



Reduction of nitrobenzene by the catalyzed Fe/Cu process

XU Wenyong*, LI Ping, FAN Jinhong

The National Engineering Research Center for Urban Pollution Control, Tongji University, Shanghai 200092, China. E-mail: inna_xu@hotmail.com

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Abstract

The polarization behavior of the couple Fe/Cu in 100 mg/L nitrobenzene aqueous solution was studied using Evans coupling diagrams. The results indicated that the iron corrosion was limited by both anodic and cathodic half-cell reactions under the neutral conditions, and cathodically controlled under the alkaline conditions. Batch experiments were performed to study the effect of solution pH, reaction duration, concentration, type of electrolyte, and dissolved oxygen (DO) on the reduction of nitrobenzene by the catalyzed Fe/Cu process. This process proved effective in the pH range of 3 to 11. The conversion efficiency of nitrobenzene at pH around 10.1 was almost the same as that under highly acid conditions (pH around 3). The degradation of nitrobenzene fell into two phases: adsorption and surface reduction, and the influence of adsorption and mass transfer became more extensive with solution concentration. The reduction rate decreased in the presence of DO in the solution, indicating that a need for aeration was eliminated in the catalyzed Fe/Cu process. Accordingly, spending on energy consumption would be reduced. Economic analysis indicated that merely 0.05 kg was required for the treatment of a ton of nitrobenzene-containing water with pH from 3 to 11. The catalyzed Fe/Cu process is cost-effective and of practical value.

Key words: nitrobenzene; Evans coupling diagram; reduction mechanisms; influencing factors

Introduction

The concentration of nitrobenzene in wastewater must not exceed a limit of 5 mg/L in China (Wu, 1998). The heightened awareness of nitrobenzene toxicity has prompted considerable research efforts toward developing new methods for removing it from groundwater.

Zero-valent iron is commonly used as a reactive medium to remove nitrobenzene from contaminated groundwater. Iron serves as a reducing agent to transform nitrobenzene compounds to their aniline analogues. Nitrobenzene reduction may occur via direct electron transfer from the iron or via indirect electron transfer from the atomic hydrogen produced from water reduction (Wang and Farrell, 2003). Agrawal and Tratnyek (1996) 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-limiting step in the zero-valent iron reduction of nitroaromatic compounds. The deviation from a completely mass transport limited behavior suggested that the reaction kinetics of nitrobenzene at the iron rotating disk electrode was influenced by both surface reaction and mass transport (Scherer *et al.*, 2001).

The zero-valent iron reduction requires anaerobic con-

ditions, and to achieve this, earlier researchers degassed the solution prior to iron reduction. Anaerobic conditions were necessary to achieve the complete reduction of nitrobenzene to aniline. Under aerobic conditions, 100% conversion of nitrobenzene was never achieved in preliminary work from the lab (Mantha *et al.*, 2001). Carbon tetrachloride was abiotically dechlorinated to chloroform and methylene chloride by zero-valent iron (Helland *et al.*, 1995). Dechlorination of CCl_4 was rapid, it also occurred under oxic conditions, although the rate was significantly slower.

Several shortcomings, including the accumulation of reduction by-products and the decrease in the activity of iron over time, have been noted (Orth and Gillham, 1996; Cheng and Wu, 2000; Jörg *et al.*, 2001; Doong *et al.*, 2003; Young-Soo and Qing, 2004). Improved methods include (1) combining ultrasound and iron to accelerate reduction and reduce the forming of oxide layers on the surface of iron by continuous cleaning through acoustic cavitation (Hung and Hoffmann, 1998); (2) increasing the surface area of iron by reducing its particle size to enhance the reactivity (Lien and Zhang, 2002; Feng and Lim, 2005); and (3) depositing a second metal as a catalyst onto the surface of the iron (Fennelly and Roberts, 1998; Cheng and Wu, 2000; Gui *et al.*, 2000; Kim and Carraway, 2000; Liu *et al.*, 2001; Morales *et al.*, 2002). Of numerous improvement methods tested, the deposition of the second metal as a catalyst onto the surface of iron is considered to

* Corresponding author. E-mail: inna_xu@hotmail.com.

