Study on the treatment of simulated azo dye wastewater by a novel micro-electrolysis filler

Zhen-Zhu Sun, Zhong-Hai Liu, Le Han, Dong-Ling Qin, Gang Yang and Wei-Hong Xing

ABSTRACT

A new type of iron-copper-carbon (Fe-Cu-C) ternary micro-electrolysis filler was prepared with a certain proportion of iron powder, activated carbon, bentonite, copper powder, etc. The effect of the new type of micro-electrolysis filler on the simulated methyl orange dye wastewater was studied. The effects of various operational parameters, such as reaction time, initial pH value, aeration rate, filler dose and reaction temperature, on the degradation rate of methyl orange were studied to determine the optimum treatment conditions, and the micro-electrolysis filler was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The experimental results show that the degradation rate of 220 mL of simulated dye wastewater with a concentration of 100 mg/L reached 93.41% ± 2.94% after 60 mL/min of aeration, with an initial pH = 2, a dose of 45 g and 125 minutes of reaction at room temperature. The new micro-electrolysis filler has a high degradation rate for methyl orange solution, which is attributed to the iron and activated carbon particles sintered into an integrated structure, which makes the iron and carbon difficult to separate and affects the galvanic cell reaction. The addition of copper also greatly increases the transmission efficiency of electrons, which promotes the reaction. In addition, the surface iron is consumed, the adjacent carbon is stripped layer by layer, and the new micro-electrolytic filler does not easily passivate and agglomerate during its use.

Key words | azo dyes, dyeing wastewater, micro-electrolysis, water treatment

INTRODUCTION

Synthetic dyes play an important role in everyday life (Khattab et al. 2012). They are widely used not only in textiles but also in paints, plastics, leather, paper, rubber and other fields (Fu et al. 2014). Azo dyes are synthetic azo compounds, that contain azo groups. There are more than 3,000 kinds of azo dyes, accounting for approximately 80% of all dyes. Upon bleaching, washing and dyeing of dye wastewater, synthetic aromatic cyclic azo dyes enter the environment via wastewater. Dye wastewater has the typical characteristics of complex composition, high concentration of pollutants, deep colour and poor biodegradability (Moreira et al. 2013; Ma et al. 2019). It has become an important source of environmental pollution (Ning et al. 2015; Zhang et al. 2018a, 2018b). In recent years, decolorization and degradation of dyeing wastewater have attracted widespread attention. Various technologies have been used to treat synthetic dyes’ wastewater such as adsorption (Elwakeel et al. 2016, 2017a, 2017b), micro-electrolysis (Yang et al. 2018), membrane filtration (Xu et al. 2018), photocatalytic degradation (Natarajan et al. 2018), biological process (Hayat et al. 2015), coagulation flocculation (Shankar et al. 2019), and chemical oxidation (Zhang et al. 2018a, 2018b).

Among the various physical and chemical methods used to treat wastewater, micro-electrolysis technology is of high interest because it is inexpensive, non-toxic and convenient (Zuo et al. 2011). Micro-electrolysis technology research in this field began in the 1980s in China, and has made rapid progress especially in recent years. It has been reported in the treatment of printing and dyeing wastewater, electroplating wastewater, petrochemical wastewater, pharmaceutical wastewater and so on (Ao et al. 2019). It is based on the principle of metal chemical corrosion, using a metal (usually iron) as the anode and a non-metal (usually carbon) as the cathode in solution to form numerous micro-galvanic cells...
for wastewater treatment, it is also known as internal electrolysis, and the corrosion cell method. There is an objective potential difference between carbon and iron, which facilitates formation of a micro-electrolysis system (Wang et al. 2015; Ning et al. 2015).

Galvanic interaction:

\[
\text{anode: } Fe - 2e^{-} \rightarrow Fe^{2+} \quad E^{0}(Fe^{2+}/Fe) = -0.44V \\
\text{cathode: } 2H^{+} + 2e^{-} \rightarrow 2[H] \rightarrow H_{2} \uparrow \quad E^{0}(H^{+}/H_{2}) = 0.00V
\]

Reaction system dissolved oxygen:

acid solution: \( O_{2} + 4H^{+} + 4e^{-} \rightarrow 2O^{-} + 4[H] \rightarrow 2H_{2}O \)

\( E^{0}(O_{2}) = 1.23V \)

neutral or alkaline solution: \( O_{2} + 2H_{2}O + 4e^{-} \rightarrow 4OH^{-} \)

\( E^{0}(O_{2}/OH^{-}) = 0.40V \)

