© by PSP Volume 25 – No. 5/ 2016, pages 1467-1475 Fresenius Environmental Bulletin

2,4-DINITROTOLUENE REMOVAL EFFICIENCY AND MECHANISMS IN TREATMENT OF CHEMICAL INDUSTRIAL WASTEWATER WITH ZERO-VALENT FE/CU BIMETAL

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ABSTRACT

Driven by chemical substitution, Fe/Cu bimetal materials were developed through copper sedimentation on iron crumbs, and characterized through a scanning electron microscope (SEM) and X-ray electron spectrometers. Fe/Cu bimetal systems were used in the treatment of 2,4-dinitrotoluene (2,4-DNT) chemical industrial wastewater, whilst the research was made on treatment efficiency and reaction rate based upon respective factors ranging from the materials, coverage rate of copper, pH and initial concentration, etc. which led us into the discussion of inner mechanisms. It was demonstrated that the best coverage rate of copper plating is 0.25%, and that Fe/Cu bimetal materials supersede simple iron crumbs regarding removal efficiency, reaction rate and adaptation. With pH set at 9.0, 11.0 and 13.0, the removal of 2,4-dinitrotoluene increased by 6.22%, 9.52% and 25.26%, changing from iron crumbs to Fe/Cu bimetal, reaching at 90.18%, 70.21% and 58.8% respectively. Fe/Cu bimetal material tackles the low degradation efficiency in alkaline environments faced by conventional micro-electrolysis and is not limited within acidic wastewater treatment.

Key Words:
Iron Crumb; Fe/Cu Bimetal; 2,4 DNT; Chemical Industrial Wastewater

INTRODUCTION

2,4-dinitrotoluene (2,4-DNT) is a type of widely used material in chemical industry, and an intermediate in fine chemicals, with strong bio-
causing cancer, causing malformation and causing mutation. Once into water bodies, it aggravates the quality and sensory properties of the water for long terms, and brings about great hazards to the environment and organisms. It has been listed in

for environmental protection (Ma et al.2013; Zhang et al). Due to the fact that these chemicals are highly stable in water bodies, conventional wastewater treatment could barely degrade and remove them from water bodies. Physical-chemical treatment, combined with bio-chemical treatment, is currently the dominant technique in the treatment of DNT chemical industrial wastewater both domestically and abroad.

In the process of treating DNT chemical industrial wastewater, a critical and restrictive step is bringing down the concentration of DNT and the toxicity of the wastewater before bio-chemical treatment. The research so far has been founded on oxidation techniques, e.g. electrochemical oxidation, Fenton oxidation and photo-catalytic oxidation. These oxidation techniques are universally too costly, making it an urgent need to find a low cost and effective way to treat DNT chemical industrial wastewater (Bozzi et al, 2005; Ma et al, 2008).

Iron-carbon micro-electrolysis, using reduction, absorption, flocculation and filtration for pollutant removal, has developed along with the utilization of iron in wastewater treatment, and is more economical compared with oxidation (Jiang et al, 2009). However, after a certain time period of running, the iron crumbs harden up and short

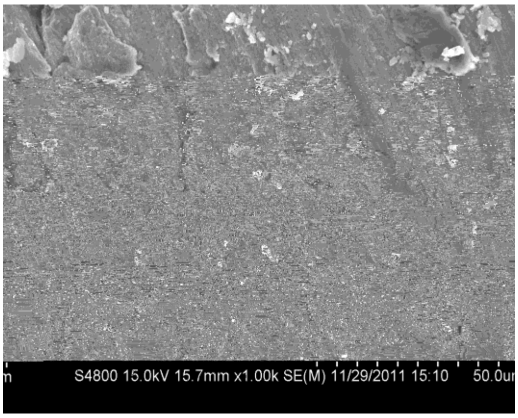
performing well under acidic conditions (Ma et al, 2008; Wang et al, 2009; B et al, 2014). Targeting at the deficiencies above, Chen used discarded iron shavings as a base matter and fabricated bimetal reduction systems such as Cu/Fe, and carried out a research on fine chemicals industrial wastewater and dyeing wastewater (Chen et al, 2011). Compared with conventional iron-carbon micro-electrolysis, bimetal systems have a wider suitable pH range (e.g. from the acidic environment to slight alkaline environment) for a good effectiveness, along with improvements in iron crumb hardening up (Ma et al, 2004). However, regarding whether Fe/Cu bimetal is suitable for

