

# Studies on degradation of Methyl Orange wastewater by combined electrochemical process

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Received 14 September 2006; received in revised form 1 February 2007; accepted 6 April 2007

Available online 8 April 2007

## Abstract

The combined process of electro-catalytic oxidation and de-colorization of wastewater contained Methyl Orange (MO) in a double-anode system, with iron plate and graphite plate as anodes and graphite plate as cathode assisted by  $\text{Co}_2\text{O}_3\text{-CuO-PO}_4^{3-}$  modified kaolin, was investigated systematically. The effects of pH, current density and electrolyte on de-colorization efficiency were also studied. Chemical oxygen demand (COD) was selected as another parameter to evaluate the efficiency of this combined degradation method on treatment of MO wastewater and the results revealed that when initial pH was 5.0, current density was  $30 \text{ mA cm}^{-2}$ , NaCl as electrolyte and its concentration was  $2.5 \text{ g dm}^{-3}$ , the color removal efficiency and COD removal can reach 100% and 89.7%, respectively. Meanwhile, the kinetics and the possible mechanism were also discussed. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Electro-catalytic oxidation; Double-anode system; Methyl Orange; De-colorization

## 1. Introduction

Dye wastewater usually consists of a number of contaminants including acids, bases, dissolved solids, toxic compounds, and colored materials which are noticeable even at very low concentrations and must be removed before the wastewater can be discharged. It is reported that approximately 5 tonne of dye discharge from dyes and coloration industries every year [1]. Due to environmental requirements in recent years, different techniques have been used, e.g. adsorption, oxidation, reduction, and electrochemical reactions. They have individual advantages, but also have some constraints causing inadequate effectiveness when applied individually [2]. For example, adsorption on activated carbon is only successful for hydrophobic dyes, chemical coagulation can produce huge volume of hazardous sludge and poses a problem of sludge disposal and cannot bring any effect for dissolved dyestuffs. Fenton's reagent is effective only when  $\text{pH} < 3.5$  [3,4]. Ozonation can result in colorless of dye wastewater, however, hazardous organic materials is slightly reduced, producing high final total organic carbon (TOC) and chemical

oxygen demand (COD) values, together with high operational cost [5–7].

Electrochemical techniques, a powerful means of pollution control, are considered as an attractive methodology for the treatment of dyeing wastewater. Electrochemical treatment was considered as a relatively proper technique and this novel technique has certain significant advantages namely: wide application, simple equipment, easy operation, lower temperature requirements and no sludge formation [8–13]. Several researchers have investigated the feasibility of electrochemical degradation of dyes with various electrode materials for wastewater treatment, such as titanium-based DSA electrodes [14], platinum electrode [15], diamond and metal alloy electrodes [16] and boron doped diamond electrodes [17,18]. Some researches also investigated electro-coagulation methods for dye removal with aluminum [19] or iron [20] electrodes. Most researches provided information on electrode materials during the dye degradation, while not much information was provided for the synergetic effect of electrochemical degradation assisted by adsorption method.

In the work described here, a previously developed model [21] describing the electrochemical treatment of wastes containing surfactant compounds was applied to study the processes occurring when wastewaters polluted with dyeing. We attempt

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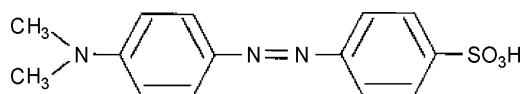


Fig. 1. Methyl Orange structure.

to identify electro-catalytic degradation of MO wastewater by electro-catalytic-oxidation and electro-coagulation combined process and the conjunctional effect when integrating the catalyst (modified kaolin) into the electro-coagulation system. Additionally, a brief discussion on the kinetic study and possible mechanism has also been proposed. Moreover, the optimal parameters (such as initial pH, current density and the concentration of electrolyte) in treating the wastewater containing MO in this combined process were also studied. The last section compares the electrochemical degradation process with  $\text{H}_2\text{O}_2$ -catalyst system.

## 2. Materials and methods

### 2.1. Reagents

All chemicals used in the experiment are of analytical grade and used without further purification. Methyl Orange (Fig. 1) is obtained from Ciba Co. (Switzerland).

