentioned iron scrap of a 100 g weight by heating, mixed it and the copper pieces evenly in a certain proportion (10:1, w/w) and held them down so that the observed density reached ~0.5 kg/l. Then put these two fillings in 500 ml wide neck ground-glass stoppered flasks, poured 300 ml the prepared 250 mg/l nitrobenzene-containing solution to be treated 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 made the flasks with the solutions possible to shake with the frequency of 140 rpm for a certain time (10, 20, 30, 40, and 60 min), then took out
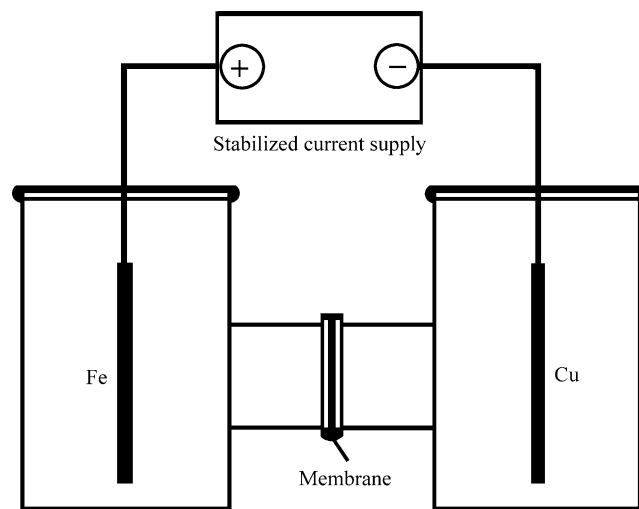

Fig. 1. Electrolytic cell for investigating the role of copper in the reduction by the catalyzed Fe–Cu process.

~50 ml sampling water from each flask, respectively, using a closer 10-ml injector and analyzed their compositions.

2.2.2. Electrolysis

Electrolysis for determining the reactions corresponding to the reduction waves at the copper cathode was conducted in a non-diaphragm electrolytic cell; electrolysis for investigating the role of copper in the reduction by the catalyzed Fe–Cu process was conducted in an electrolytic cell separated into two compartments by a permeable cellulose acetate membrane (Fig. 1). Each compartment is of size $5\,cm \times 5\,cm \times 10\,cm$. In the latter case, electrode processes were investigated in the anode compartment and cathode compartment, respectively. As shown in Fig. 1, an iron piece sized $9\,cm \times 3.5\,cm$ was used as anode, and a copper piece sized $9\,cm \times 3.5\,cm$ was used as cathode.

Electrolyzed the nitrobenzene-containing solution with 1200 mg/l for investigating the role of copper in the reduction by the catalyzed Fe–Cu process having the current under control at 0.5 A for a certain time, then took out some anolyte and catholyte, respectively, measured their pH and conductance and analyzed their compositions with GC/MS.

2.2.3. Cyclic voltammetry scanning

Twenty millilitres of 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 ~2 h and acetone for ~2 h separately to clean its surface.

2.2.4. Analytical methods

Finnigan Voyager gas chromatographic and mass spectrographic instruments were applied to analyzing compositions

of organic compounds in the water after the treatment. Ten milliliters water was extracted with 1 ml dichloromethane of analytical (AR) grade before injecting onto 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 °C and the column temperature started at 50 °C for 2 min, was ramped to 250 °C at a rate of 20 °C/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% phenylpolydimethylsiloxane is 0.25 μm) was used in the analytical process. Dodecane was used as the internal standard (IST) while determining the concentration of the nitrobenzene-containing aqueous solutions after the treatment by the catalyzed Fe–Cu process. The conversion rate of nitrobenzene was calculated via Eq. (3).

$$Y(C_6H_5NO_2) = \frac{C_0 - C}{C_0} \times 100\% \tag{3}$$

where Y (%) is the conversion rate of nitrobenzene, C_0: the initial concentration of the nitrobenzene-containing aqueous solution. C: the concentration of the nitrobenzene-containing aqueous solution treated for a certain time by the catalyzed Fe–Cu process.

