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Original Research Paper

A Novel Application of Micro Electrolysis-Fenton Process on High-strength Acidic Dye Wastewater

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ABSTRACT

A combined process, micro electrolysis-Fenton process was chosen as the pre-treatment performance of high-strength dyestuff wastewater. The software tool ANLYSIS CFX® was employed on simulation of the reactor. Meanwhile, comparative experiments were carried out and it was determined that the micro electrolysis-Fenton process was superior to the traditional one in terms of treatment effect. Optimal conditions were attained by experimental conditions changing. The results show that under optimal conditions, the BOD_5/COD ratio could be increased from 0.08 to 0.46 and the COD removal rate could be more than 75%. This process was highly efficient in organic matter removal and biodegradability improving.

INTRODUCTION

It is estimated that ca. 1 million tons of dye is manufactured every year. At the same time, more than 15.1% of the world dye production is discharged into the environment during synthesis, processing and using. Besides the negative effects on water appearance, which makes it repulsive to consumers, the presence of organic matter in the natural waters is directly associated with toxicity and carcinogenicity caused by dyes, surfactants, suspended solids, organochlorinated compounds, etc. that can be present in the effluents (Cisneros 2002).

Kinds of techniques such as biodegradation, membrane filtration, adsorption, coagulation, classic Fenton's agent, incineration and lime precipitation have been developed to solve these problems caused by those toxic or refractory organic matters in industrial effluents (Oktem 2007, Wei 2010, Garcia 2007, Mascolo 2010, Ghoreishi 2003). A few of them have led into industrial applications. However, most of these treatments result in secondary pollution, since they transfer the toxic or refractory substances from the liquid phase to other phases such as the sludge, used membranes, and saturated adsorbents, which cause another environmental problem (Benkli 2005). Therefore, there has been an increasing interest in some other technologies, e.g. electrolysis processes that is an alternative destructive treatment in which chemical species are reduced into smaller fragments and even to the point of mineralization. The electrochemical technologies were found to be successful in removing pollutants in various industrial wastewaters (Ahn 1999, Ghoreishi 2003, Chen 2004, Mantzavinos 2004). Nevertheless, all these techniques are too expensive to be afforded and difficult to be effectively utilized. Meantime, conventional biological processes which are thought to be economic are not effective for treating dyestuff wastewater because many commercial dyestuffs are nonbiodegradable or toxic to the organisms being used and result in the problems of sludge bulking, rising sludge and pinpoint floc (Nelson 1991). Therefore, to enhance the treatment efficiency from the view of economy, it is necessary to change the characteristics and improve the biodegradability by certain pre-treatment processes.

In this way, the aim of present work is to optimize the performance conditions on organic load and toxicity reduction, biodegradability improvement and other degradation behaviours of real dyeing effluents.

MATERIALS AND METHODS

Materials: Fresh dye effluent samples were collected from a dyestuff chemical plant located in Nanchang, in south China region. The dye effluent was characterized by high organic load, and toxic and nonbiodegradable in nature (Table 1).

Swarf was recycled form a certain machine factory. Sodium hydroxide (NaOH, analytical grade), hydrochloric acid (HCl, certified), granular activated carbon (GAC, φ3mm × 5mm), and all other agents were purchased from local chemical company, and were used as received without previous purification.

Experimental Procedures: The procedure of the microelectrolysis-Fenton pre-treatment process is shown in Fig. 1. After pH adjustment, the raw wastewater was delivered into the microelectrolysis reactor with/without aerating. Then, it was filled into the Fenton's agent reactor. After mixing with PAM and $Ca(OH)_2$, it was transferred into the clarifier. It can be treated by the biological process after the pre-treatment.

Analytical methods: The mineralization rates were calculated by COD decrease. The toxicity reduction and biodegradability improvement were evaluated by the ratio of BOD_5/COD (Sarria 2002). To eliminate the influence of the remaining H_2O_2, samples were heated up to 70°C after pH adjustment to 10. All the techniques used in analysis followed standard methods (Kurt 2002).

RESULTS AND DISCUSSION

Performance of the Microelectrolysis Process

Simulation of the reactor: To make the reaction conditions clear in the reactor, the software tool ANLYSIS CFX® was employed for simulating the reactor. It was assumed that all the particles in the reactor are in the same size without shape changing, distributed homogeneously; the liquid is incompressible fluid without heat transferring. As shown in Fig. 2 and Fig. 3, there are few dead zones, reflux, eddy currents and the pressures are nearly the same as the real ones. The flow patterns are much better than the conventional one's,

Table 1: Dye wastewater characteristics.