Kaolin, provided by Shanghai Reagent Co., China, are composed of  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$  (surface area:  $20 \text{ m}^2 \text{ g}^{-1}$  and pore volume:  $0.5 \text{ cm}^3 \text{ g}^{-1}$ ).

The concentration of Methyl Orange in wastewater used in the experiments was  $400 \text{ mg dm}^{-3}$ .  $\text{NaCl}$  ( $0.15 \text{ mol dm}^{-3}$ ) or  $\text{Na}_2\text{SO}_4$  ( $0.15 \text{ mol dm}^{-3}$ ) was used as electrolyte, and  $\text{NaOH}$  or  $\text{HCl}$  in proper amounts was used to get the suitable pH value.

### 2.2. Catalyst preparation and characteristics

$\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$  modified kaolin was prepared by impregnation method as our early paper [21]. The catalyst has

the BET surface of  $38 \text{ m}^2 \text{ g}^{-1}$  compared with the neat kaolin of  $20 \text{ m}^2 \text{ g}^{-1}$  BET surface. By the modification process, the previous kaolinite structure has disappeared and a new pored structure has been formed.

### 2.3. Set-up of wastewater treatment

The schematic diagram of experimental set-up of EC cell with catalyst is shown in Fig. 2. Double anode and single cathode were positioned vertically and parallel to each other with an inter gap of 0.5 cm. The materials used for the anode are ion plate and graphite plate, and that used for the cathode is graphite plate. The superficial surface of working electrode ( $3.4 \text{ cm} \times 6 \text{ cm}$ ) was  $20.4 \text{ cm}^2$ . Ten grams of smashed catalyst was introduced in the solution to form a multi-phase electrochemical oxidation reactor, with a working volume of  $0.15 \text{ dm}^3$ . The solution was constantly stirred at 100 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated DC power supply, WYK302B2, Xi'An, China. The current and voltage were adjustable between 0–2.5 A and 0–35 V, respectively.

### 2.4. Analysis techniques

All the experiments runs were conducted in duplicate and analysis of each parameter was done triplicate for each run. The coefficient of variation obtained was not more than 5% for the three determinations and for the experiment runs conducted in duplicate. The initial pH of the solution was tested using an Orion 290 pH meter. COD during the electrolysis was determined by an open reflux, dichromate titrimetric method as described in standard methods [22]. All parameters are measured according to standard methods for examination of water and wastewater [23]. During the degradation tests, dye concentration was determined by double beam UV-vis spectrophotometer (UV-7504, China). The maximum absorbency visible wavelength (470 nm)

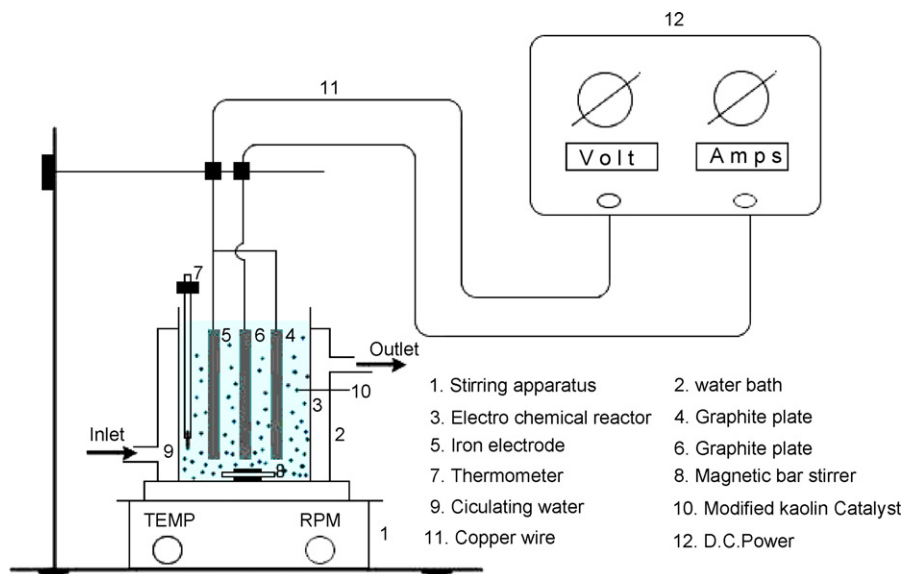


Fig. 2. Schematic diagram of experimental set-up of EC cell.

was detected and used as color removal index. Color removal ratio was calculated as our previous paper [24].