Some products (such as active hydrogen, hydrogen peroxide, hydroxyl radical and ferric flocculants) generated at the electrode have high activity and can participate in redox reactions and electrocoagulation with many pollutants, which can induce the decolouration and degradation of pollutants (Li et al. 2015). In the process of the galvanic cell reaction, iron loses electrons to form iron ions, and \( H^{+} \) gains electrons to generate new ecology \([H]\). It has high activity and can react with unsaturated groups in dye molecule, reducing azo bonds, destroying chromogenic groups, and eventually breaking the dye molecules into small molecules so as to reduce the chroma. When the micro-electrolysis reaction is completed, the pH of the wastewater is adjusted to alkalinity, iron ions can react with hydroxide to form ferric hydroxide colloid. The newly formed ferric hydroxide colloid has a very strong flocculation effect that can flocculate and precipitate many suspended substances in wastewater.

Traditional micro-electrolytic materials mainly use iron and carbon. A ternary micro-electrolysis filler is prepared by adding copper to the original material. The advantage of the ternary micro-electrolysis filler is that copper and iron can form a bimetallic reduction system, which can strengthen the cathodic reaction, accelerate the electron transfer rate and improve the reaction efficiency of micro-electrolysis (Cao & Wu 2012).

The purpose of this study was to investigate the feasibility of using micro-electrolysis technology for the treatment of azo dye-containing wastewater. Methyl orange, one of the most commonly used azo dyestuffs, was selected as the simulated printing and dye wastewater. The effects of various operational parameters, such as reaction time, initial pH value, aeration rate, filler dose and reaction temperature, on the degradation rate of methyl orange were optimized to achieve the highest degradation efficiency. Finally, the mechanism underlying the degradation of methyl orange in the micro-electrolysis process was explored, providing basic theoretical guidance for the treatment of natural printing and dye wastewater.

**MATERIALS AND METHODS**

**Materials**

The reduced iron powder used in the experiment was analytical reagent (AR) grade, 50 mesh, and purchased from Aladdin Company (USA). Ammonium oxalate was provided by Yonghua Chemical Technology Co., Ltd (Jiangsu China). Methyl orange was obtained from Tianjin Chemical Reagent Research Institute. Co., Ltd. The concentration of methyl orange used in the experiment was 100 mg/L. Copper powder was obtained from Sinopharm Chemical Reagent Co., Ltd. Powdered activated carbon, 200 mesh, was purchased from Jiangsu Zhuxi Activated Carbon Co., Ltd. All of the above-mentioned chemicals were of analytical grade and were used directly without further purification. Bentonite of chemical purity (CP) was purchased from Shanghai Trial Four Hervey Chemical Co., Ltd.

**Micro-electrolysis filler preparation process**

The experiments were performed under the optimum preparation conditions: iron carbon mass ratio (m (Fe) : m (C)) = 4:1, iron carbon mass fraction = 75%, m (Fe) : m (Cu) = 10:1. At the same time, a certain amount of ammonium oxalate was added as a pore-making agent. A certain amount of pure water was added and stirred continuously until the sticky state. Then, the raw materials were kneaded by hand into spherical particles with a diameter of 1.5 cm. Then, in the vacuum dryer (DZF-6020, Yiheng Scientific Instruments Co., Ltd, Shanghai), the filler was dried at 95 °C for 30 min to prevent cracking during high-temperature roasting. Finally, in the vacuum tube furnace (SG-GL 1,200 K, Daheng Optical Precision Machinery Co., Ltd, Shanghai), the filler was roasted at a high
temperature (800 °C) in a N₂ atmosphere for 2 h and cooled to room temperature.

**Micro-electrolysis reactor**

The reactor for batch static experiments was constructed with an air pump (SB-648A, Songbao Electrical Appliances Co., Ltd, Zhongshan), a rubber tube, an air flow rotameter (LZB-3WB, KEDE, Changzhou), an aerator, and a glass column (Ø 3.5 cm × 30 cm), and a schematic diagram is shown in Figure 1. A certain amount of micro-electrolysis filler was placed in the glass column, and then 220 mL simulated wastewater (methyl orange at a concentration of 100 mg/L) was added to the glass column to submerge the Fe-C filler. The pH of the solution was determined by a laboratory pH/conductivity meter (MP 521, Shanghai Sanxin Instrument Factory Co., Ltd, Shanghai). The air generated by the air pump entered the flowmeter and then dispersed as many small bubbles into the solution through the aerator. The micro-electrolysis degradation process occurred on the packed bed, the surface of the filler was corroded continuously, and the aeration agitated the wastewater continuously to remove the falling substances over time. All experiments were carried out in batch mode at room temperature.