DNT chemical industrial wastewater, or the effectiveness and reaction mechanisms, we have noticed barely any report by far. This led us to use iron crumbs as the base matter and build Fe/Cu bimetal systems for the treatment of DNT chemical industrial wastewater, and made a research on treatment efficiency and reaction rate based upon respective factors ranging from the materials, coverage rate of copper, pH and initial concentration etc. We optimized the conditions of the reaction systems, aiming at offering some certain reference to the practical utilization of Fe/Cu bimetal systems in the treatment of nitro-containing aromatic compounds chemical industrial wastewater.

MATERIALS AND METHODS

REAGENTS AND INSTRUMENTS

The 0.1 cm diameter iron crumbs were obtained from a machinery plant in Linhai, Zhejiang Province. Chemicals used are graded AR (analytical reagent). Instruments used in the experiment include DELTA-320 pH meter (DELTA, China), UV-7504 (A) ultraviolet visible spectrophoto1 135.98 5



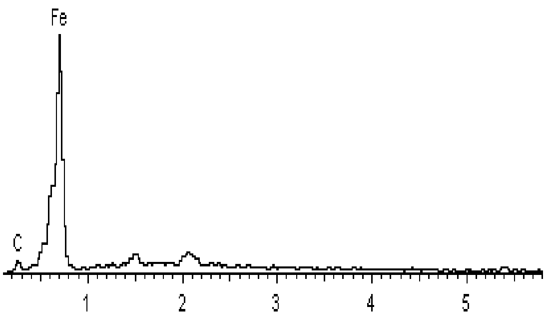
(a) SEM Image of Iron Crumbs

(b) SEM Images of Cu/Fe Bimetal

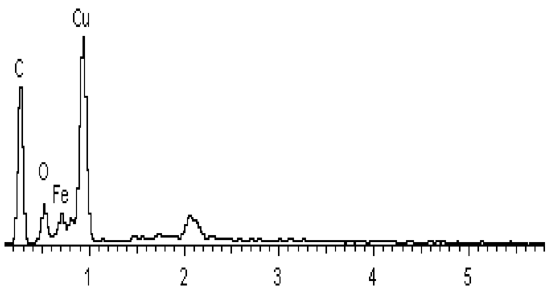
FIGURE 1
SEM Images.

X-ray Energy Dispersive Spectroscopy (EDS) Image. Fig. 2 shows X-ray EDS images of iron crumbs and Cu/Fe bimetal of 0.25% copper rate. Table 1 shows the results element contents) of the samples. EDS image of the iron crumbs shows Fe and C as the predominant elements, taking up 79.91% and 18.22% of weight percentage respectively. EDS image of Cu/Fe bimetal shows the existence of Cu, Fe, C and O, indicating that Cu/Fe bimetal has been created as the iron crumbs

percentage of O is only 9.43%, whilst Fe and Cu takes 18.69% of atomic percentage, which indicates that during the fabrication of the materials, just a part of the zero-valent elements were oxidized, and that zero-valent Cu/Fe systems still exist in the Cu/Fe bimetal materials.