### 3. Results and discussion

#### 3.1. Effect of initial pH

In general, MO has two chemical structures dependent on pH value of solution. Quinoid structure is a main form at low pH value while azo structure at high pH. It is expected that pH value of solution possibly affected electro-catalytic reaction on electrode surface. Therefore, the effect of initial pH of MO wastewater on de-colorization efficiency was investigated in this work. Apparently, appropriate pH is benefit to the cleavage of the azo bond.

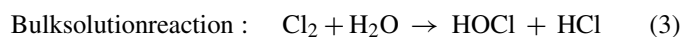
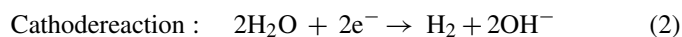
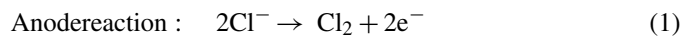
As can be seen from Fig. 3, a significant difference on de-colorization was noted with NaCl as electrolyte at initial pH 2, 5, 9 and 11, respectively. It was observed that MO molecules were readily decomposed when initial pH was 5.0. The efficiency of decomposition was, however, considerably effectively in the appropriate acidic solution (the de-colorization efficiency can reach 84%) than that of in the alkaline solution when initial pH was 11 (the de-colorization efficiency was only 31%), indicated that the catalytic activity of the modified kaolin in acid solutions is higher than that of in the basic media.

In this combined electrochemical degradation process, electro-coagulation process was combined with catalytic oxidation process. The pollutant was mainly degraded by electro-catalytic oxidation, because modified kaolin has very strong adsorption and catalytic property. When operated at moderate pH, the sweep flocs  $\text{Fe}(\text{OH})_3$  and other hydroxyl species, produced on the sacrificial anode, coagulated with modified kaolin, which promoted the degradation process and made the suspended particles to deposit. As Fig. 3 shows, the best initial pH was 5 and could meanwhile achieve 95% de-colorization efficiency of MO after 60 min, which can be explained that when in this pH region, the degradation process can occur effectively

by both catalytic-oxidation and chemical coagulation.  $\text{Fe}^{3+}$  ions may undergo hydration to form  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$  and other species under moderate acid conditions. A lowest de-colorization efficiency was observed at pH above 11, which is probably due to less  $\text{Fe}(\text{OH})_3$  formation and low catalytic activity.

#### 3.2. Effect of supporting electrolyte

Fig. 4 shows two supporting electrolytes ( $\text{Na}_2\text{SO}_4$  and NaCl) and their concentration on de-colorization efficiency. As can be seen, when  $\text{Na}_2\text{SO}_4$  was substituted by NaCl, the de-colorization efficiency increased from 68.8% to 95% after 60 min, which fully indicated that introduction of NaCl as electrolyte can enhance the degradation efficiency and shorten reaction time, maybe due to the reaction between the generated chlorine/hypochlorite and dye molecule. The pollutants were oxidized by chlorite/hypochlorite that were then reduced to chlorite ion.



This was classified as indirect oxidation and also promoted electro-catalytic oxidation of pollutant. Moreover, the increased NaCl can result in a rise of current density at the same voltage. Therefore, the effect of NaCl dosage in terms of de-colorization efficiency has been studied. Increasing the concentration of NaCl up to  $2.5 \text{ g dm}^{-3}$  accelerated the removal rate, enabling complete mineralization of the MO to an extent of 99% de-colorization efficiency in 60 min [21]. A further increase in NaCl concentration (up to  $5 \text{ g dm}^{-3}$ ) did not bring about any improvement in de-colorization efficiency, so the optimal NaCl concentration used in the successive experiments was  $2.5 \text{ g dm}^{-3}$ .

