



Electro-catalytic degradation of methylene blue wastewater assisted by Fe₂O₃-modified kaolin

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ABSTRACT

The electrochemical oxidation of methylene blue (MB) wastewater assisted by Fe₂O₃-modified kaolin in a 200 mL electrolytic batch reactor with graphite plate as electrodes was investigated. The catalyst was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effects of pH, current density and introduction of NaCl on the efficiency of the electrochemical degradation process were also studied. It was found that Fe₂O₃-modified kaolin has higher catalytic activity in the electrochemical degradation of MB wastewater. 96.47% chemical oxygen demand (COD) removal was obtained in 40 min of electrochemical treatment of MB wastewater at pH 3, current density was equal to 69.23 mA cm⁻².

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1. Introduction

As international environmental standards are becoming more stringent, technological systems for the removal of organic pollutants such as dyes have been recently developed. 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluent [1]. Conventionally the dyes wastewater can be treated by biological, physical and chemical methods [2,3]. Biological treatment processes are often ineffective in removing dyes which are highly structured polymers with low biodegradability [4]. And, various physicochemical techniques, such as chemical coagulation, adsorption on active carbon, reverse osmosis and ultrafiltration [2], are usually used to treat the wastewater contained dyes. But these methods are only available to the lower dye concentrations. In recent years, ozonation [4,5], photooxidation [5–7] and Fenton's reagent [8] have been reported as alternatives because of its high effective, but the high cost of these methods leads to further consideration.

Methylene blue (MB) is a prototype of dyestuffs that have wide applications, including coloring paper, temporary hair colorant, dyeing cottons and wools. Although not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans. MB is particularly resistant to biodegradation [9,10]. Although there have been numerous reports of photocatalytic MB degradation over TiO₂-based photocatalysts, most of the studies

were performed under UV light irradiation [10,11]. Recently, Zhao et al. [12] reported that some dyes could be degraded under visible light irradiation on TiO₂ by a self-photosensitized process, but MB is excluded. Up to now, only a few studies have been reported on MB dye degradation under visible light irradiation [12,13]. Furthermore, the catalytic efficiency is limited by the light absorption characteristics of TiO₂-based photocatalysts. Electrochemical technologies used to treat various wastewaters have been extensively investigated for the last two decades, researchers have been focused on the efficiency of oxidizing various pollutants on different electrodes and improvement of the electrochemical stability of electrode materials. Up to now, many works have been done to develop high performance anodes in respect of high catalytic activity, long life, etc. including glassy carbon electrode [14], carbon felt [15], Pt/Ti [16] and graphite [16]. Zhou and Lei [17] employed activated carbon as catalyst to degrade *p*-nitrophenol with electrocatalytic oxidation process, revealed that activated carbon played a important role in degrading *p*-nitrophenol.

Kaolin, which is quite abundant in the earth's upper crust, is an important raw material for manufacturing and investigating, and because kaolin was previously found to be effective in stabilizing metals [18] and catalyzing oxidation reactions [19]. For a long time, kaolin has been used to capture heavy metals such as Cr, Pb, Cd, and Ni at an elevated temperature [20]. Fewer reports have been found to use modified kaolin as an active catalyst to catalyze wastewater degradation process.

The aim of this work is to study the conjunctive effect when integrating the catalyst (modified kaolin) into the electrochemical system and find out the optimal parameters in treating MB wastewater. Moreover, a brief assessment of the treated wastewater on environment was made to study the possibility of its recycle.

