

Catalytic decolorization of azo-stuff with electro-coagulation method assisted by cobalt phosphomolybdate modified kaolin

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Abstract

The new catalytic decoloration of C.I. Acid Red 3R with electro-coagulation (EC) method assisted by cobalt phosphomolybdate modified kaolin has been studied. The result showed that this process could effectively remove the C.I. Acid Red 3R contained in wastewater and its color removal efficiency could reach up to 98.3% in 7 min. The kinetics of the catalytic decolorization of Acid Red 3R was also studied. The decolorization reaction order was dependent on the initial concentration $[R]_0$ with respect to the concentration of C.I. Acid Red 3R. At lower $[R]_0$ the order was first, which then decreases with increasing $[R]_0$. The operating parameters such as initial pH, current density and temperature were also investigated. A possible reaction mechanism was proposed.

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1. Introduction

The worldwide production of dyes and pigments has been estimated at between 750,000 and 800,000 tonnes/year [1,2] with around 12% of all organic dyes lost during the various stages of production. This considerable loss explains why the effluents originating from the textile industry generally present strong coloration, which interferes with the photosynthesis in aquatic environments. In addition, some dyes (and their sub products) can be considered carcinogens or mutagens and they may also contain levels of heavy metals that breach environmental standards.

Conventionally, the dyes wastewater is treated through biological, physical and chemical methods [3,4]. Biological treatment processes are often ineffective in removing dyes that are highly structured polymers with low biodegradability [5]. Various physicochemical techniques, such as chemical coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration [3,4], are the normal ways to treat the dyes. But these methods are available to the low concentrations, and cannot deal with the high concentrations. In recent years, ozonation [5,6] and

photooxidation [7] have been reported as alternatives since they were regarded to be very effective. But the high cost of these methods leads to further consideration.

Electro-coagulation (EC) has been successfully tested to treat various industrial wastewater in recent years [8]. EC is a process consisting of creating a floc of metallic hydroxides within the effluent to be cleaned, by electro-dissolution of soluble anodes. Compared with traditional flocculation and coagulation, electro-coagulation has in theory, the advantage of removing the smallest colloidal particles: the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It also has the advantage of producing a relatively low amount of sludge. Therefore, EC has been widely used to treat waters containing food and protein wastes, oil wastes, synthetic detergent effluents mine wastes and heavy metal-containing solutions. This method can also be used to remove phosphate, for defluoridation of water, to treat potable water [8].

In the environmental protection, the BOD_5/COD_{Cr} ratio is a standard of biochemical nature. If the BOD_5/COD_{Cr} ratio is more than 0.3, it is considered that the biochemical nature is well. So the wastewater is supposed to be treated with biochemical method. If the ratio of BOD_5/COD_{Cr} is less than 0.1, it is considered that the wastewater has the low biodegradability, so it should be decolorized by physical–chemical methods, and the

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BOD₅/COD_{Cr} ratio of C.I. Acid Red 3R was attributed to this range. However, C.I. Acid Red 3R as representative of azo-stuff is an electro-active material: the molecule of azo-stuff may decompose to two molecular aromatic amine, when reacting with azo reductases and aromatic amine can induce pathological changes, so it is harmful to our human being.

On the basis of our previous investigations [9,10], the multi-functional CoPM/kaolin along with a pilot electrochemical cell was applied to treat C.I. Acid Red 3R wastewater in this work. The objective of our work was to study the influence of several process parameters such as initial pH, current density, temperature, initial dyestuff concentration on the treatment of wastewater contained C.I. Acid Red 3R and find out the desired conditions in which the electro-coagulation treatment more effectively. The kinetics and mechanism of this process were also studied. This model system may be applicable to color removal in a textile wastewater stream.

2. Experimental details

2.1. Materials

All chemicals used in the experiment were analytically pure grade. Kaolin, provided by Shanghai Reagent Co., China, are composed of Al₄[Si₄O₁₀](OH)₈ (surface area: 20 m² g⁻¹ and pore volume: 0.5 cm³ g⁻¹). Co(NO₃)₂·6H₂O, NH₄H₂PO₄ and MoO₃ were purchased from Xi'an Reagent Co. and used without further purification.

C.I. Acid Red 3R is typical of the azo-dyestuff and its molecular structure was shown in Fig. 1. Its azo-bond is a chromophore and its naphthalence ring makes this molecule have a stable chemical property. The substituted group such as -OH, -SO₃Na, made Acid Red 3R have the property of better solubility.