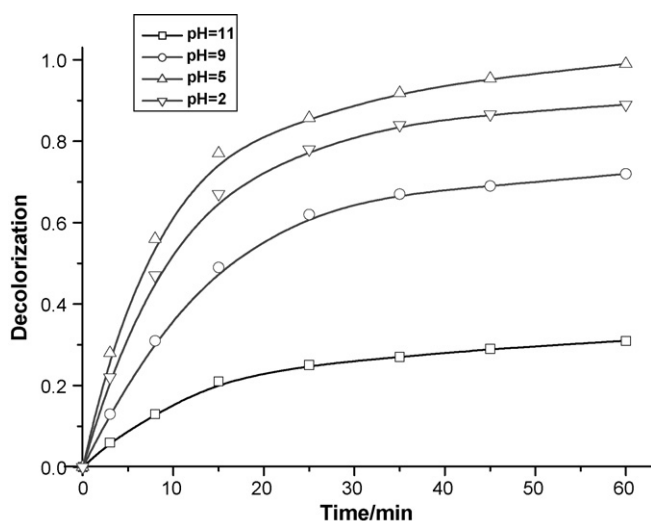


Fig. 3. Effect of initial pH on de-colorization efficiency of MO (room temperature; current density:  $30 \text{ mA cm}^{-2}$ ; NaCl:  $2.5 \text{ g dm}^{-3}$ ; MO:  $400 \text{ mg dm}^{-3}$ ).

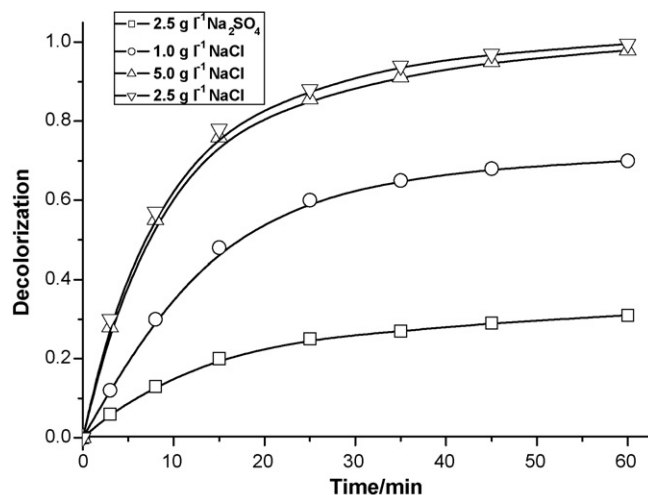


Fig. 4. Effect of different supporting electrolyte and their concentration on dye removal (room temperature; initial pH: 5.0; current density:  $30 \text{ mA cm}^{-2}$ ; MO:  $400 \text{ mg dm}^{-3}$ ).

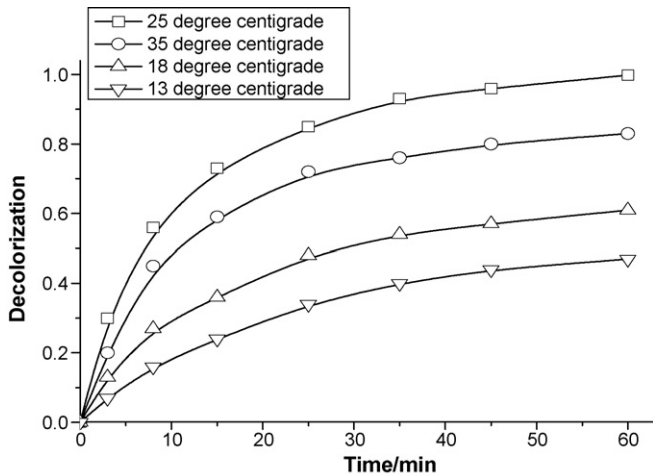


Fig. 5. Effect of reaction temperature on electrochemical degradation of MO (initial pH: 5.0; current density: 30 mA cm<sup>-2</sup>; NaCl: 2.5 g dm<sup>-3</sup>; MO: 400 mg dm<sup>-3</sup>).

### 3.3. Effect of temperature

Fig. 5 displays the de-colorization efficiency at different operating temperatures. Generally, high temperature can enhance the activity of catalyst. Hence, the dye degradation and evolution of oxygen are accelerated synchronously with temperature increasing.