3. Results and discussion

3.1. The cyclic voltammograms of nitrobenzene at the graphite and the copper electrodes

Fig. 2 represents the cyclic voltammetric response obtained in 100 mg/l nitrobenzene in 0.1 M Na$_2$SO$_4$ aqueous solution for: (a) the graphite and (b) the copper electrodes at a scan rate of 4 V/s.

It is observed from the Fig. 2a that no response can be found at the graphite electrode, that is nitrobenzene is not capable of being reduced directly at the graphite electrode. No other than hydrogen evolution wave is shown at the graphite electrode, so, the nitro-group is mainly reduced by the hydrogen evolved at cathode.
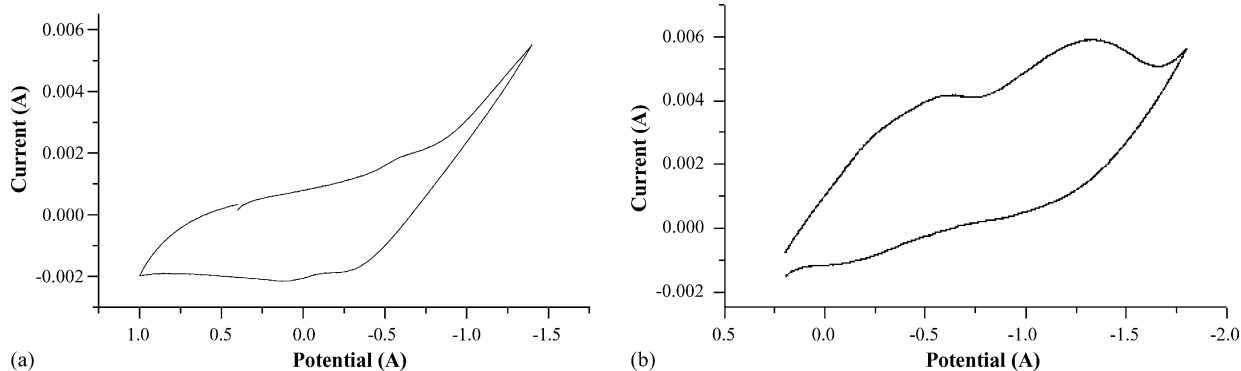
Cast iron is an alloy of pure iron, carbon and some other impurities. Carbon and impurities are dispersed evenly as very small granules in cast iron. Numerous corrosion cells are formed when the cast iron is immerged in an electrolyte solution. In this case pure iron comes as anode, and carbon comes as cathode [29].

The half reaction at the iron anode can be represented by Eq. (1).

$$\text{Cathode} \quad 2H^+ + 2e \rightarrow 2H \rightarrow H_2 \tag{4}$$
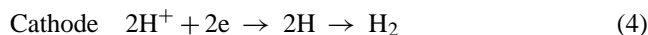
in a neutral or acidic medium the nascent state H produced after electrode reactions take place and Fe^{2+} are enabled to reduce many components in the wastewater. For many metals the nexus between hydrogen evolution overpotential η and current density j can be expressed via Tafel's equation [21]:

$$\eta = a + b \log j \tag{5}$$

where a, b are the constants that are determined by experimental means. Cast iron has a rough surface, and its great true surface area is nearly the equivalent of reducing current density j. According to Eq. (5), hydrogen evolution overpotential η inevitably falls, when current j density drops. Meanwhile, the growth of the surface also enhances the probability of hydrogen evolution [21]. Nitrobenzene is reduced indirectly at the cathode in Master Builder's iron and more specifically it is reduced by the hydrogen evolved at cathode in a great measure. Acidity of the solution therefore, favors the reduction considerably. The results of the experiment shown in Fig. 2b are in accordance with the theoretical mechanism.