**Analysis method**

(1) Establishing standard curve of methyl orange: the absorption peak of methyl orange at 465 nm was obtained by using an ultraviolet-visible spectrophotometer (LAMBDA 950, Perkins Elmer Co., USA). The absorbance of methyl orange was measured by using a DR 2800 portable spectrophotometer (DR 2800, HACH Company, USA). The wavelength was set at 465 nm to detect the absorbance of methyl orange at the corresponding concentration in the solution. The relationship between the absorbance of methyl orange and the corresponding concentration was plotted using Origin software. The fitting equation is $Y = 5.6551X - 0.0668$, $R^2 = 0.9995$ ($Y$ denotes concentration, $X$ denotes absorbance).

(2) Determination of the degradation rate: samples were taken at regular intervals and diluted. Then, the concentration was measured by a portable spectrophotometer, and the corresponding degradation rate was calculated. The degradation rate of methyl orange was calculated by the following formula, where the initial mass concentration is expressed by $C_0$, and the reaction time is expressed by $C_t$.

Methyl orange degradation rate = \( \frac{C_0 - C_t}{C_0} \times 100\% \)

**RESULTS AND DISCUSSION**

**Pretreatment**

As the activated carbon in the filler has a certain adsorption effect on methyl orange, before the filler is used, the filler is placed in an adequate methyl orange solution and soaked for 240 min to remove the influence of the adsorption.
It can be seen from Figure 2 that the concentration of methyl orange remains basically unchanged after 180 min, so soaking the filler for 10 h is sufficient to saturate the activated carbon adsorption. In addition, methyl orange is weakly alkaline in an aqueous solution, so the effect caused by micro-electrolysis cannot be considered.

Effect of reaction conditions on the degradation rate

The effects of reaction time on the degradation rate of methyl orange were investigated. The concentration of methyl orange in the test solution changed over time. The curve in Figure 3(a) reveals that the degradation rate of methyl orange increases rapidly with increasing reaction time in the range of 0–60 minutes and then gradually becomes flat with increasing reaction time. The degradation rate increased slowly after 120 minutes. Considering the energy consumption and other factors, such as the later experimental time points, the reaction time was finally determined to be 125 minutes.

The rate of aeration not only affects the recycling performance of wastewater but also affects the dissolved oxygen content in the solution. Therefore, the effect of aeration rate on the degradation of methyl orange in solution was studied. Figure 3(b) shows that the degradation rate of methyl orange increases with increasing reaction time under different aeration rates. When the aeration rate was 10 mL/min, the degradation rate was relatively low. Upon increasing the aeration rate, the degradation rate of methyl orange gradually increased. This may be mainly because the wastewater could not be stirred sufficiently when the aeration rate was low, which affected the contact between the wastewater and filler. When the reaction time reached 75 minutes, the degradation rate curves of methyl orange under 60 mL/min and 90 mL/min aeration essentially overlapped. At this time, the increase in the aeration rate was not obvious. Therefore, the removal efficiency shows an obvious difference between without aeration and with aeration. However, the degradation efficiency does not increase substantially with the increase in the aeration amount. Hence, the aeration rate was controlled at 60 mL/min in the following experiment, under which the degradation rate of methyl orange reached 92.55% ± 2.55%.

The pH value significantly affects the efficiency of the micro-electrolysis reaction (Li et al. 2011). Furthermore, the pH value of natural printing and dye wastewater is relatively high. Hence, the effect of pH was evaluated during the treatment of methyl orange in the reactor. Figure 3(c) shows that the degradation rate of methyl orange increases gradually with increasing reaction time at different initial pH values. The degradation rate is highest at an initial pH of 2. This is because, in acidic environments, the potential difference between iron and carbon poles is large, promoting the micro-electrolysis reaction to produce more active substances such as Fe$^{2+}$ and [H], which promotes the redox reaction and improves the treatment effect (Kalyani et al. 2009; Jamaluddin & Abdullah 2016). If the pH is continuously lowered, not only will a large amount of acid be used, but the consumption rate of filler will also increase rapidly. With increasing initial pH, the degradation rate of methyl orange will decrease significantly. This is because the increase in pH reduces the potential difference between iron and carbon and weakens the micro-electrolysis ability. Therefore, it was concluded that an acidic environment (pH < 5) is more effective than an alkaline environment (pH > 8) for the degradation of methyl orange. Indeed, hydrogen is produced at pH values of <4, which is beneficial for the degradation of methyl orange. Considering these factors, the pH was maintained at 2 during the following experiments.