2.2. Set-up

The iron and graphite double-anode and steel cathode were positioned vertically and parallel to each other with an inter gap of 1.5 cm as Fig. 2 shown. The effective surface area of the electrodes was 10.5 cm². One hundred and fifty milliliters aqueous solutions were carried out in the reactor. The wastewater was put into the outer column cylinder and was constantly stirred

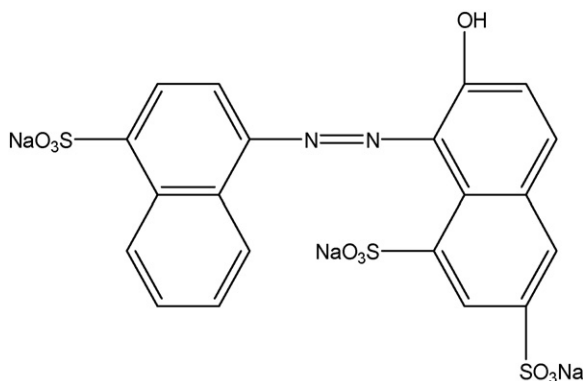


Fig. 1. The molecular structure of Acid Red 3R molecular formula: C₂₀H₁₁N₂-Na₃O₁₀S₃; classification: mono-azo; λ_{max}: 510 nm, MW = 604.473.

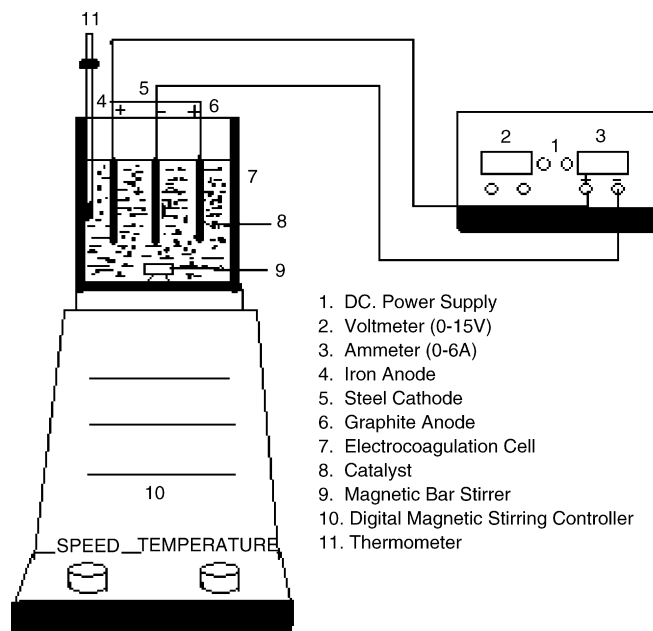


Fig. 2. The iron and graphite double-anode system of the EC process.

at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The temperature of the reaction system can be controlled by the thermostat of the magnetic stirring apparatus.

The electric power was supplied with regulated dc power supply, WYK302b, Xi'an, China. The current and voltage were adjustable between 0 and 6 A and between 0 and 15 V.

The concentration of C.I. Acid Red 3R in wastewater used in the experiment was 500, 800, 1200, 1500 mg l⁻¹, respectively, 0.75 mol l⁻¹ Na₂SO₄ was used as electrolyte, and NaOH or H₂SO₄ in proper amounts was used to get the suitable pH value. The temperature of the electrochemical reaction was maintained at 25 °C. The voltage applied was 10 V.

2.3. Preparation of catalyst (CoMP/kaolin)

CoMP was prepared as the literature [11]: NH₄H₂PO₄, MoO₃ and Co(NO₃)₂·6H₂O were mixed in relevant proportions. After careful grinding, the mixture was put into a crucible and heated under air atmosphere at 300 °C for 12 h. This treatment results in decomposition of ammonium molybdate and cobalt nitrate. After cooling and grinding, the oxide mixture is allowed to react at 650 °C for 4 h to obtain the CoMP materials. Then CoMP was blended with kaolin, grinding, annealed at 650 °C for 4 h to obtain the CoMP/kaolin catalyst.

2.4. Analysis techniques

Color index was analyzed by a double beam UV-vis spectrophotometer (UV-7504, China). The absorbance at maximum wavelength was detected and used as color removal index. Color removal ratio was calculated as follows:

$$R_{\text{color}\%} = \frac{\text{ABS}_0^{510} - \text{ABS}^{510}}{\text{ABS}_0^{510}} \times 100\%$$