Nitrobenzene gives two reduction peaks corresponding to the irreversible electrochemical reduction at the copper electrode (Fig. 2b), one was at −0.58 V, another one was at −1.32 V. In order to determine the reactions corresponding to the reduction waves at the copper cathode, electrolysis was conducted for $t \sim 16$ h having the cathodic potential under control at −1.32 V (versus S.C.E) 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, which spelled reduction of the intermediate product to aniline at −1.32 V or thereabout at the copper electrode.

Fig. 2. Cyclic voltammograms of 100 mg/l nitrobenzene in 0.1 M Na$_2$SO$_4$ aqueous solution: (a) at the graphite electrode and (b) at the Cu electrode.

As remarked, the reduction process proceeds through nitroso and hydroxylamino intermediates (Eqs. (6)–(8)), when nitrobenzene is reduced to aniline at electrodes [5,30,31].

Elimination reaction

$$ArNO_2 + 2e + 2H^+ \rightarrow ArNO + H_2O \qquad (6)$$

Addition reaction

$$ArNO + 2e + 2H^+ \rightarrow ArNHOH \qquad (7)$$

Substitution reaction

$$ArNHOH + 2e + 2H^+ \rightarrow ArNH_2 + H_2O \qquad (8)$$

The reduction potentials for reactions (6) and (7) are very similar, so polarography performed on acid to neutral aqueous solutions gives only two 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. Nitroso will not accumulate as it is capable of being reduced at the more positive potential compared to nitrobenzene [3]. 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.

Formally, the overall reaction can be written as:

$$ArNO_2 + 6e + 6H^+ \rightarrow ArNH_2 + 2H_2O \qquad (9)$$

On the evidence of the experimental data shown in Fig. 2b, hydroxylamine corresponds to the more negative reduction potential than nitrobenzene, in other words it is harder to reduce directly at the copper electrode than nitrobenzene.

3.2. The influence of pH on the reduction mechanisms of nitrobenzene at the copper electrode

Fig. 3 shows the voltammograms for the reduction of nitrobenzene in 0.1 M Na$_2$SO$_4$ aqueous solution at the copper electrode under: (a) acidic (pH $\sim$ 3.0) and (b) alkaline (pH $\sim$ 9.0) conditions.

In the process of the cathodic scanning, the nitrogen atom in the nitro-group obtains one electron at first. Then this electron transfers to the oxygen atom due to its electron-withdrawing effect. After that, the nitrogen atom obtains a new electron. As a consequence both the nitrogen and oxygen atoms in the nitro-group possess an unshared electron pair and are ready to obtain proton(s) [32]. The probability of the association reaction between the obtained electrons nitro-groups and hydrogen ions grows in the acidic medium, which causes magnification of the current through the solution (Fig. 3a). The increase in number of hydrogen ions favors the addition and substitution reactions at the electrode. Two reduction peaks shown in Fig. 2b overlapped partly because of the fast electrode reaction rate; diffusion to the electrode surface tends to be the rate-controlling step in this case. The elimination reaction for the formation of nitroso-group (Eq. (6)) is easy to occur under alkaline conditions since the structure of the nitrogen atom that is closely associated with a hydroxyl and a hydrogen bond simultaneously is relatively labile. The current through the solution rises when nitroso-groups increase in number. Accordingly, the current corresponding to the peaks rises obviously (Fig. 3b).

The experimental results of our research team also showed that the catalyzed Fe–Cu process was superior to Master Builders' iron in treating nitrobenzene-containing water. This advantage was particular noticeable under alkaline conditions. This phenomenon was basically caused by the difference in reduction mechanisms between these two technologies (Fig. 4). pH of alkaline nitrobenzene-containing 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 $\sim$ 9.5). Moreover, it will not give rise to a hydrogen ion shortage like in Master Builders' iron and further slowing up the reduction and in this way one of the weak points of the latter is covered.