However, when the operating temperature was above 25 °C, the degradation efficiency decreased, which was probably due to the adsorbed pollutants derived from catalyst surface. On the other hand, it is obvious that when temperature increase above 25 °C generation of chlorine/hypochlorite will decrease, which was proved by the experimental results: when the experiment was operated at these conditions: initial pH: 5.0, current density: 30 mA cm<sup>-2</sup>, NaCl: 2.5 g dm<sup>-3</sup>; MO: 400 mg dm<sup>-3</sup>, 40.1 and 17.2 mg dm<sup>-3</sup> chlorine/hypochlorite were produced

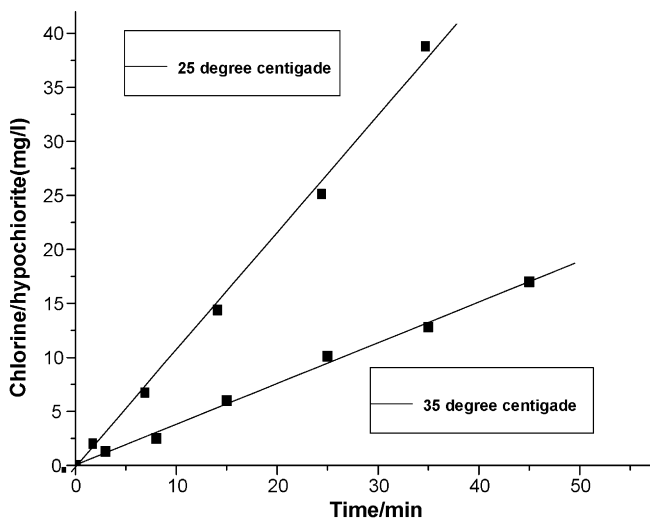


Fig. 6. Effect for reaction temperature on generation of chlorine/hypochlorite (initial pH: 5.0, current density: 30 mA cm<sup>-2</sup>, NaCl: 2.5 g dm<sup>-3</sup>; MO: 400 mg dm<sup>-3</sup>).

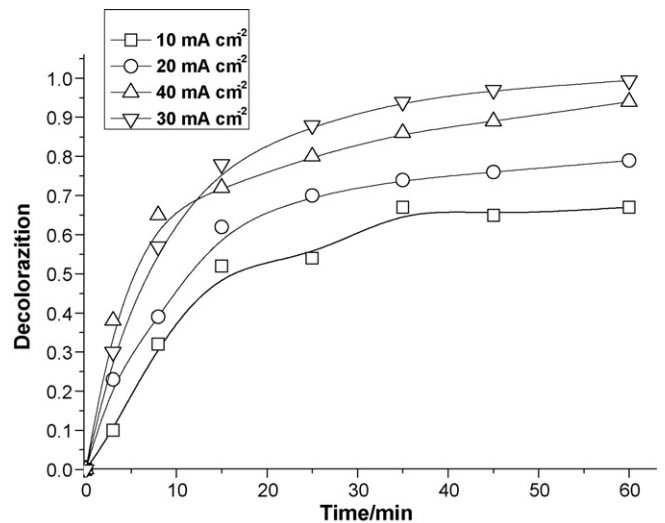


Fig. 7. Effect of applied current density on de-colorization of MO (initial pH: 5.0, current density: 30 mA cm<sup>-2</sup>; NaCl: 2.5 g dm<sup>-3</sup>, MO: 400 mg dm<sup>-3</sup>).

at 25 and 35 °C, respectively (Fig. 6). Consequently, the best de-colorization results can be achieved at 25 °C.

### 3.4. Effect of current density

Different current densities (10–40 mA cm<sup>-2</sup>) were applied to investigate the electro-catalytic degradation of MO in NaCl solution (2.5 g dm<sup>-3</sup>) at a 400 mg dm<sup>-3</sup> initial dye concentration at a solution pH of 5 and a temperature of 25 °C (Fig. 7). It can be found that de-colorization efficiency increased with increasing the applied current density, because of the increased production of oxidant such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. But when operating at higher current densities (above 30 mA cm<sup>-2</sup>), there was a moderate decrease on de-colorization, which can be attributed to the fact that increasing current density increases the over potential required for the generation of oxidants. At the same time, more energy will be consumed at higher current density applied. Therefore, the optimal current density for the successive electro-catalytic degradation is 30 mA cm<sup>-2</sup>.