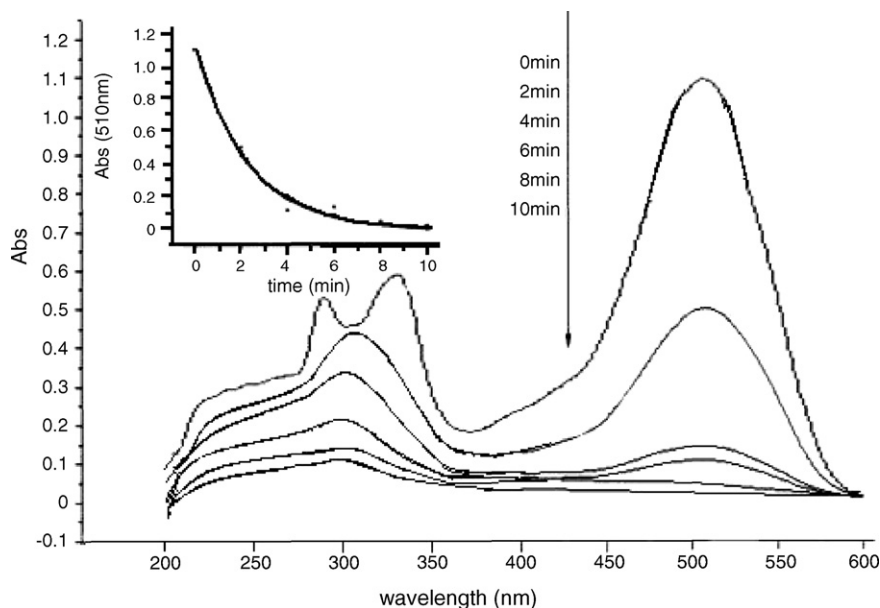


Fig. 3. Time-resolved absorption spectra of the reaction system.

where ABS^{510} is the maximum value of absorbance at 510 nm, ABS_0^{510} is the absorbance of the initial solution. The initial pH of the solution was measured using an Orion 290 pH meter.

An IR spectrometer, model IR Eouinx55 (Germany) was used for sample IR spectrometer analyse. X-ray diffraction (XRD) measurements of the catalyst powder were recorded using D/Max-3c (Janpan Rigalcu) diffractometer equipped with Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

3. Results and discussion

3.1. Kinetics

Although the color can be removed in the absence of the catalyst, this process needs longer time. When the catalyst was introduced, this process can be accelerated. A gradual loss of the absorbance of C.I. Acid Red 3R with catalyst was shown in Fig. 3. The observed rate constant, k was determined from first-order kinetic plot, $\ln A_t = \ln A_0 - k_0t$, as shown in Fig. 4, where A_t is concentration of the dye at time = t , and A_0 is concentration of the dye at $t=0$ min. The k value was determined at different temperatures and used to estimate the activation parameters (Table 1). It is clear that the reaction of higher rate constant is associated with lower activation energy and enhancement of temperature leads to proportional increase of rate constant.

As can be seen in Fig. 4, the reaction rate in the presence of catalyst was higher than that of no catalyst with the rate constant of 0.6047 and 0.4522 min^{-1} , respectively. When $t = 7$ min, the color percent removal was 95.18% with the absence of the catalyst, while, in the presence of the catalyst, the color removal could reached up to 98.3%.

The dependence of the reaction rate on the initial concentration of C.I. Acid Red 3R, C_0 , was investigated. As shown in Fig. 5, the initial rate has a first-order dependence on C_0 at lower concentrations and calculates as: $r = kC_0$. However, with

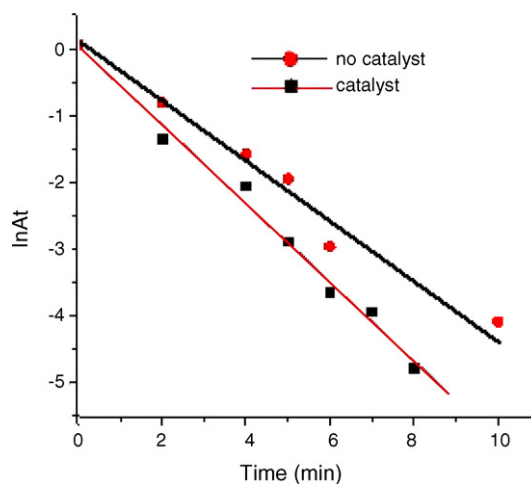


Fig. 4. First-order plot of the reaction of 500 mg l^{-1} of Acid Red 3R.

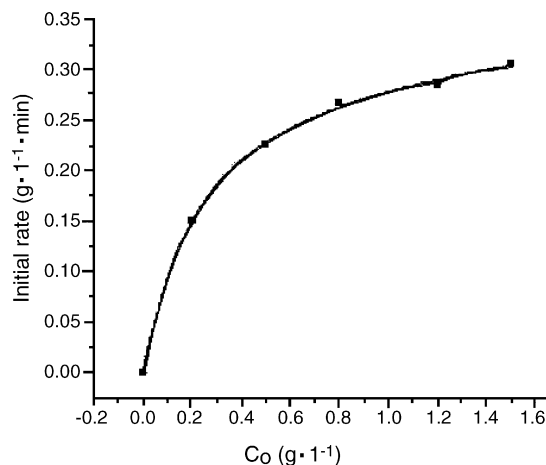


Fig. 5. Dependence of the initial reaction rate on the initial concentration of Acid Red 3R, C_0 (cobalt phosphomolybdate catalyst: 3 g l^{-1} , room temperature = 20°C).