3.3. The role of Cu in the reduction by the catalyzed Fe–Cu process

As remarked earlier, electrolysis of an aqueous solution of nitrobenzene with 1200 mg/l was carried out in the diaphragm electrolytic cell to determine the role of copper in the reduc-
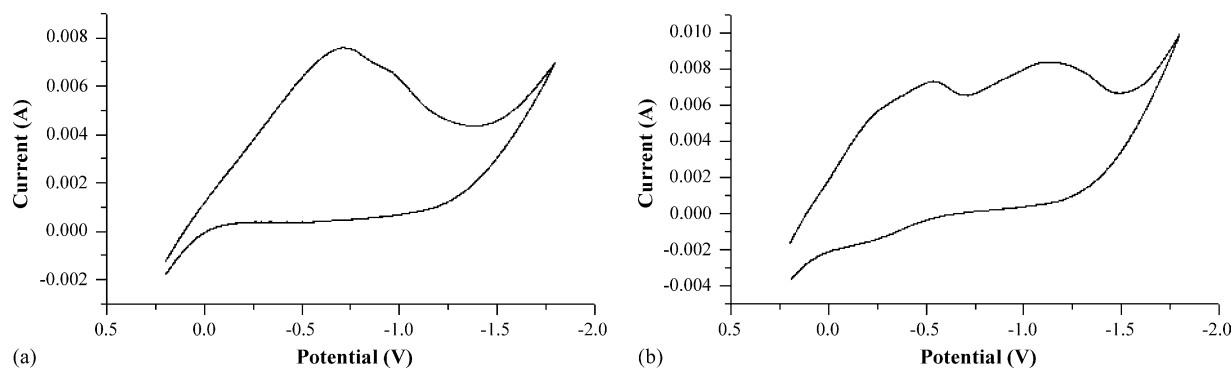

Fig. 3. Cyclic voltammograms of 100 mg/l nitrobenzene in 0.1 M Na$_2$SO$_4$ aqueous solution at the copper electrode at acidic and alkaline pH: (a) pH of the solution was adjusted to 3.0 and (b) pH of the solution was adjusted to 9.0.
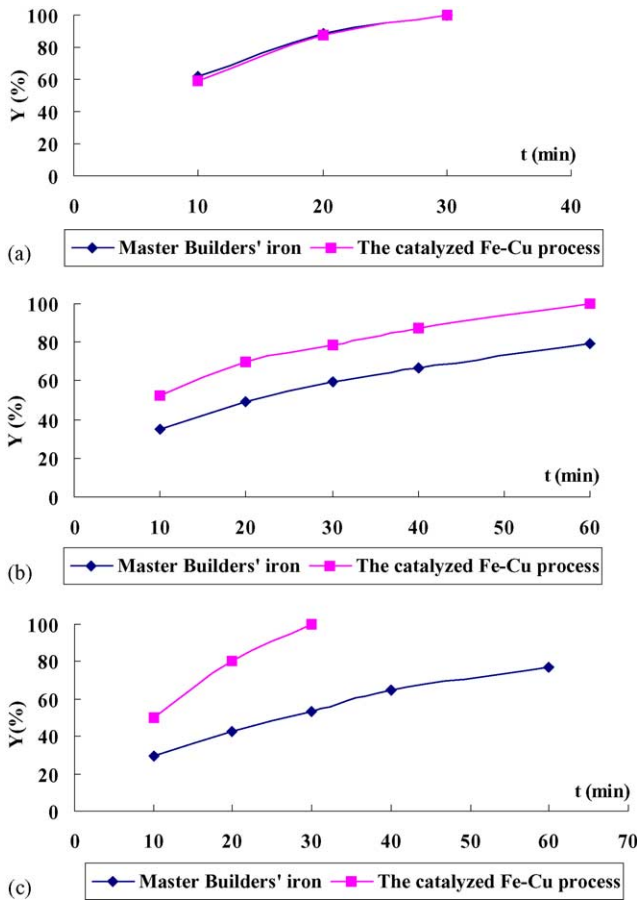
(a)

(b)

(c)

Fig. 4. The parallels of the treatment effect between the catalyzed Fe–Cu process and Master Builders' iron. The initial concentration of the nitrobenzene-containing aqueous solution ≈ 250 mg/l. (a) The pH of the water to be treated was adjusted to 3.0; (b) pH of the water to be treated equaled to 7.5; and (c) pH of the water to be treated was adjusted to 9.5.

tion by the catalyzed Fe–Cu process. The experimental results are shown in Tables 1 and 2 and Figs. 5 and 6.