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be promising, in view of the simplicity of preparation and the rapid and complete reduction.

A low-cost and highly effective Cu/Al bimetal was developed by Lien and Zhang (2002) for treatment of halogenated methanes in near neutral and high pH aqueous systems. The presence of Cu on Al significantly enhanced rates of degradation of halogenated methanes and reduced toxic halogenated intermediates. Roles of Cu may involve protecting Al against the undesirable oxidation with water, enhancing the reaction rates through galvanic corrosion, and increasing the selectivity to a benign compound.

The authors' early study (Xu *et al.*, 2005) indicated that nitrobenzene was reduced directly on the surface of copper rather than by the hydrogen evolved at the cathode in the catalyzed Fe/Cu process. Both acidity and alkalinity favored the direct reduction at the Cu electrode. The direct pathway played a great role in the reduction because reducing nitrobenzene directly at the Cu electrode was easier than reducing it by the hydrogen evolved at the cathode. Copper could be regarded as an electrocatalyst in this case.

The corrosion depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions (Liu and An, 2002). Evans coupling diagrams are used extensively to study the effect of various factors on corrosion rates (Melitas and Farrell, 2002). The overall rate of iron corrosion may be limited by either the anodic or the cathodic half-cell reactions under open-circuit conditions. Under anodically controlled conditions, the rate at which oxidants are able to accept electrons is faster than the rate at which iron is able to release electrons. In contrast, cathodically controlled corrosion occurs when the rate at which iron is able to release electrons is faster than the rate at which oxidants are able to accept electrons.

The goal of this research was to investigate the polarization behavior of Fe/Cu in nitrobenzene solution and the mechanisms involved in its reduction from solution by Fe/Cu bimetallic media. Toward this end, the batch experiments were performed under different reaction conditions to study the effect of various influencing factors such as solution pH, reaction duration, concentration, type of electrolyte, and DO on the reduction of nitrobenzene by Fe/Cu bimetallic media. The iron consumption necessary for the reduction was also determined.

1 Experimental

1.1 Reagents and instruments

The waste scrap iron (scrap cast iron) with a surface area of 0.3–0.4 m²/g was received from the Mechanical Factory of Tongji University, China and washed with soap to remove oil. The catalyst was pure copper tinsel with 0.12-mm thickness offered for sale in the market, and was cut into thin pieces of size 5 cm × 1 cm before the experiments. Water for the batch experiments was prepared with ordinary distilled water. The electrolyte for electrochemical measurements was prepared with double distilled water. Sodium sulfate (0.1 mol/L) was used as a

supporting electrolyte. Sulfuric acid or sodium hydroxide was used to adjust electrolyte pH value. All reagents applied in the process of the experiments were analytical grade (AR) materials.

The HYG-A shaker (Taicang Experimental Equipment, China) was used to perform the batch experiments. Electrochemical measurements were performed with a conventional three-electrode configuration. The home-made Fe and Cu electrodes with an area of 1.44 cm² were used as working electrodes in the measurements of polarization curves. A Pt electrode served as an auxiliary electrode and a 232 saturated calomel electrode (SCE) (Shanghai Analytical Instrument, China) was used as a reference electrode. All electrochemical measurements were conducted using a CHI600A electrochemical station (Shanghai Chenhua Instrument, China), as was the stochastic software applied to collecting data and plotting the polarization curves. The portable sensION2 pH/ISE meter (Hach, USA) was used to measure pH.