Quantity (td^{-1})	COD (mg/L)	(BOD_5/COD) ratio	pH	Salinity (%)
150	13000-15000	≤ 0.08	1-2	3-5

which could help the microelectrolysis reaction. It means higher efficiency, less reaction time and reactor volume needed.

Swarf granularity dependency: More and more primary cells formed as the size of the swarf lessen, which means the increasing of the specific surface areas. The COD removal rate increased with reduction of swarf sizes (Fig. 4). Nevertheless, it fell when the swarf was too small in size. As more and more swarf lost in the effluent, the COD removal rate reduced. Thus, the original swarf without any pre-treatment on size was used and it showed economic and environmental friendly.

Effect of iron/GAC volume ratio: To investigate the influence of the iron/GAC volume ratio on COD removal, series of tests were carried out (Fig. 5). The COD removal increased as the ratio stepped up; around 1 it gave the greatest removal (30.3%), and then decreased quickly. Few cells were formed as the ratio was too high or low. When they were equal on volume, the most cells would work and the highest organic removal be obtained.

Effect of pH: The solution pH has influence on the potential differences of the cells. In 60 min reaction with pH adjusted from 0 to 6, iron/GAC volume ratio 1:1, COD removal efficiency was obtained (Fig. 6). The COD removal rate increased as the pH stepped up and a pH at 1 gave the greatest removal (30.1%), then it fell down. The lower the

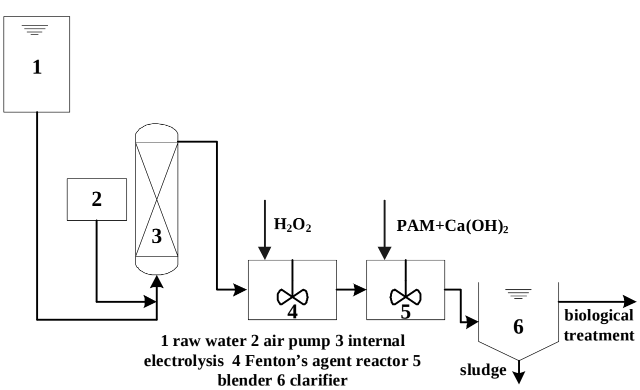

Fig. 1: Flow pattern simulating in the reactor.

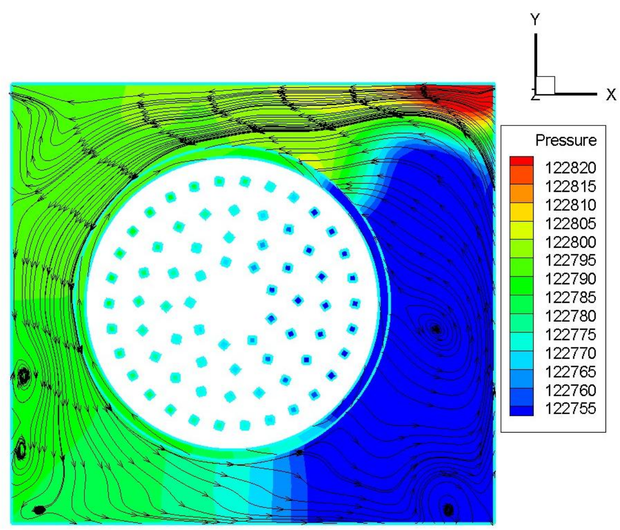

Fig. 2: Pressure profile simulating in the reactor.

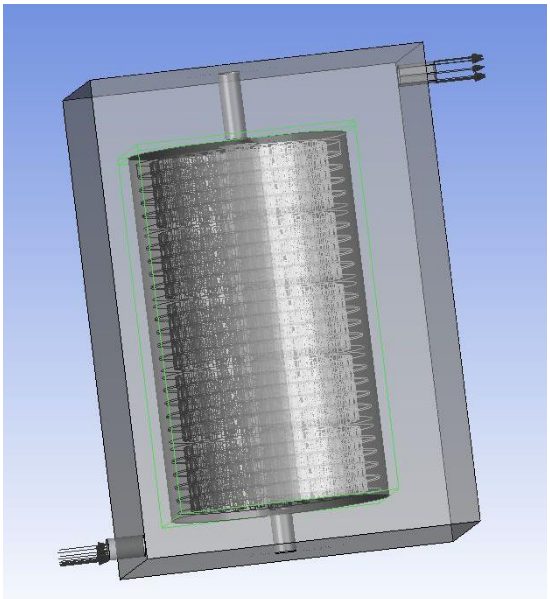

Fig. 3: Schematic diagram of experimental set-up.