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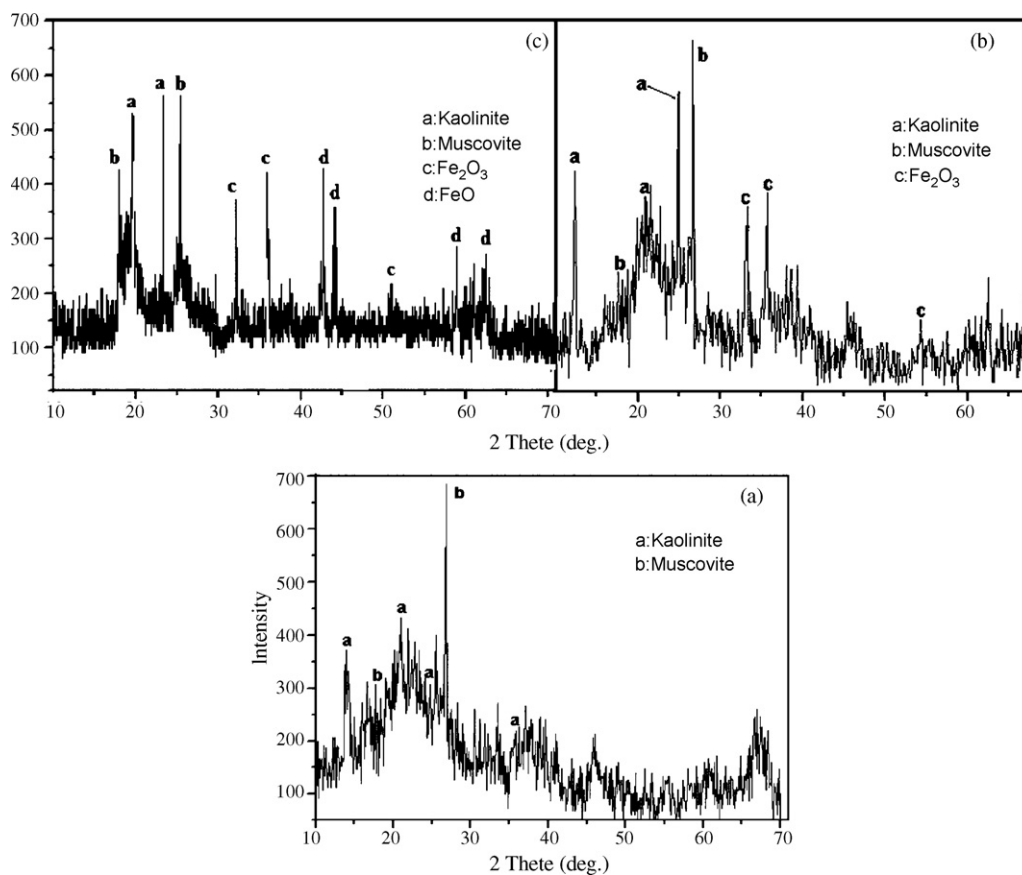


Fig. 1. XRD patterns of neat kaolin (a), Fe₂O₃-modified kaolin before reaction (b) and after reaction (c).

2. Experimental

2.1. Materials

All chemicals were analytical grade and used without further purification. Kaolin, provided by Shanghai Reagent Co., China, is composed of Al₄[Si₄O₁₀][OH]₈ [surface area: 20 m² g⁻¹ and pore volume: 0.5 cm³ g⁻¹]. 0.3 g L⁻¹ synthetic MB represented dye wastewater used in the experiment. NaOH or H₂SO₄ in proper amounts was used to get the suitable original pH value.

2.2. Preparation of catalyst

10 g FeCl₃, 100 g kaolin and 150 mL water were agitated with stirring for 4 h, then the pH of the solution was adjusted to neutral condition with 0.5 M NaOH solution. After that, the sample was aged at room temperature for 24 h and filtrated, washed until free from chlorine iron, followed by drying at 373 K for 4 h. To immobilize the metal, the prepared dried slurry was calcined at 873 K for 4 h.