1.2 Experimental methods

1.2.1 Batch experiments

The above-mentioned iron scrap with a weight of 100 g was dried by heating at 120°C, thereafter, 100 g of the dry iron scrap was thoroughly mixed with Cu pieces in a desired proportion (10:1, W/W) and held down so that the observed density reached approximately 0.5 kg/L. The mixture was then placed in a 500-ml wide neck ground-glass stoppered flask, and 300 ml of solution containing nitrobenzene was added to the flask which was then covered. Following this, the flask with water was placed in the HYG-A shaker and shaken at 140 r/min for the desired time (30, 60, 90, 120 min). A 50-ml aliquot was sampled from the flask with a close 10-ml injector and analyzed its composition with Voyager GC/MS (Finnigan Corporation, USA).

1.2.2 Electrochemical measurements

Polarization behavior of Fe/Cu was studied to determine whether iron corrosion was anodically or cathodically controlled in the catalyzed Fe/Cu process. A 20-ml aliquot of aqueous organic solution was purged with nitrogen gas continuously for about 1 min to drive away the oxygen dissolved in the water, and then stabilized for 10–15 s. The homemade copper electrode lay soaked in 10% (W/W) hydrochloric acid for 2 h and acetone for 2 h, respectively, to clean its surface. The iron electrode was polished with fine sandpaper and rinsed thoroughly with highly purified water.

1.2.3 Analytical methods

A Finnigan Voyager spectrometer (GC-MS) was used to analyze the compositions of organic compounds in the water after the treatment. Ten milliliters of 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 flow rate of helium, a carrier gas, was set at 1 ml/min. The MS was operated in electron impact mode (70 eV). Injection

port temperature was 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 nonpolar capillary column of model DB/5 (30 m in length, 0.25 mm in diameter, with the thickness of 0.25 μm) was used in the analytical process. Dodecane was used as the internal standard (IS) in the measurements of the concentration of the aqueous solutions containing nitrobenzene after the treatment by the catalyzed Fe/Cu process. The conversion rate of nitrobenzene was calculated via the following equation.

$$Y_{C_6H_5NO_2} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

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

2 Results and discussion

2.1 Polarization behavior of Fe/Cu in NB aqueous solution (Evans coupling curves)

The Evans coupling curves of Fe/Cu in anaerobic 100 mg/L nitrobenzene aqueous solution are shown in Fig.1. Under acid conditions, the anodic polarization curve of iron do not intersect the cathodic curve of copper (Fig.1a). Perhaps it is because iron corrosion is initiated easily at acid pH. The catalysis of the Cu electrode is not clear. It can be seen from Figs.1b and 1c that the anodic polarization curve of iron reveals three regions, the first is characterized by the active dissolution of iron, the second is quite flat in the potential range -0.71 to 1.10 V under neutral conditions and -0.65 to 1.15 V under alkaline conditions and the third started around 1.10 V, exhibiting a sharp increase of current with potential. This is because some oxides such as $Fe(OH)_2$ and FeO are produced with increasing potential at the anode, which form the resistance layer to the transfer of ions and diffusion and cause the passivation of iron. After reaching the upper limit of the passivation potential the protective film is oxidized into highly-valent $Fe(OH)_3$, Fe_3O_4 , and so on.

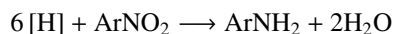
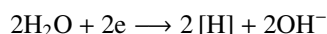
The cathodic polarization curves intersect the anodic curve in its transition zone at pH 7.5 and 10.1. This means that contact corrosion could be initiated in the system.

Both the driving force ($E_{0,C} - E_{0,A}$) and corrosion current j_{corr} under alkaline conditions are greater than those under neutral conditions. The relative magnitudes of the “slopes” cathodic polarizability $P_c = (E_{0,C} - E_{corr})/\log j_{corr}$ and anodic polarizability $P_a = (E_{corr} - E_{0,A})/\log j_{corr}$ determine whether the anodic, cathodic, or both reactions are limiting the overall rate of iron corrosion. P_c and P_a are almost the same at neutral pH; the iron corrosion is limited by both the anodic and cathodic half-cell reactions. $P_c \gg P_a$ under alkaline conditions, indicating that corrosion is cathodically controlled.