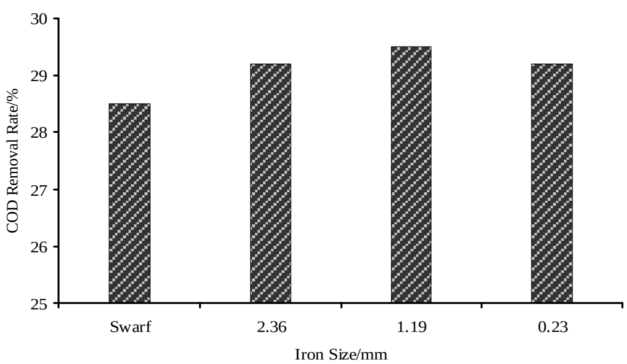

Fig. 4: Effect of iron granularity on COD removal.

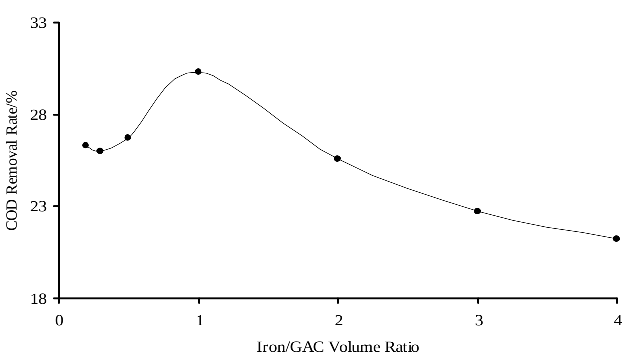

Fig. 5: Effect of iron/GAC volume ratio on COD removal.

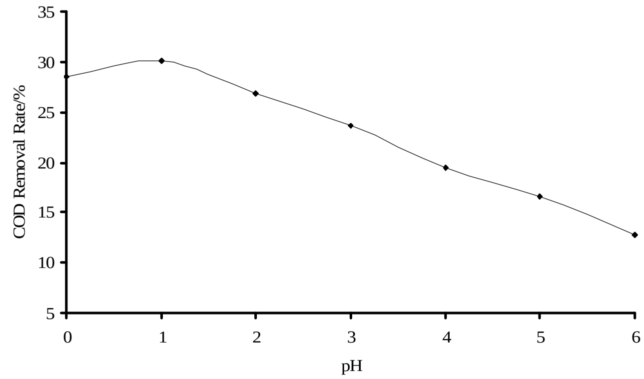

Fig. 6: Effect of pH on COD removal.

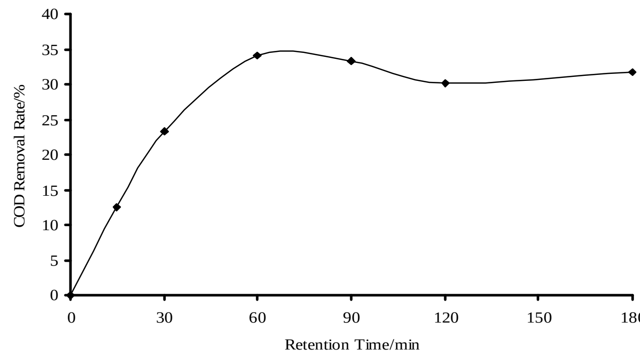

Fig. 7: Effect of retention time on COD removal.

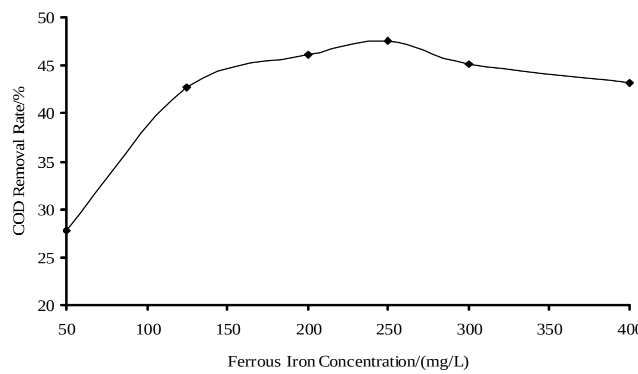

Fig. 8: Effect of Fe^{2+} concentration on COD removal.

pH is, the bigger the potentials are. The anode of the cell became passive as the pH was too low.

Reaction time dependency: As reaction time increased the COD removal rate stepped up (Fig. 7). After 60 min reacting, the increment was little and it dropped some time for the organic desorbing from the GAC. The reactor volume would be bigger as the retention time increased and the cost would be increased.