As shown in Figure 3(d), the degradation rate of methyl orange increases rapidly with increasing filler dose. This is because the greater the filler dose, the greater the number of micro-cells that form on the filler, so the degradation effect of the micro-electrolysis reaction will be accelerated. At doses of 45 g and 60 g, the degradation rate of methyl orange begins to rise most rapidly and then tends to increase slowly. After the reaction time reaches 100 minutes, even if the dose of filler is increased, the degradation rate of methyl orange will not increase greatly. The filler dose is too small...
to achieve complete degradation, and the excessive dose of filler will cause material waste. Thus, the dose of filler used is 45 g. Under these conditions, the degradation rate of methyl orange reached 91.48% ± 2.13%.

As shown in Figure 3(e), the degradation rate of methyl orange in solution increases with increasing reaction temperature. When the temperature is 5 °C, 25 °C and 40 °C, the degradation rate of methyl orange is 84.4% ± 2.32%,

Figure 3 | Effect of reaction conditions on the degradation rate of methyl orange. (a) room temperature, initial pH value 3, aeration rate of 40 mL/min and filler dose of 50 g; (b) room temperature, initial pH value 3, a filler dose of 60 g, and a reaction time of 125 min; (c) room temperature with an aeration rate of 60 mL/min, a filler dose of 60 g and a reaction time of 125 min; (d) room temperature with 60 mL/min aeration, 125 min reaction time and pH value 2; (e) 60 mL/min aeration, 125 min reaction time, pH value 2 and 45 g filler dose. Data are the mean ± S.D. (n = 3) from three independent experiments. Statistical analysis was performed using one-way ANOVA followed by Student’s t-test. (P < 0.05).
93.41% ± 2.94% and 96.1% ± 1.75%, respectively. The degradation rate of methyl orange increases greatly when the reaction temperature increases from 5 °C to 25 °C. When the reaction temperature increases from 25 °C to 40 °C, the degradation rate increases to a certain extent, but the enhancement effect is not significant. The main reason for this result is that with increasing temperature, the rate of thermal motion between molecules increases, the proportion of active molecules increases, and the rate of micro-electrolysis reaction and the treatment effect are accelerated. Maintaining the reaction temperature at 40 °C in the actual treatment process requires a substantial amount of heat consumption, and the filler can achieve a higher degradation rate at room temperature; thus, the experimental reaction temperature is set to room temperature.

**Methyl orange degradation mechanism**

Figure 4 shows typical UV–vis spectra of the solution and the methyl orange solution treated for reaction times of 0, 30, 60, 90, and 120 min. A spectrophotometer was used to scan methyl orange at a wavelength of 150–700 nm. Methyl orange molecules contain an azo bond, and the colour of the dye is caused by the azo bond of the chromogenic group (Chen et al. 2011). Methyl orange has two distinct absorption peaks; the peak at 464 nm is caused by the electron transition of the macro-conjugated system formed by the azo bond and the whole molecule and the absorption peak at 269 nm is caused by the electron transition of the benzene ring conjugate system, which is related to the benzene ring (Fan et al. 2009; Zhang et al. 2012). The results show that the absorption peak of the chromogenic group azo bond (−N=N−) of methyl orange at 464 nm decreases with increasing reaction time, which indicates that the azo structure of methyl orange is destroyed and that the methyl orange is broken into small molecules with a benzene ring structure.

Therefore, a possible degradation mechanism of methyl orange is shown in Figure 5. First, iron loses electrons, and then the electrons react with hydrogen ions in solution on the carbon cathode to form nascent hydrogen [H]. The strong activity of [H] can cause the azo bond (−N=N−) in methyl orange molecules to break down and reduce to aniline, and some [H] can produce H2. At the same time, Fe0 and Fe2+ can react with methyl orange to form aniline small molecule substances. After the micro-electrolysis reaction is completed, if the pH of the wastewater is adjusted to alkaline, Fe2+ and Fe3+ can react with OH− to form Fe(OH)2/Fe(OH)3 colloids. The newly produced colloids...
have good flocculation and sedimentation effects and can precipitate part of the organic matter.