2.2 Influencing factors on the conversion of NB by the catalyzed Fe/Cu process

2.2.1 Effect of pH

The reduction of nitrobenzene by the catalyzed Fe/Cu process is because of net effect of the following pathways (Xu *et al.*, 2005):



Nitrobenzene reduction occurs via indirect electron transfer from atomic hydrogen produced from water reduction (a) or via direct electron transfer from iron (b) under acid conditions, so hydrogen ion H^+ is of great importance to the reduction. However, the pathway (b) seems to be particularly evident because of vigorous self-corrosion of iron (Fig.1). Both the anodic and cathodic reactions determine the contact corrosion rate under neutral conditions; additionally, reducing nitrobenzene directly at the copper electrode is easier than reducing it with atomic hydrogen (Xu *et al.*, 2005). Therefore, the reduction by iron (b) and the direct pathway on the copper surface (c) play a major role in the system. The contact corrosion is determined by the cathodic reactions under alkaline conditions. The elimination reaction for the formation of the reduction intermediate product, nitrosobenzene occurs easily under alkaline conditions, which favors the direct reduction at the copper electrode (Xu *et al.*, 2005). Additionally, the pathway (b) cannot help enormously in the reduction at higher pH. The direct pathway (c) on the Cu surface therefore features at this rate.

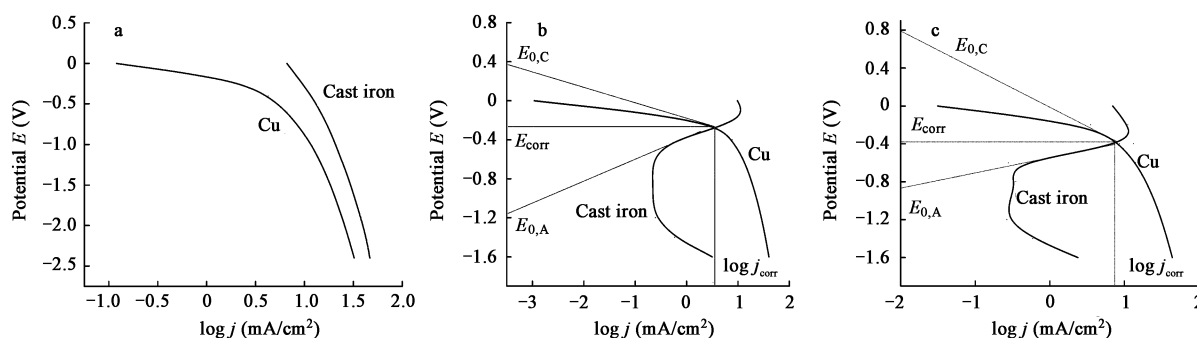


Fig. 1 Evans coupling curves of Fe/Cu in 100 mg/L nitrobenzene aqueous solution at pH 3.1 (a), pH 7.5 (b), and pH 10.1 (c).

The batch experiments were performed according to the steps described in Section 1.2.1 to study the effect of solution pH on the reduction. The experimental results in Fig.2 indicated that the conversion rate of 250 mg/L nitrobenzene decreased with pH under acid conditions. Under alkaline conditions it first increased with rising pH, and then dropped. In general, the conversion rate of 250 mg/L nitrobenzene by the catalyzed Fe/Cu process decreased in the following order: pH 3.0 > pH 10.1 \approx pH 9.5 > pH 5.0 > pH 7.5 > pH 12.3. The catalyst copper improved the reduction, especially under slightly alkaline conditions: the conversion rate at pH around 10.1 was almost the same as that under highly acid conditions (pH around 3), and reached 100% in 30 min.

The batch experiments were also performed for 500 mg/L nitrobenzene solutions with different pH. As shown in Fig.3, the conversion rate reached 100% after 60, 100, 70, and 90 min reaction at pH 3.0, 7.5, 10.1, and 11, respectively. In other words, it decreased in this order: pH 3.0 > pH 10.1 > pH 11.0 > pH 7.5. Copper helped the reduction greatly at pH around 10.1, and the direct pathway (c) dominated in the system. The catalyzed Fe/Cu process could be used to treat slightly alkaline wastewater containing nitrobenzene, as it would not give rise to a hydrogen ion shortage and further slowing up the reduction with time.