As shown in Table 1, conductance and pH changed with time because of dissolution of iron in the anode compartment and reduction of nitrobenzene and water. The conductance moved up because of oxidation and dissolution of iron and reduction of water at first, then dropped on account of formation of black magnetic ferroferric oxide Fe_3O_4 in the anode compartment. In the cathode compartment the conduc-

Table 1

The change of conductance and pH of the catholyte with time (electrolytic current $I = 0.5$ A, cathode area $S = 31.5$ cm^2)

Time of electrolysis (h)	Conductance (ms)	pH
1	27.7	12.5
1.5	34.5	12.7
2	42.6	12.8
2.5	47.3	12.9
3	46.6	13.0
3.5	44.8	13.0
4	45.2	13.0
4.5	45.8	13.1

Table 2

The change of conductance and pH of anolyte with time (electrolytic current $I = 0.5$ A, anode area $S = 31.5$ cm^2)

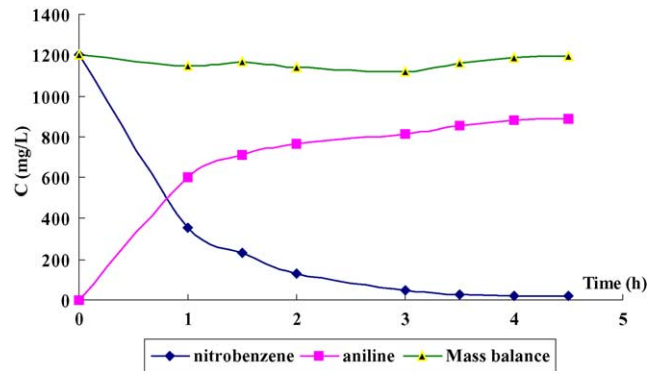| Time of electrolysis (h)	Conductance (ms)	pH
1	26	2.3
1.5	32.6	2.4
2	38.3	2.5
2.5	42.6	2.8
3	35.6	3.0
3.5	28.6	3.3
4	23.7	3.5
4.5	18.8	6.3

Fig. 5. Concentration vs. time plot showing conversion of nitrobenzene and production of aniline in the cathode compartment with time. The initial concentration of the nitrobenzene-containing aqueous solution ≈ 1200 mg/l.

tance changed because of the direct reduction and hydrogen evolution. On the evidence of the experimental data shown in Figs. 5 and 6, nitrobenzene was reduced much faster in the cathode compartment, which means that the direct pathway played a major part in the reduction by the catalyzed Fe–Cu process. In the cathode compartment the total nitrogen hardly changed in the process of electrolysis (Fig. 5), 70.53% nitrobenzene was reduced to aniline after the 1 h electrolysis, and 98.27% nitrobenzene was reduced to aniline after 4.5 h electrolysis.
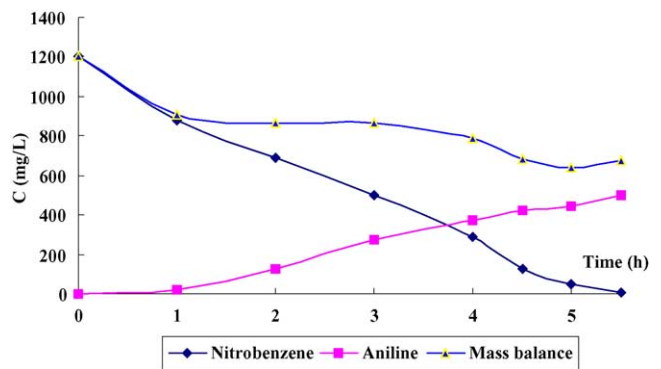

Fig. 6. Concentration vs. time plot showing conversion of nitrobenzene and production of aniline in the anode compartment with time. The initial concentration of the nitrobenzene-containing aqueous solution ≈ 1200 mg/l.