2.3. Treatment of methylene blue wastewater

The experiments were conducted with the cell of 200 mL capacity with constant temperature of 308 K. Two porous graphite electrodes were fixed vertically and parallel to each other with an inter-gap of 1.0 cm. The true surface of graphite electrode (5.2 cm × 5 cm) was 26 cm². Certain amount of catalyst powder was put into 100 mL 0.3 g L⁻¹ MB solution dissolved Na₂SO₄ or NaCl as electrolyte, forming a multi-phase electrochemical oxidation slurry bed. The electrolyte was maintained by constantly stirring the solution at 200 rpm using a magnetic stirrer. Electric

power was supplied by regulated DC power supply, WYK302b, Xi'an, China.

2.4. Analytical method

The pH of the solution was measured using an Orion 290 pH meter. The chemical oxygen demand (COD) was chosen as the parameter by which to evaluate the process of oxidation and was determined according to standard methods [21]. X-ray diffraction (XRD) measurements of the catalyst powder were recorded using D/Max-3c (Japan Rigaku) diffractometer equipped with Ni filtered CuKα radiation (λ = 1.5406 Å). Solid morphology was determined by scanning electron microscopy (SEM, Quanta 200, Holland). An IR spectrometer, model IR Eouinx55 (Germany) was used for sample IR spectrometer analysis.

2.5. Environmental estimate

The experiment of environmental estimate of treated wastewater was conducted in laboratory, in a climate controlled model greenhouse with a heating system and an evaporative cooling system. The set point minimum and maximum temperatures in the greenhouse were 288 and 293 K. The minimum day and maximum night relative humidities were 60% and 90%, respectively. The plants were planted 2 cm apart and the irrigation was supplied once a day at 9:00 am. Leaf blade was collected sixth per 2 h a day from 9:00 am to 19:00 pm. The amount of total chlorophyll was determined by a spectrophotometer at wavelengths 652 nm, according equation:

$$Ct = \frac{Abs^{652} \times 1000}{34.5}$$

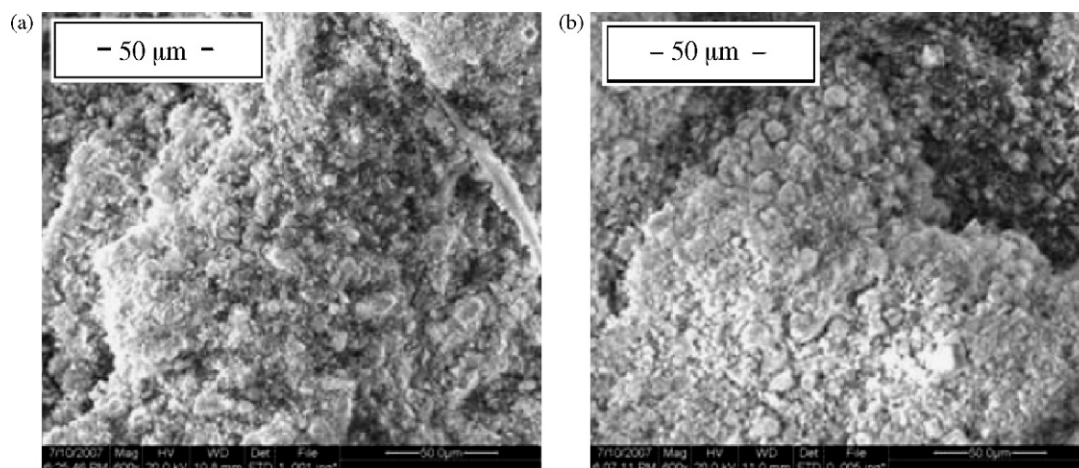


Fig. 2. SEM of Fe₂O₃-modified kaolin before (a) and after reaction (b).

where C_t (mg L⁻¹) was the total amount of chlorophyll. Abs^{652} was the total value of chlorophyll absorbency at 652 nm.