2.2.2 Effect of reaction duration

The experiments were performed to study the effect of reaction duration on the reduction by the catalyzed Fe/Cu process. As shown in Fig.4, the reaction duration had a notable impact on the conversion rate of nitrobenzene. In the first 20 min the conversion rate reached 50%, in the latter 70 min it increased moderately, and approached 100% only after 90 min reaction. The total nitrogen balance never reached 100% in the system, indicating that the reactant or products were adsorbed onto the electrode surface, or intermediate products occurred. GC/MS analysis showed that nitrobenzene was reduced to aniline by the catalyzed Fe/Cu process, and no other intermediate product was found in the samples (data not shown). Therefore, total

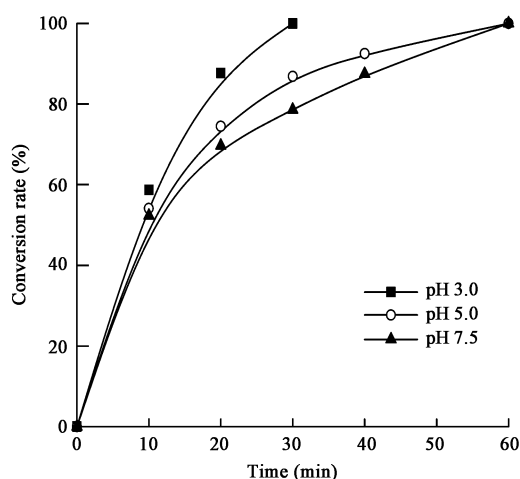


Fig. 2 Effect of solution pH on the reduction of 250 mg/L nitrobenzene aqueous solution by the catalyzed Fe/Cu process.

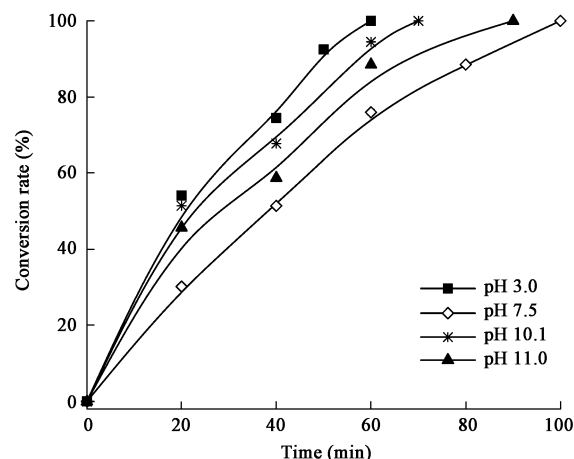
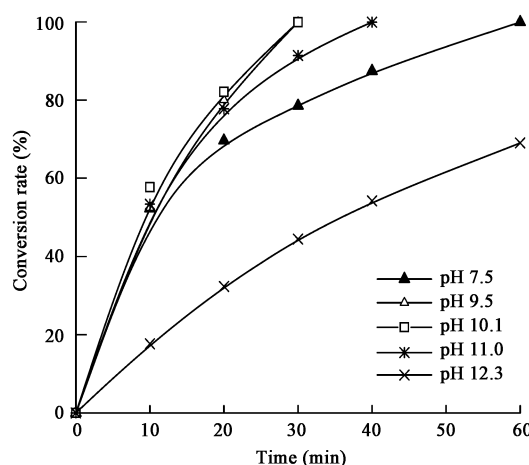


Fig. 3 Effect of solution pH on the reduction of 500 mg/L nitrobenzene aqueous solution by the catalyzed Fe/Cu process.

nitrogen imbalance in the system was attributed to adsorption. A 62% nitrobenzene was removed after 20 min reaction, among which 36% was removed by adsorption, and 26% nitrobenzene was reduced to aniline. Then total nitrogen reached a minimum of 65%. This was because the degradation fell into two phases: adsorption and reduction. In the adsorption phase nitrobenzene transferred to the surface of the iron scrap with an immense surface area, and in the reduction phase the adsorbed nitrobenzene was reduced to aniline. After 90 min reaction, 90% nitrobenzene was reduced to aniline and the rest was removed by adsorption.