(a) EDS Image of Iron Crumbs



(b) EDS Image of Cu/Fe Bimetal

FIGURE 2
EDS Imagesc[( )] TJETBT1 0 0 7h -c[( )] TJETBT1 0 0 7h

each of four 500 mL sized small packed-bed reactors 100g of iron crumbs, the copper rate of which being respectively 0%, 0.1wt%, 0.25wt% and 0.5wt%. Put in 2,4 DNT wastewater of 100

As shown in Fig. 4, after 2 h of reaction, the degradation rate of 2,4-DNT in relation to iron crumbs with no copper was around 95% at pH of 3.0, 5.0 and 7.0, and 83.96%, 59.25%, 33.54%, respectively as pH goes up to 9.0, 11.0 and 13.0, which indicates that from pH 9 to pH 13, the removal rate of DNT significantly drops as pH goes up. h of reaction, the degradation rate of 2,4-DNT in relation to Fe/Cu bimetal (copper rate 0.25wt%) was around 98% at pH of 3.0, 5.0 and 7.0, and 90.18%, 70.21%, 58.8% respectively as pH goes up to 9.0, 11.0 and 13.0.

Comparing iron crumbs without copper and Fe/Cu bimetal, we can see that at pH of 3.0, 5.0 and 7.0, both could give a satisfying removal rate above 95% on DNT, yet Fe/Cu bimetal is better at pH of 9.0, 11.0 and 13.0, respectively 6.22%, 9.52% and 25.26% higher compared to iron crumbs, which indicates that as alkalinity increases, Fe/Cu bimetal is better than iron crumbs. The results imply

RESEARCH INTO REACTION MECHANISMS

Researches into Process Products in Reaction. Put into packed-bed reactors filled with Fe/Cu bimetal (copper rate 0.25%) 2,4 DNT wastewater of pH 7 and 100mg/L in concentration. Samples were taken regularly for ultraviolet spectrum scanning analysis, Fig. 7 for the outcomes of UV spectrum scanning.

As shown in Fig. 7, the absorption peak at 250nm wavelength gets weaker and weaker as the reaction goes on, and disappears at 120min; at the same time, the absorption peak at 215nm wavelength gets stronger gradually and reaches the highest at 120min. Based on the analysis of UV spectrum scanning outcomes, 2,4-DNT gets mostly degraded, whilst new matters are generated in the reactions.

TABLE 2
Kinetic Parameters of 2,4-DNT Degradation by Iron Crumbs and Fe/Cu Bimetal.

Iron Filings	Kinetics Equation	Fe/Cu	Kinetics Equation

FIGURE 6
Reaction Rate of 2,4-DNT Degradation by Iron Crumbs and Fe/Cu Bimetal.

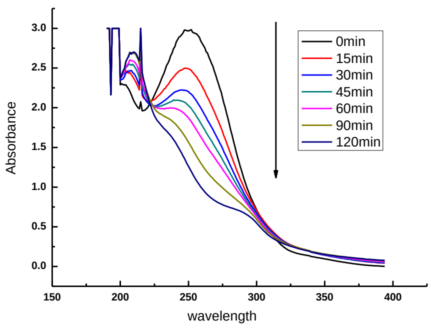


FIGURE 7
Ultraviolet Spectrum Scanning Graphs of Cu/Fe.

Variations of pH and Iron Ion Concentration. As shown in Fig. 8, during the treatment of 2,4-DNT wastewater by Fe/Cu bimetal, pH increases as the reaction goes on but not significantly, remaining between 7 8. At the starting period, stripping of iron ions is observed, reaching 1.23mg/L, and drops to 0.52mg/L as the reaction goes on, and fluctuates between 0.68mg/L and 0.86mg/L afterwards. It is believed that during redox reactions, electrons are lost from iron atoms, generating iron ions in the solution. Meanwhile, some H+ are consumed, leading to pH increase, and thus Fe(OH)2 is generated as iron ions are combined with OH-, leading to the decrease of iron ion concentration in the system and pH maintaining between 7-8(Scherer et al.2001;Liu et al.2005).