3. Results and discussion

3.1. Characteristic of catalyst

3.1.1. XRD analysis

The phase behavior of neat kaolin and Fe₂O₃-modified kaolin was measured by X-ray diffractometer and shown in Fig. 1. The presence of characteristic peaks as an attributive indicator of kaolinite ($2\theta = 12.3^\circ, 20.28^\circ, 24.86^\circ, 35.86^\circ$) and of muscovite ($2\theta = 17.88^\circ, 26.62^\circ$) was detected in neat kaolin and Fe₂O₃-modified kaolin, indicating that the stable Al–O octahedron structure remained and less of losses in layered crystallinity structure at 873 K. For Fe related species (Fig. 1b), the diffraction peak ($2\theta = 33.14^\circ, 35.61^\circ$ and 54.34°) assigned to Fe₂O₃ can be clearly detected, indicating that modification of the neat kaolin by Fe species has been succeeded, and the layered structure of kaolin kept constant. After the reaction, the Fe species presented itself as the mixture of Fe₂O₃ and FeO (Fig. 1c), maybe indicating that the Fe₂O₃ species in the catalyst has been involved in the MB decoloration. In addition, less than 1.5 ppm of Fe²⁺ and Fe³⁺ were detected in the treated water, suggesting that the catalyst was stable in the MB degradation process.

The chemical analysis data of the modified kaolin (the molar ratio of Na₂O:Fe₂O₃:SiO₂:Al₂O₃ = 1.5:0.2:2.5:1) before reaction indicated that the modified treatment has been successfully carried out and caused a moderate change in the composition of kaolin. After the reaction, the composition of the modified kaolin was also analyzed, the result indicated that little changes have been detected, except that the mixture of Fe₂O₃ and FeO has been replaced 100% Fe₂O₃ in the modified kaolin before reaction, which was consistent with the XRD result.

3.1.2. SEM

The morphology of Fe₂O₃-modified kaolin before and after reaction examined by SEM and representative micrographs was shown in Fig. 2 [22]. It was observed that the layered crystallinity structure and pored structure of kaolin existed after modified with Fe₂O₃ (Fig. 2a), which was consistent with the XRD analysis. After the MB degradation reaction, the porous structure of the Fe₂O₃-modified kaolin has also been existed, but a little more compacted (Fig. 2b) than before reaction.

3.2. Application of the catalyst in the electrochemical degradation of MB

3.2.1. Effect of initial pH on COD removal

Fig. 3 shows the effect of initial pH on COD removal catalyzed by Fe₂O₃-modified kaolin within 40 min of the reaction. It was noted that initial pH strongly affected electrochemical degradation efficiency: the COD removal reached 96.43% in pH 3 within 40 min, while lower COD removal was observed at high pH value. Tang and Huang [23] reported that the high acidity enhances free radical formation, therefore organic materials are easily oxidized [24]. While in basic media [25], hydrogen peroxide derived from the surface of electrodes, an oxidant in the Fenton's reaction, was unstable and decomposed into O^{•-} and water, according to Eq. (1):



therefore losing some of its oxidation ability, so the oxidation proceeded slowly in basic condition.

3.2.2. Effect of current density on COD removal

The current density, being a surrogate parameter, is found to influence the treatment efficiency of the electrochemical degradation processes [26,27]. Therefore, the applied current density was varied to examine its effect on the COD removal (Fig. 4). The results clearly showed that increasing current density contributed

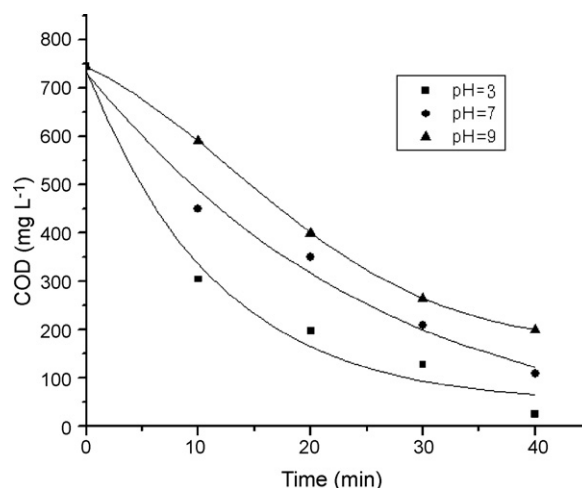


Fig. 3. Effect of pH on COD removal with time ($T=308\text{K}$; current density = 69.23 mA cm^{-2} ; catalyst dosage = 30 g L^{-1} ; electrolyte = 1.0 g L^{-1} NaCl).