2.2.3 Effect of concentration

The batch experiments were conducted to study the effect of solution concentration on the reduction by the catalyzed Fe/Cu process (Fig.5). The conversion rate reached 50% in the first 10 min, when the initial concentration changed in the range 200–900 mg/L; in the latter 50 min it decreased evidently with concentration. In the solutions of higher concentration (1,400–1,900 mg/L), the conversion rate reached 23% in the first 20 min, and then decreased slightly with concentration. This was because the degradation of nitrobenzene occurred on the metal



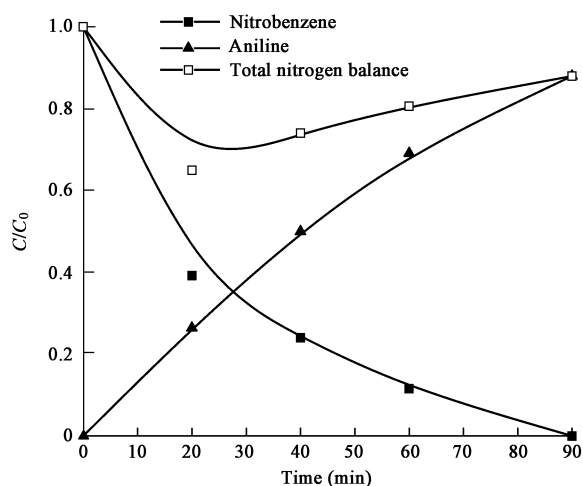


Fig. 4 Effect of reaction duration on the reduction of 500 mg/L nitrobenzene aqueous solution by the catalyzed Fe/Cu process (pH 7.5).

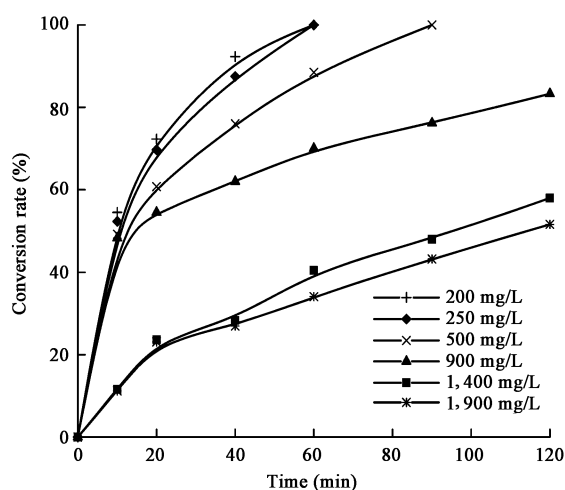


Fig. 5 Effect of initial solution concentration on the reduction by the catalyzed Fe/Cu process (pH 7.5).

surface, the adsorption of nitrobenzene caused competition for the reactive sites on the iron surface. GC/MS analysis showed that aniline occurred later in the solutions of higher concentration (1,400–1,900 mg/L) (data not shown), indicating that the influence of adsorption and mass transfer expanded with solution concentration. Adsorption and mass transfer in the liquid phase were the rate-limiting step of the electrode reaction in the solutions of higher concentration.