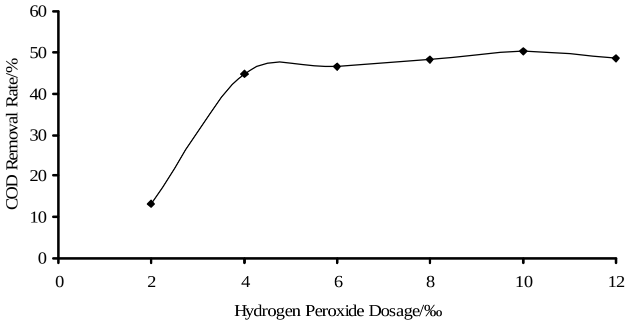

Fig. 9: Effect of hydrogen peroxide dosage on COD removal.

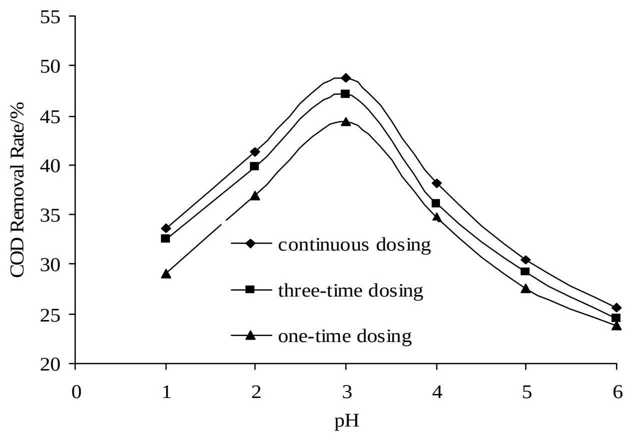

Fig. 10: Effect of different dosing methods on COD removal.

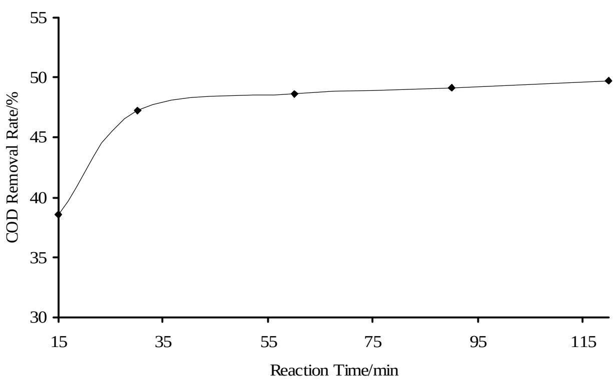

Fig. 11: Effect of reaction time on COD removal.

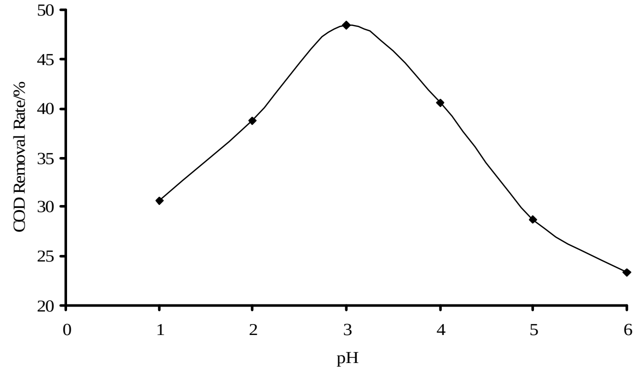

Fig. 12: Effect of pH on COD removal.

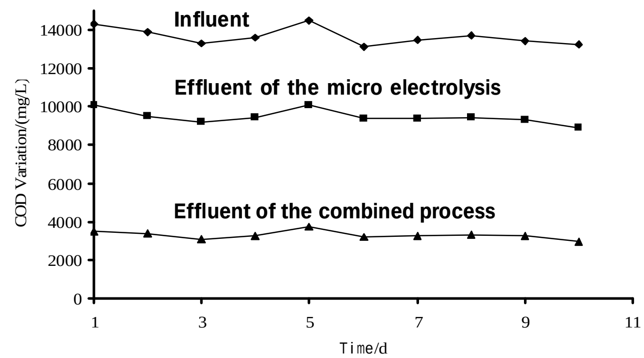

Fig. 13: Performance of the microelectrolysis-Fenton process.