The reduction rate slowed along with time in the cathode compartment because, as remarked earlier (Fig. 2b), the reduction peaks of the intermediate products moved in the more negative direction. In other words, they became harder to reduce. The conversion rate of nitrobenzene reached more than 70% in the first hour of electrolysis, 18.55% nitrobenzene was reduced to aniline in the second hour of electrolysis, 7% nitrobenzene was reduced to aniline in the third hour, and merely 2.2% nitrobenzene was reduced to aniline in the last $1\frac{1}{2}$ h.

The reduction of nitrobenzene by Fe^0 is a heterogeneous process involving the oxidation and dissolution of iron in conjunction with the reduction of nitrobenzene under acidic conditions [2].

$$ArNO_2 + 6H^+ + 3Fe \rightarrow ArNH_2 + 2H_2O + 3Fe^{2+} \quad (10)$$

It appeared that the reaction (10) played an important role in the anode compartment because the anolyte was strongly acidic (pH $\sim$ 2.3). Nevertheless the results obtained differed in various stages. The concentration of nitrobenzene decreased by a margin in the first hour of electrolysis, during this time a very small amount of aniline came into existence in the anode compartment; the conversion rate of nitrobenzene dropped successively in the first 3 h with the producing rate of aniline increasing simultaneously. After the 3 h electrolysis the conversion rate of nitrobenzene went up a little, 1 h thereafter the conversion rate started slowing, perhaps it was because adsorption of nitrobenzene to the iron surface had played an important role in the beginning of the electrolysis. In the first hour of electrolysis only a small amount of aniline (22.61 mg/l) was produced in the anode compartment. In the second hour of electrolysis the producing rate of aniline increased, however, the amount of the aniline produced in the anode compartment still remained far less than that should be produced, if the nitrobenzene converted was reduced completely, that is to say most of nitrobenzene converted was not reduced to aniline immediately but adsorbed to the surface of the iron electrode. After the surface of the iron electrode adsorbed sufficient nitrobenzene molecules, the reduction rate started increasing. Afterwards the reduction rate slowed with time, because the reduction products became harder to reduce. The reduction of water occurred at the copper electrode and must be regarded as well in the cathodic reduction.

On the evidence of the experimental data shown in Figs. 5 and 6, we found the producing rate of aniline in the cathode compartment much greater than in the anode compartment Additionally, the total nitrogen cut down in the anode compartment during the electrolysis; it meant that a percentage of nitrobenzene may not be desorbed by the surface of the iron electrode during the electrolysis.

In the general, the reduction of nitrobenzene by the catalyzed Fe–Cu process owes to the net effect of the following pathways:

(a) $2H_2O + 2e \rightarrow H_2 + 2OH^-$,
$Fe + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$
$3H_2 + ArNO_2 \rightarrow ArNH_2 + 2H_2O$

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

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

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

From what is mentioned above we have reached a conclusion that the contribution of the pathway (b) to the reduction of nitrobenzene was inconsiderable in the first hours of electrolysis in the anode compartment, adsorption to the iron surface seemed to play a big part in the reduction rate controlling in the beginning. In the latter hours the contribution of the pathway (b) grew in strength, after the 4 h electrolysis, the reduction rate began to slow with time. As an amount of hydrogen ions was required to reduce nitrobenzene in the system, pH rose along with the time (Table 2). The pH rose gently at first, because the reduction rate was not high in the beginning. However, along with the raise of the reduction rate, pH went up by a margin (2.3–6.3).