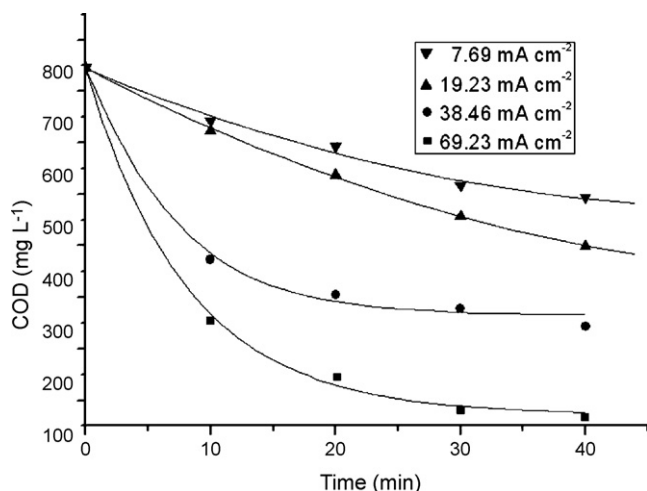


Fig. 4. Influence of applied current density on the evolution of COD ($T=308\text{ K}$; initial pH 3; catalyst dosage = 30 g L^{-1} ; electrolyte = 1.5 g L^{-1} NaCl).

to COD removal, because of the increased production of H_2O_2 at higher current densities. The reason is that increasing current density increases the over potential required for the generation of H_2O_2 on the cathode according to the reaction [Eq. (2)]:



More hydroxyl radicals can be formed when H_2O_2 interacted with the catalysis of modified kaolin with the increase in applied current density. So, the optimum applied current density for success was 69.23 mA cm^{-2} .

3.2.3. Effect of modified kaolin on COD removal

To evaluate the synergetic effect of modified kaolin with the electro-catalysis process, COD removal efficiencies treated in the same electro-catalytic conditions (69.23 mA cm^{-2}) without the modified kaolin was compared. Only 35.20% COD removal was obtained with 1.0 g NaCl as electrolyte in pH 3 within 40 min, indicating that COD was removed by electro-catalytic conditions more effectively than by single electro-catalysis.

3.2.4. Effect of chloride ions on COD removal

Fig. 5 shows the effect of electrolyte Na_2SO_4 and NaCl on COD removal during the oxidation of the wastewater catalyzed by mod-

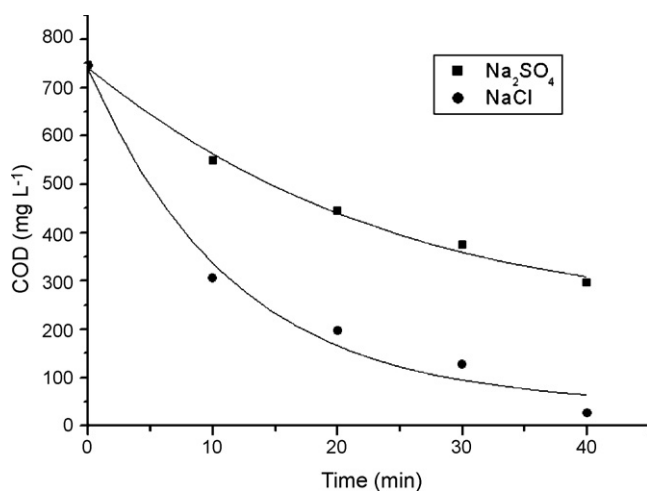


Fig. 5. Effect of electrolyte on COD removal with time ($T=308\text{ K}$; initial pH 3; current intensity = 69.23 mA cm^{-2} ; catalyst dosage = 30 g L^{-1} ; electrolyte = 1.0 g L^{-1} Na_2SO_4 or NaCl).