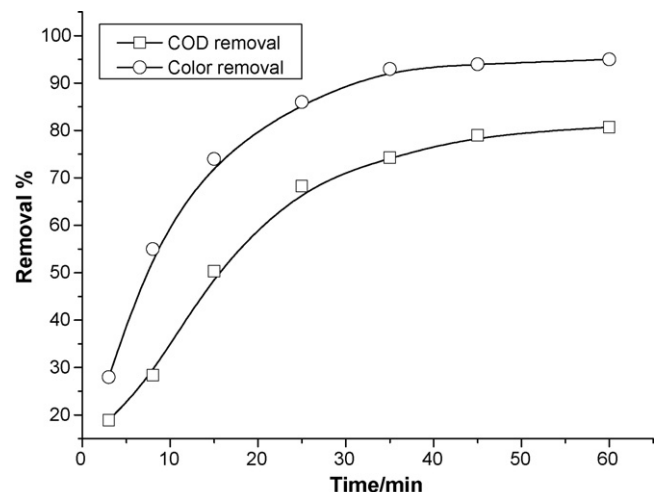


Fig. 8. COD and color removal at optimal conditions.

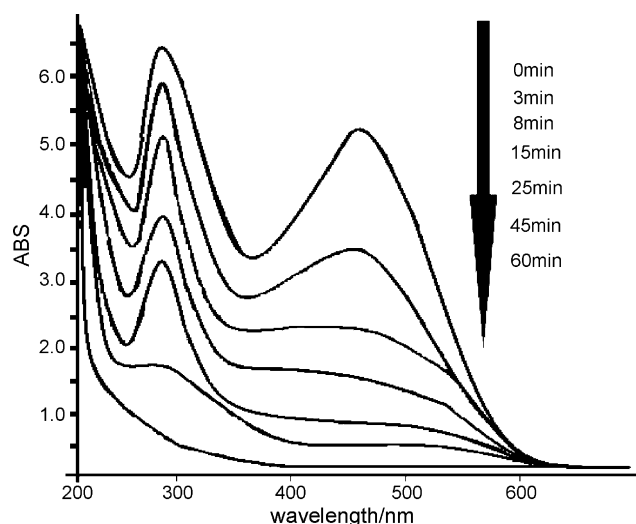


Fig. 9. UV-vis spectra during the electrochemical degradation of MO (initial pH: 5.0; NaCl:  $2.5 \text{ g dm}^{-3}$ , 10 g smashed catalyst, room temperature, MO:  $400 \text{ mg dm}^{-3}$ ).

### 3.5. Electrolysis time on COD and color removal

Effect of time on COD and color removal under the optimal conditions (initial pH: 5.0; room temperature; NaCl:  $2.5 \text{ g dm}^{-3}$ ; MO:  $400 \text{ mg dm}^{-3}$ ) was investigated. As can be seen from Fig. 8, COD and color removal increased as a function of time elapsed. After 60 min of the treatment, COD and color removal reached the maximum of 89.6% and 95%, respectively.

### 3.6. UV-vis spectral changes during the degradation process of Methyl Orange wastewater

A typical UV-vis spectrum of MO as a function of electrolysis time (60 min) was inspected (Fig. 9). A peak observed at 272 nm was assigned to azo structure of dye. The visible peak at 470 nm was attributed to aromatic rings in dye molecules. However, these two absorbency peaks decrease evidently after the treatment, it may be concluded that the conjugated bonds of MO must be destroyed and the molecules are broken into small ones.

## 4. Proposed mechanism

To further investigate the de-colorization process of MO, it is necessary to study the possible mechanism. Initially, it is well-known that the removal of dye is due to the cleavage of chromophore bond in the dye molecule. The whole degradation involves two main processes: catalytic-oxidation and electro-coagulation.

### 4.1. Kinetic studies

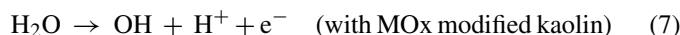
An exhaustive kinetic study has been carried out on the combined degradation of MO. Before addition of catalyst to the solution of MO, no remarkable change on the color was observed. However, when the catalyst was introduced, the oxida-

tive reaction was started and a gradual loss of the absorbance of MO was observed as Fig. 10 shown.