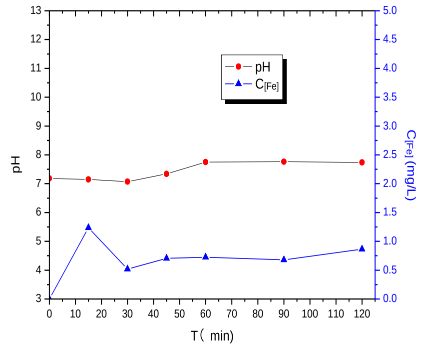
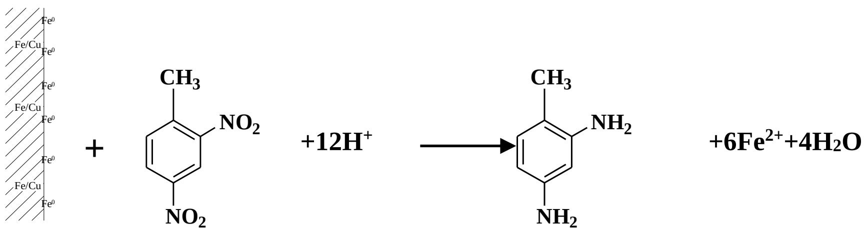


FIGURE 8
Variation of pH and Iron Ion Concentration.

Discussion on Reaction Mechanisms. In accordance with a research into the phenomenon of the experiment in this paper, the mechanisms of DNT wastewater treatment by zero-valence Fe/Cu bimetal could be approached from four perspectives, namely (1) direct electron transfer on the surface of Fe/Cu bimetal, (2) micro primary battery effects, (3) the effects of bimetal and 4 adsorption of the corrosion products of Fe^0 (Xu et al.2008; Liang et al.2010].

(1) Direct electron transfer on the surface of Fe/Cu bimetal.



(2) Micro primary battery effects.

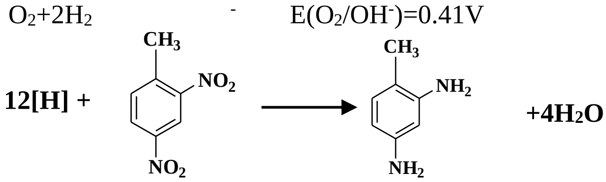
Anode (Fe): Fe $^{2+}$ E Fe^2 /Fe = 0.44V

Cathode (C): $2H^+$ $_2$ E H^+/H_2 = 0V

Cathode reactions are as follows with the existence of oxygen:

O_2+4H^+ $_2O$ $E(O_2)=1.23V$

O_2+2H_2 $^-$ $E(O_2/OH^-)=0.41V$



(3) Effects of bimetal. In the bimetal system of copper and iron, copper as the cathode improves the reaction rate of the micro primary battery, and also provides a reaction surface for the reduction reactions of DNT, which enhances the reaction rate of the system (Liang et al.2010).

(4) Adsorption of the corrosion products of Fe^0. The removal of DNT also was resulted from the adsorption of the corrosion products of Fe^0.

CONCLUSIONS

(1) The optimized copper rate on iron crumbs is 0.25%. With pH set at 9.0, 11.0 and 13.0, the removal rate increased by 6.22%, 9.52% and 25.26% changing from iron crumbs to Fe/Cu bimetal, reaching at 90.18%, 70.21% and 58.8% respectively. Fe/Cu bimetal material tackles the low degradation efficiency in alkaline environments faced by conventional micro-electrolysis and is not limited within acidic wastewater treatment.

(2) The reaction rate of 2,4-DNT degradation by Fe/Cu bimetal is higher than that of iron crumbs under all pH conditions, implying that the fabrication of Fe/Cu bimetal systems does a good job in accelerating the reaction rate.

(3) The mechanisms of DNT wastewater treatment by zero-valence Fe/Cu bimetal could be approached from three perspectives, namely (1) direct electron transfer on the surface of Fe/Cu bimetal, (2) micro primary battery effects, and (3) the effects of bimetal.

ACKNOWLEDGEMENTS

This work was financially supported by Public Technology Applied Research Fund of Zhejiang Province Science and Technology Department (2013C33020), Environmental Science and Technology Project of Zhejiang Province (2013B018), Priority Academic Program Development of Jiangsu Higher Education Institutions and Research Fund for Plant Evolutionary Ecology Innovative Research Team.

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