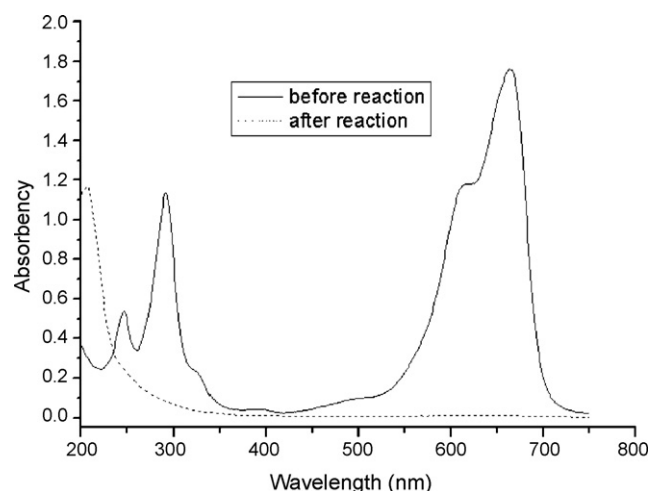
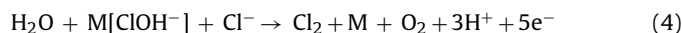
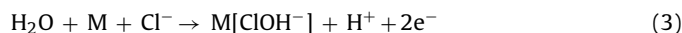


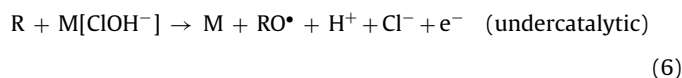
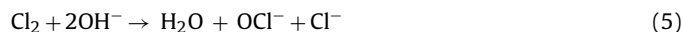
Fig. 6. UV-vis spectra of MB before and after reaction.

ified kaolin at pH 3. The results show that chloride ions have a significant effect on the COD removal due to the formation of strong oxidant [Cl_2 , ClO_2 , OCl^-]. Proper concentrations of chloride ions and salts in water can improve the performance and effectiveness of the electrochemical process and also decrease its energy consumption. The addition of NaCl electrolyte resulted in an increase in COD removal due to the chloride oxidation on the anode surface or in the aqueous medium [28]:

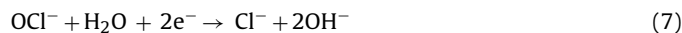
Anode reaction (M: porous graphite):



In aqueous medium (R: organics, RO: the oxidized organics):



Cathode reaction:



3.2.5. UV-vis and FT-IR spectrophotometric investigations of MB before and after treatment

It can be seen from Fig. 6 that two major absorbance peaks of methylene blue can be seen at 291 and 663 nm, due to benzene ring and heteropolyaromatic linkage. After reaction, these two peaks almost totally disappeared, which indicated the benzene ring and heteropolyaromatic linkage of methylene blue were almost destroyed.

The typical IR spectra in the region $2000\text{--}500\text{ cm}^{-1}$ of methylene blue before and after treatment were shown in Fig. 7. The disappearance of two peaks at 1598 cm^{-1} after treatment for 40 min indicated the total destruction of the aromatic part of a dye molecule. The peaks at 1393 and 1530 cm^{-1} are due to the $\text{C}=\text{N}$ and $-\text{CH}_3$ symmetric deformation. The disappearance of the two peaks indicates the total destruction of $\text{C}=\text{N}$ bond in heteropolyaromatic linkage and $-\text{CH}_3$ structure. The appearance of two new peaks at 1638 , 1388 cm^{-1} , due to asymmetric stretching of $\text{N}=\text{O}$ bond, $\text{N}-\text{O}$ stretching vibration and $\text{N}-\text{H}$ bonding vibration, respectively, indicated the degradation has been proceeded during the electrochemical reaction.