The kinetic measurements were conducted under pseudo-first-order condition. The observed rate constant,  $k_0$ , was determined from first-order kinetics plot,  $\ln A_t = \ln A_0 - k_0 w t$ , as shown in Fig. 10, where  $A_t$  is the absorbance at time  $t = t$ ,  $A_0$  is the absorbance at  $t = 0$ , and  $w$  is the amount of the catalyst used. The  $k_0$  value per g of dry catalyst (pgdr) was determined for the catalyst at optimal temperature and used to evaluate the activation parameters. It is well-known that the reaction of higher rate constant is associated with lower activation energy, which indicates that MO was easily attacked by oxidizing agent such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), OH radicals when the catalyst was introduced. The activity of the catalyst in  $\text{H}_2\text{O}_2$  decomposition was found to follow the same order [24,25].

### 4.2. Proposed mechanism

The degradation of pollutants by combined electrochemistry was concluded due to OH radicals produced by catalytic oxidation of modified kaolin and adsorption process of electro-generated  $\text{Fe}(\text{OH})_3$  “sweep flocs”. The catalytic oxidation process involve the following several steps: (i) mass transfer of  $\text{O}_2$  formed from anode toward the surface of cathode, slight OH radicals also generated form the anode, (ii) in moderate acidic conditions,  $\text{H}_2\text{O}_2$  is continuously produced by two-electron reduction of oxygen on the cathode surface.



(iii)  $\text{H}_2\text{O}_2$  were decomposed and also produced highly reactive hydroxyl radicals in the presence of heterogeneous catalyst, (iv) the reaction between OH radicals and organic pollutants adsorbed on the surface of catalyst. The role of the catalyst is not only to participate in catalyzing the formation and the decomposition of  $\text{H}_2\text{O}_2$  but also to adsorb the pollutants making the

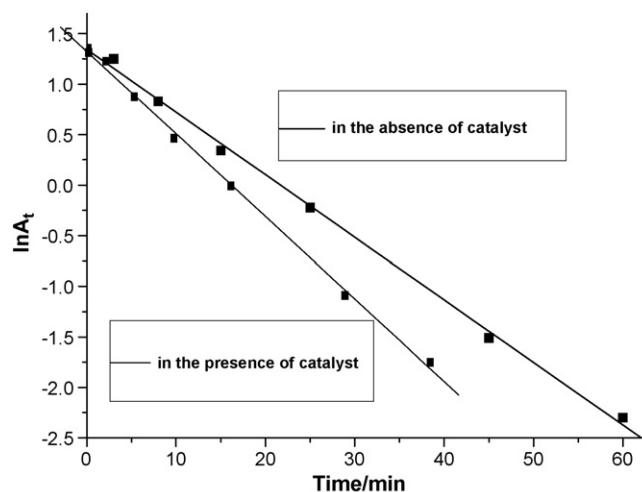


Fig. 10. First-order plot for the reaction of  $400 \text{ mg dm}^{-3}$  MO at  $\lambda = 470 \text{ nm}$  on de-colorization.



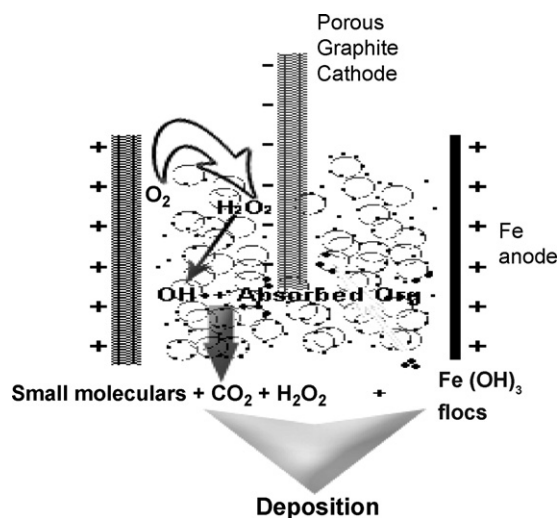
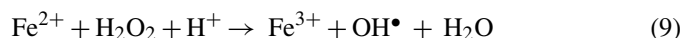


Fig. 11. Schematic diagram of the proposed mechanism.

further degradation readily occur on its surface [8,9,21]. On the other hand, electro-coagulation process involves the generation of coagulants in situ by dissolving electrically iron ions from ion anode [13]. The generation of iron ions takes place at the anode.