An experiment was conducted to estimate the contribution of the pathway (d) to the reduction: measured two aqueous solutions of 250 mg/l nitrobenzene of the same volume, then added 1% iron (II) sulfate (w/w, %) to these 2 solutions, in addition to 1% iron (II) sulfate added a certain amount of copper powder (2 g) to the second solution. The reactions were conducted for a certain time ($t \sim 20$ min) under the acidic conditions (pH $\sim$ 2) and stirring. The experimental results showed that the percentage of nitrobenzene did not diminish with time in the first solution, and it did not change even 1 day later; in the second solution the quantity of nitrobenzene decreased slowly with time, the conversion rate of nitro-group reached 42.9% 1 day 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 played a big part in the reduction by the catalyzed Fe–Cu process.

In a review paper, Wu and Jin [33] pointed out that the dark green ferrous hydroxide $Fe(OH)_2$ formed by Fe (II) at pH $\sim$ 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:

$$C_6H_5NO_2 + 6Fe(OH)_2 + 4H_2O \rightarrow C_6H_5NH_2 + 6Fe(OH)_3$$

$$(11)$$
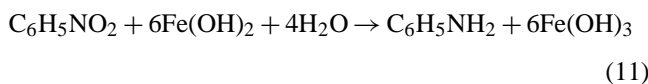
In order to study the effect of this reaction in the catalyzed Fe–Cu process, a similar to above experiment was conducted at pH $\sim$ 8 (pH was adjusted with NaOH). The dark green $Fe(OH)_2$ produced was able to reduce nitrobenzene in the solution in 5 min, afterwards $Fe(OH)_2$ was oxidized into brownish-yellow ferric hydroxide $Fe(OH)_3$. The reaction lasted 25 min, when the copper powder existed in the system. However, the conversion rate was a little higher in
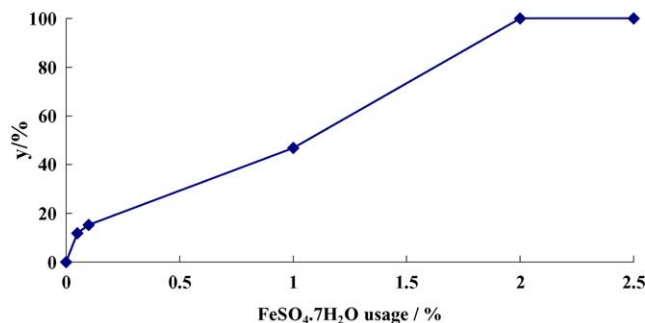
Fig. 7. The influence of Fe (II) usage on the treatment of nitrobenzene.

the latter case. The results showed that the addition of copper powder raised the utilization ratio of Fe(OH)$_2$ as a reductant with reducing the reduction rate.

An additional experiment was conducted to study the influence of Fe (II) usage on the treatment efficiency of nitrobenzene. It is observed from Fig. 7 that the conversion rate increased along with the growth of Fe (II) usage. According to the reaction (Eq. (11)) 6 mol of 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$_4$·7H$_2$O was consumed during the reduction. This showed 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. To reduce nitrobenzene directly at the copper electrode is easier than to reduce it with hydrogen, the pathway (c) therefore dominated in the system, and in this case copper could be regarded as electrocatalyst.

The influence of copper usage on the reduction by the catalyzed Fe–Cu process was also investigated in this paper: mixed the iron scrap of 100 g with the copper pieces evenly in different proportions (10:1, 6:1, 5:1, 4:1, w/w), then carried out the experiments according to the procedures stated in Section 2.2.1. From the experimental data shown in Fig. 8 it can be seen clearly that copper usage has great influence with the treatment efficiency, specifically, the latter increased along with the growth of copper usage. Copper increased the reduction rate.