2.2.4 Effect of type of electrolyte

The experiments were performed to study the effect of type of electrolyte on the reduction by the catalyzed Fe/Cu process: four portions of the iron scrap of 100 g weight were dried by heating, and then copper was added to them, respectively, in a certain proportion (10:1, W/W). Also 900 mg/L nitrobenzene solutions were prepared in four different electrolytes of 0.1 mol/L: CuSO_4 , NH_4Cl , NaCl , and Na_2SO_4 , respectively. Subsequently, the steps described in Section 1.2.1 were followed. As shown in Fig. 6, the electrolytes had a noticeable impact on the degradation of nitrobenzene. They accelerated the galvanic

corrosion rate and increased the conversion efficiency of nitrobenzene accordingly. Chlorine ion was capable of destructing the protective film on the surface of iron and further accelerating its corrosion (Xia *et al.*, 2003). Iron displaced copper from CuSO_4 solution with the formation of incompact cupreous particles on the iron surface, which led to further acceleration of the galvanic corrosion and increase in degradation efficiency.

2.2.5 Effect of DO

The experiments were performed under aerobic, anoxic, and oxygen-free conditions to study the effect of DO on the reduction by the catalyzed Fe/Cu process. Three portions of the iron scrap of 100 g weight was dried by heating, copper was added to them, respectively, in a certain proportion (10:1, W/W). Subsequently, the steps described in Section 1.2.1 were followed. Following this the first solution was aerated by stirring the solution for 30 min with a magnetic stirrer, in an open wide neck flask and then closed, the second flask was closed as soon as the solution was prepared, and the third solution was purged with N_2 for 30 min to remove DO. The flasks with the filling and solutions were then stored in the shaker of model HYG-A and shaken at 140 r/min for a certain time. A 50-ml aliquot was sampled from the flask with a close 10-ml injector, and its composition was analyzed with GC-MS (data not shown). The results (Fig. 7) indicated that the reduction speeded up with a decrease of DO in the solution. Perhaps it was because oxygen competed for the electrons provided by iron and accordingly inhibited the reduction of nitrobenzene. It could also refer to the capture of the reactive sites on the filling by oxygen or to the rapid formation of ferrites and hydroxides of iron in the presence of oxygen, which led to the passivation of iron and decline in the conversion rate of nitrobenzene.

Compared to the Master Builder's iron, a need for aeration is eliminated in the catalyzed Fe/Cu process; accordingly, spending on energy consumption will be reduced. It actually helps to make the most of the catalysis of copper and reducing capacity of iron. Furthermore, the iron-based sludge will decrease in amount after the

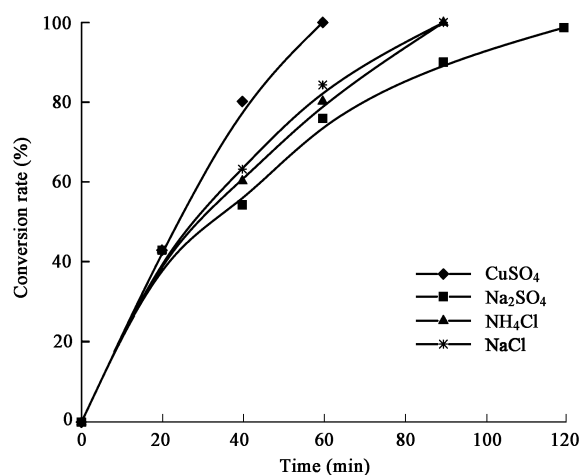


Fig. 6 Effect of the type of electrolyte on the reduction of 900 mg/L nitrobenzene aqueous solution by the catalyzed Fe/Cu process (pH 7.5).

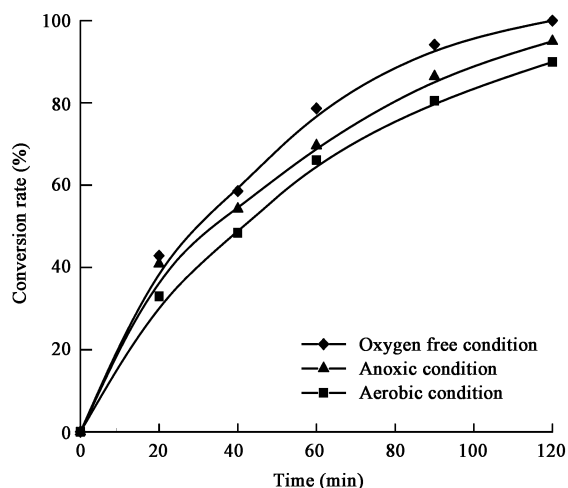


Fig. 7 Effect of DO on the reduction of 900 mg/L nitrobenzene aqueous solution by the catalyzed Fe/Cu process (pH 7.5).

reduction. Therefore, the reduction is cost-effective. With all these advantages this process can be considered to be of practical value.