$\text{Fe}^{2+}$  reacted with  $\text{H}_2\text{O}_2$  in the acidic conditions to form OH radicals:



The excess of  $\text{Fe}^{3+}$  formed precipitates as  $\text{Fe}(\text{OH})_3$  “sweep flocs” have large surface area which are beneficial for a rapid adsorption of soluble pollutants and trapping of colloidal particles like suspended kaolin particles [15]. These flocs are polymerized as:



and are easily removed from aqueous medium by sedimentation. Secondary anodic reactions occur also during electro-coagulation. For example, in acidic conditions, with NaCl as electrolyte, native and free chlorine and hypochlorite are formed. Contaminants are then expected to be removed by the combined action of both their homogeneous degradation with OH radicals produced following Eq. (6) and coagulation with the  $\text{Fe}(\text{OH})_3$  precipitate. Furthermore, for all the parameter effect tested, the rate of degradation almost varies in the initial 20 min, this should ascribe to the great porous structure of the fresh catalyst, when the catalyst was introduced, the pollutants was immediately absorbed and concentrated, thus the rate of degradation enhanced. In other words, electro-catalytic oxidation played very important role in electrolysis processes. The main reaction mechanism of degradation of pollutant is summarized in Fig. 11.

#### 4.3. Comparison with $\text{H}_2\text{O}_2$ -catalyst system

To prove the possible mechanism proposed, another experiment has been conducted with  $\text{H}_2\text{O}_2$ -catalyst system to

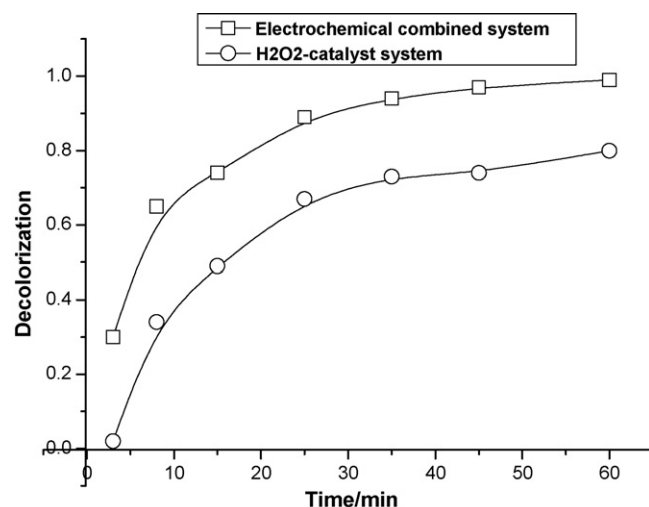


Fig. 12. Comparison of de-colorization rate under two different systems.

compare with that of combined electrochemical process. The de-colorization under two different systems is presented in Fig. 12. Two millilitres of 30%  $\text{H}_2\text{O}_2$  was added dropwise into the system per 10 min; it may be observed obviously that the de-colorization rate could barely reach 72% after 60 min with  $\text{H}_2\text{O}_2$ -catalyst system, which should be ascribed to the decompositions of  $\text{H}_2\text{O}_2$  in the presence of catalyst. However, it can also be seen from Fig. 12 that the de-colorization under  $\text{H}_2\text{O}_2$ -catalyst system was slower than that of electrochemical combined process, which demonstrated that reactions occurred in electrochemical combined system was not only the decomposition of  $\text{H}_2\text{O}_2$  generated by electrochemical reaction but also by other reactions (e.g. direct oxidation on electrodes).

## 5. Conclusions

The electro-catalytic oxidation treatment of Methyl Orange wastewater assisted by  $\text{CuO}-\text{Co}_2\text{O}_3-\text{PO}_4^{3-}$  modified kaolin in a double-anode system with iron plate and graphite plate as anode and graphite plate as cathode were investigated. The result of this study revealed the following: When the process was operated at pH of 5, room temperature and supporting electrolyte NaCl concentration of  $2.5 \text{ g dm}^{-3}$ , it can be achieved 100% color removal and 89.7% COD removal. The whole degradation of MO in our combined electrochemical reactor involved two eminent processes: catalytic oxidation and electro-coagulation, which is different from the path that proceeds in  $\text{H}_2\text{O}_2$ -kaolin system. It may also be concluded that the electrochemical degradation assisted by kaolin adsorption effect can improve the whole process of dyeing wastewater treatment.

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