**Scanning electron microscopy (SEM) analysis**

The appearance of the Fe-C filler used in this study is shown in Figure 6. Overall, the Fe-C filler was black and globular, and its particle diameter was approximately 15 mm. The SEM image of the filler (B) showed that it contained various pore structures, similar to other micro-electrolysis fillers in previous studies (Yang et al. 2017). It can be seen from Figure 6(b) and (c) that the difference in microstructure of the micro-electrolytic filler before and after use is obvious, the surface of the filler is clean and uniform before use, and after the reaction, the filler is corroded, and a small amount of amorphous particles are present on the surface. In addition, the surface of the filler is corroded but still uniform, which indicates that zero-valent iron and activated carbon particles are sintered into an integrated structure so that iron and carbon are not easily separated, the iron on the surface is consumed, and the adjacent activated carbon is peeled layer by layer. At the same time, because of aeration, the aggregates and sediments on the surface of the filler can be removed, and the surface of the filler can be updated over time so that the passivation and agglomeration of the traditional micro-electrolytic filler does not easily occur. Therefore, the filler can effectively solve the problems of passivation, blocking and bonding.

![Figure 6](https://iwaponline.com/wst/article-pdf/79/12/2279/595989/wst079122279.pdf)

Figure 6 | (a) Appearance of the filler; (b) SEM images before filler use; (c) SEM images after filler use.
X-ray diffraction (XRD) analysis

Fe-Cu-C ternary micro-electrolytic fillers were studied by XRD. As shown in Figure 7, there is an obvious diffraction peak at 44.9, which is the characteristic diffraction peak of FeO. The peaks at 43.3, 50.4, and 74.2 correspond to the diffraction peaks of copper (Wu et al. 2015; Yu et al. 2019). In addition to metallic elements, some metal oxides are present. The characteristic diffraction peaks of Fe3O4 occur at 65.2 (Huang et al. 2018). This may be because during the preparation of the filler, a small amount of water still remains in the interior after drying and reacts with iron powder to produce ferric oxide at high temperatures.

Comparison of degradation rate for methyl orange with various micro-electrolysis materials

Table 1 shows a comparison of the maximum degradation rate of micro-electrolysis materials found in the recent literature, and the best operating parameters are also presented. A direct comparison of degradation rate is difficult due to different experimental conditions; however, these data are sufficient to show that the Fe-Cu-C ternary micro-electrolysis filler have a degradability of the same order of magnitude as other micro-electrolysis fillers (and better in some cases). It should be noteworthy that the advantage of Fe-Cu-C ternary micro-electrolysis filler is that copper can enhance the cathode performance and make the electron transfer rate produced by the galvanic cell reaction more efficient. Moreover, in the reaction process, because various raw materials are sintered together, there will be no separation of anode and cathode. The high degradation rate of the Fe-Cu-C ternary micro-electrolysis towards methyl orange reveals that the Fe-Cu-C ternary micro-electrolysis filler could be promising for practical applications in methyl orange dye degradation from wastewater.

CONCLUSION

The optimum process conditions for the treatment of simulated printing and dye wastewater by using new micro-electrolytic fillers are as follows: aeration rate, 60 mL/min; initial pH, 2; filler dose, 45 g; and reaction time, 125 minutes at room temperature. The degradation rate of simulated dye wastewater reaches 93.41% ± 2.94%, which indicates an excellent degradation ability. UV-vis analysis showed that the degradation of methyl orange was due to the destruction of the azo bond of its chromogenic group, which converted it into small molecules containing a benzene ring. Under high-temperature roasting, the filler forms an integrated structure, and the effective components, such as iron and carbon, are closely contact. During the reaction process, the filler is peeled off layer by layer, so the problem of solidification and passivation of the filler does not easily
occur. And the Fe-Cu-C ternary micro-electrolysis filler could be promising for practical applications in dye degradation from wastewater.

**ACKNOWLEDGEMENTS**

This research was supported by the Prospective Joint Research Project of Industry, University and Research in Jiangsu Province (BY2016005-11), and National Science and Technology Support Plan (no. 2015BAE111B03).

**REFERENCES**


Zhang, C., Dong, Y., Li, B. & Li, F. 2018a Comparative study of three solid oxidants as substitutes of H₂O₂ used in Fe (III)-oxalate complex mediated Fenton system for photocatalytic elimination of reactive azo dye. *Journal of Cleaner Production* 177, 245–253.

Zhang, L., Yue, Q., Yang, K., Zhao, P. & Gao, B. 2018b Analysis of extracellular polymeric substances (EPS) and ciprofloxacin-degrading microbial community in the combined Fe-C microelectrolysis-UBAF process for the elimination of high-level ciprofloxacin. *Chemosphere* 193, 645–654.


First received 13 February 2019; accepted in revised form 29 June 2019. Available online 9 July 2019.