On the whole, the water responded well to the reduction, when pH varied from acidic to slight alkaline. In other words the catalyzed Fe–Cu process is able to extend Master Builders' iron to a wider scope of application. A need of aeration is eliminated in this process; accordingly, spending in energy consumption will be reduced. Copper is not plated on the iron by exposing the iron to a solution of Cu^{2+}, the process therefore is simplified; in addition, the reduction is
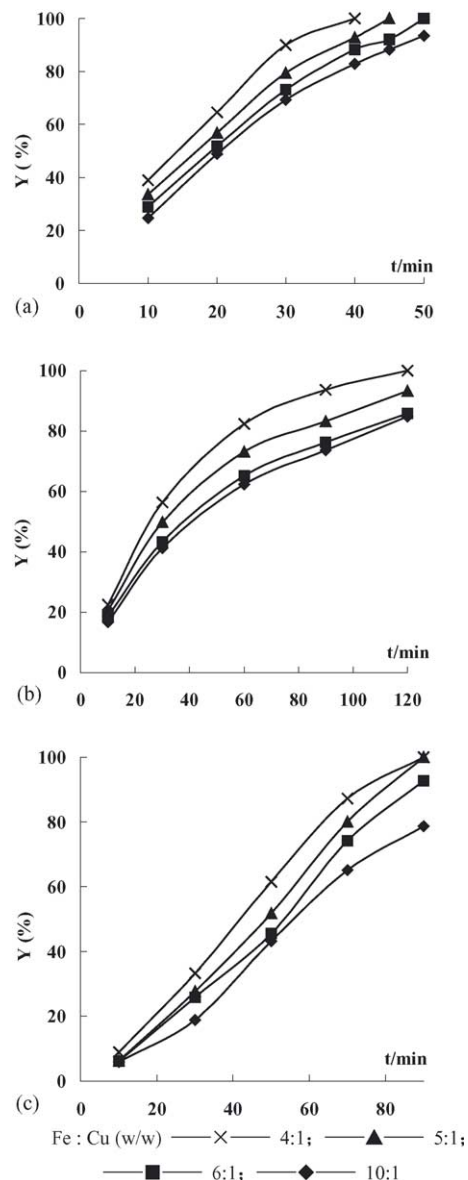

Fig. 8. The influence of copper usage on the reduction by the catalyzed Fe–Cu process. The initial concentration of the nitrobenzene-containing aqueous solution ≈500 mg/l. (a) The pH of the water to be treated was adjusted to 2.0; (b) pH of the water to be treated equaled to 7.5; and (c) pH of the water to be treated was adjusted to 10.0.

cost-effective. With all these advantages the catalyzed Fe–Cu process can be considered as of vital importance.

4. Conclusions

In this study the difference in reduction mechanisms between Master Builders' iron and the catalyzed Fe–Cu process was put forward after studying the electro-reductive characteristics of nitrobenzene at the copper and graphite (carbon) electrodes. In the catalyzed Fe–Cu process nitrobenzene is reduced directly on the copper surface rather than

by the hydrogen evolved at cathode like in Master Builders' iron. Both acidity and basicity favor the direct reduction at the copper electrode. The catalyzed Fe–Cu process was superior to Master Builders' iron in treating nitrobenzene-containing water, this advantage was particular noticeable under alkaline conditions, accordingly, this process can be used to treat alkaline 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, in this way one of the weak points of the latter is covered. The direct pathway played a leading role in the reduction by the catalyzed Fe–Cu process. To reduce nitrobenzene directly at the copper electrode is easier than to reduce it by the hydrogen evolved at cathode because hydrogen is a less facile reductant. The direct reduction occurred prior to hydrogen evolution at the copper electrode. Copper could be regarded as an electrocatalyst in the reduction by the catalyzed Fe–Cu process. The reduction rate of nitrobenzene slowed along with time in the cathode compartment because the reduction products became harder to reduce. After the surface of the iron electrode adsorbed sufficient nitrobenzene molecules in the anode compartment, the reduction rate increased. Afterwards the reduction rate started slowing again with time. The electro-catalyst copper increased the reduction rate. The catalyzed Fe–Cu process is of practical value.

Acknowledgments

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