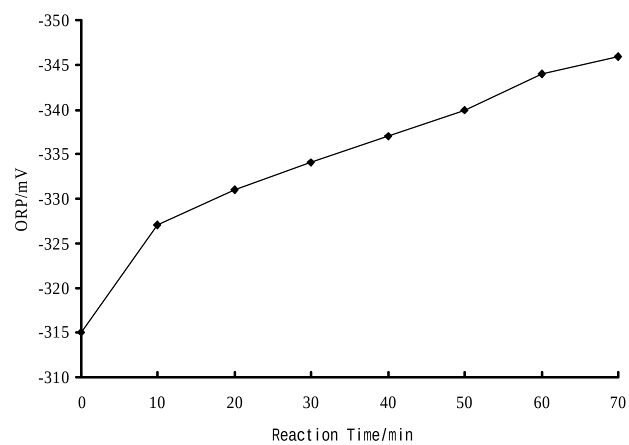

Fig. 14: Variation of ORP by reaction time.

Performance of the Fenton's Agent

Effect of Fe^{2+} concentration: Fe^{2+} plays a role of excitation and transfer. With H_2O_2 dosage 4‰, COD removal variation on Fe^{2+} concentration changing was obtained (Fig. 8). COD removal rate stepped up quickly till [Fe^{2+}] increased to 125mg/L and it dropped when [Fe^{2+}] > 250mg/L. More Fe^{2+} would take more OH·. However, redundant OH· reacted with each other and made it a waste (Wang 2002). Thus, the concentration of Fe^{2+} between 125mg/L and 250mg/L was recommended. When the effluent pH was 2, [Fe^{2+}] was about 200mg/L.

Influence of H_2O_2 dosage and the way of H_2O_2 dosing: In 30 min reaction at pH 4 and H_2O_2 dosage of 2‰, 4‰, 6‰, 8‰, 10‰, 12‰, COD removal efficiency was obtained (Fig. 9).

Table 2: Biodegradability improvement.

Type	Influent	Effluent of the micro electrolysis	Effluent of the combined process
BOD_5/COD ratio	≤ 0.08	0.26	0.46

COD removal rate increased quickly when H_2O_2 dosage changed from 2‰ to 4‰, and became slow as the dosage became more than 4‰. Meantime, the way of H_2O_2 dosing had significant influence on organic removing. It was found that the continuous dosing is superior to one-time dosing and three-time dosing (Fig. 10). Large amount of H_2O_2 dosage in a short time means a waste of money.

Reaction time dependency: At room temperature, with H_2O_2 dosage 4‰ and pH 3, COD removal rate variation with reaction time was obtained (Fig. 11). It increased significantly at first and became slow after 30 min.

Effect of pH: Fenton's agent works under acidic condition and Fe^{2+} precipitated under alkalinous and neutral conditions. The reaction equations are shown as below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \quad ...(1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OH\cdot_2 \quad ...(2)$$

$$OH\cdot_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O\cdot_2 \quad ...(3)$$

The largest COD removal was attained around pH 3 (Fig. 12). Chain reaction (1) was inhibited when pH > 6 and chain reactions (2) and (3) were inhibited when pH < 3. Meantime, pH had an effect on the balance between Fe^{2+} and Fe^{3+} which affected the oxidizability of the Fenton's agent greatly.

Performance of the Microelectrolysis-Fenton's Agent Process

Performance of the combined process: The performance of the combined pre-treatment process is shown in Fig. 13, under a condition of Fe/GAC volume ratio 1, pH = 2, reaction time 60min; and pH = 3, 4‰ H_2O_2 continuous dosing, reaction time 30 min. As COD of the influent varied from 13000mg/L to 15000mg/L, the total removal rate was above 75%. It offered the following biological treatment a stable supply.

Biodegradability improvement: BOD_5/COD ratio was taken as the parameter of biodegradability to evaluate the performance of the combined pre-treatment process. As shown in Table 2, the BOD_5/COD ratio was increased from 0.08 to 0.46 with an increment of 0.38. It is concluded the organic-high refractory dyestuff wastewater was successfully pre-treated to biodegradable (Symons 1960).

Comparison of the combined process and the classic Fenton's agent process: The rate rise of the oxidation-reduction potential was stable in 60min reaction time (Fig. 14). It means that the microelectrolysis was steady and Fe^{2+} was released smoothly. At the same time, H_2O_2 was dosed continuously. It made all the agents fully used. While in the classic one, OH· was released in short time and always made it waste.

CONCLUSIONS

The obtained results prove that the microelectrolysis-Fenton process applied on raw dyestuff wastewater as pre-treatment resulted in removing a large amount of recalcitrant compounds as well as in decreasing toxicity and improving biodegradability. More detailed studies would be necessary in order to optimize these techniques for industrial scale and sequencing biological treatment. Nevertheless, studies such as this one already indicate that it is possible to implement this kind of waste pre-treatment, particularly in the dyestuff industry, since the matrices of this kind of effluents are not amenable to biodegrade.

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