2.3 Economic analysis

The catalyzed Fe/Cu process reduces nitrobenzene to aniline and improves biological degradability of wastewater accordingly. However, it can hardly remove COD completely from wastewater. Therefore, it is strongly suggested that this process be used in combination with the conventional biological technology. Copper is a catalyst that increases the rate of reaction without being consumed in the process. Iron scrap is a consumable; accordingly, its consumption forms a principal component of the operating cost.

The experiments were performed to determine the iron consumption necessary for the removal of 100 mg/L nitrobenzene from solutions with different pH. Resolvable iron (including Fe^{2+} and Fe^{3+}) consumption was 26.45, 13.19, 9.31, and 3.73 mg/L for the solutions with pH 3.0, 7.5, 10.1 and 11.0, respectively. The total iron (including the resolvable and precipitable iron) consumption was 37.25, 40.36, 41.18 and 46.95 mg/L, respectively. All in all, the total iron consumption was less than 50 mg/L, i.e., merely 0.05 kg iron was needed for the treatment of a ton of water containing nitrobenzene, with pH from 3 to 11. Immediate precipitation of oxides and hydroxides of iron was observed under alkaline conditions. As pH increased, the effect became more evident. Under acid and neutral conditions the precipitation followed the increase of pH caused by the reduction of nitrobenzene.

3 Conclusions

The polarization behavior of the couple Fe/Cu in 100 mg/L nitrobenzene aqueous solution was studied using Evans coupling diagram. The results indicated that factors favoring either the anodic or cathodic reactions would increase the iron corrosion rate at the neutral pH. The corrosion of iron was cathodically controlled under the

alkaline conditions. The catalyzed Fe/Cu process proved to be effective in the pH range 3 to 11. The conversion efficiency of nitrobenzene at pH around 10.1 was almost the same as that under the highly acid conditions (pH around 3). The direct electron transfer from iron seemed to be particularly evident because of the vigorous self-corrosion of iron under highly acid conditions. Under alkaline conditions the reduction enhanced with increasing pH first, and then weakened and reached a maximum at pH around 10.1, because the direct pathway was dominant in the system then. The degradation fell into two phases: adsorption and reduction. In the adsorption phase nitrobenzene transferred to the surface of the iron scrap with an immense surface area, and in the reduction phase the adsorbed nitrobenzene was reduced to aniline. Mass transfer in the liquid phase was the rate-limiting step of the electrode reaction in the solutions of higher concentration (1,400–1,900 mg/L) because adsorption of the reactant caused the competition for reactive sites. The reduction rate decreased in the presence of DO in the solution. Oxygen might have competed for the electrons provided by iron and accordingly inhibited the reduction of nitrobenzene. Additionally, the reactive sites on the filling could have been occupied by oxygen. A need for aeration was eliminated in the catalyzed Fe/Cu process; accordingly, spending on energy consumption would be reduced, and the iron-based sludge would decrease in amount during the reduction as well. Merely 0.05 kg was needed for the treatment of one ton of water containing nitrobenzene, with pH from 3 to 11. Immediate precipitation of oxides and hydroxides of iron was observed under alkaline conditions. As pH increased, the effect became more evident. Under acid and neutral conditions the precipitation followed the increase of pH caused by the reduction. The catalyzed Fe/Cu process was of practical value because it made the most of the catalysis of copper and the reducing capacity of iron. Copper was not plated on the iron by exposing the iron to a solution of Cu^{2+} , the process was therefore simplified.

Acknowledgements

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