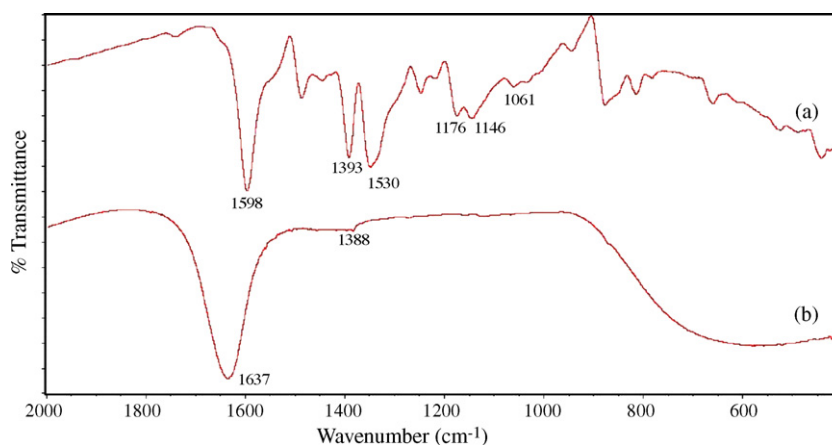


Fig. 7. Changes of MB in FT-IR spectra before (a) and after (b) reaction.

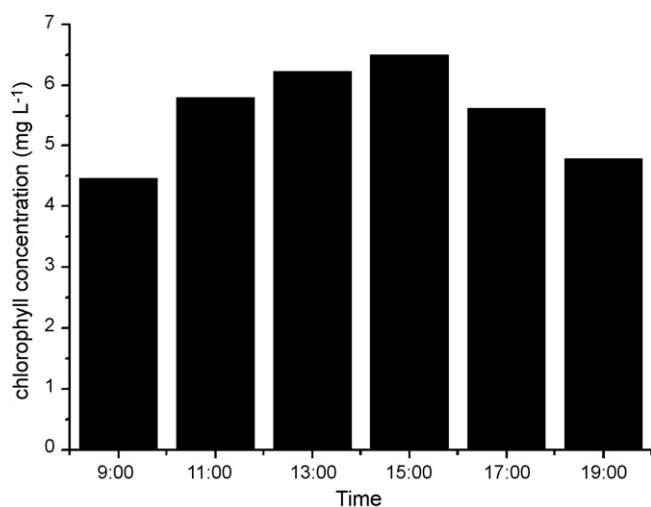


Fig. 8. Changes of chlorophyll concentration of plant as the function of time.

3.2.6. Toxicity studies towards clover

In order to evaluate whether the treated MB water was suitable for irrigation, a brief environmental influence assessment was performed. Total chlorophyll concentration is a unifying parameter for indicating the effect of specific interventions. The results were shown in Fig. 8. It can be seen from Fig. 8 that the treated wastewater has little effect on the content of chlorophyll, the overall chlorophyll content gradually increased when the treated wastewater was irrigated into the soil, and then the chlorophyll content reduced rapidly from 15:00 to 17:00 pm, the overall content of chlorophyll varied from 4.477 to 5.61 mg L⁻¹, however, it was interesting to find its content gradually recovered to normal level at 19:00 pm, which indicated that the treated wastewater could satisfy the demand of irrigating.

4. Conclusion

The electro-catalysis degradation of MB wastewater assisted by Fe₂O₃-modified kaolin has been carried out successfully. XRD and SEM show that the layered structure existed in neat and modified kaolin. Optimal operating conditions such as initial pH and current density were also studied. It was found that when the initial pH was 3, current density was 69.23 mA cm⁻² and the catalyst dose was 30 g L⁻¹, the COD removal rate can reach 96.47% in 40 min. The removal of MB wastewater might be attributed to strong ox-

idant that produced from the synergetic effect of between modified kaolin and electrochemical system.

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