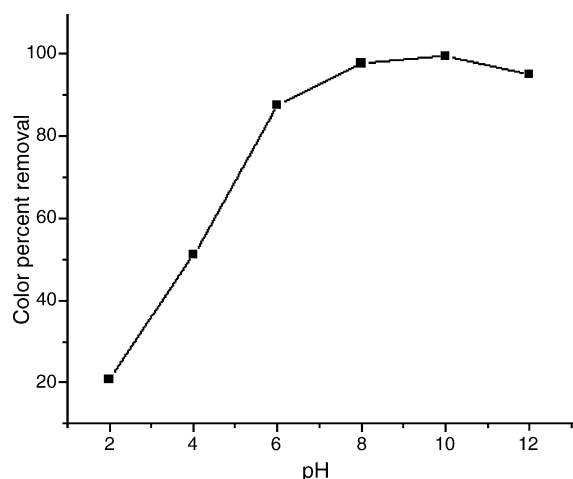


Fig. 6. Effect of initial pH on the color removal efficiency ($C_0 = 500 \text{ mg l}^{-1}$, electrolyte: Na_2SO_4 0.75 mol l^{-1} , $m_{\text{catalyst}} = 3 \text{ g l}^{-1}$, room temperature = 20°C).

increases of C_0 the order of reaction decreases and almost a limiting rate was reached at higher concentrations. The reaction rate increased with increasing the amount of catalysts.

3.2. Effect of operating variables on color removal

3.2.1. Effect of the initial pH on color removal

The initial pH is an important parameter influencing the performance of the EC process [12]. To examine its effect, the initial pH of the samples was adjusted to 2, 4, 6, 8, 10, 12 with the addition of H_2SO_4 or NaOH . The color removal of dye solutions in various initial pH at the same reaction time (7 min) were shown in Fig. 6.

It can be seen from Fig. 6 that the color removal efficiency increased from 20 to 98.3% when the initial pH varied from 2 to 8, it can be concluded that an initial pH of 8 or higher is optimal for the color removal of dye solutions, which can be ascribed to that there are more metallic hydroxide flocs formed in alkaline solution which can react with the dye to form the intermediate that can be decomposed by the catalyst, moreover maybe due to that the CoMP modified kaolin catalyst has higher catalytic activity in the alkaline initial pH conditions, so an initial pH of 8 or higher is optimal for the color removal dye solutions [13–16].

3.2.2. Effect of current density on color removal

Current density is the most important parameter for controlling the reaction rate in all EC processes. It is well known that the amount of current density determines the coagulant production rate, adjusts the rate and size of the bubble production, and hence affects the growth of flocs [17,18]. Fig. 7 showed the effect of current density applied ($10\text{--}70 \text{ mA cm}^{-2}$) on the color removal in the EC process. Increasing the current density causes a corresponding increase in the oxidized iron production from electrodes, so the higher the current density is, the higher the color removal efficiency.

When operating at higher current densities, there was a better reactor performance and lower operating cost. However, when the applied current varied above 50 mA cm^{-2} in the alkaline

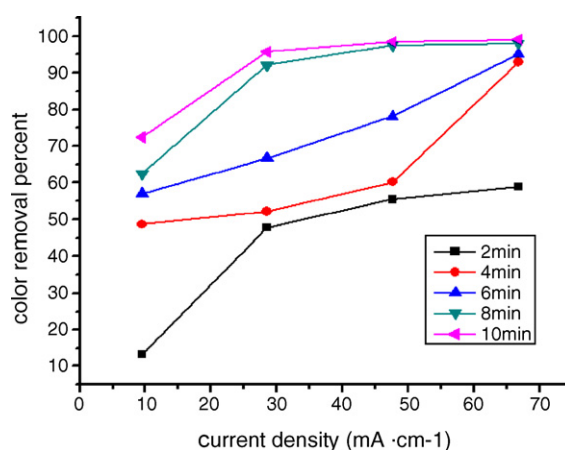


Fig. 7. Influence of applied current density on the color percent removal (3 g l^{-1} catalyst; $C_0 = 500 \text{ mg l}^{-1}$, electrolyte: Na_2SO_4 0.75 mol l^{-1} , initial pH 10, room temperature).

conditions ($\text{pH} > 8$), there was a little increasing on color removal and the cell temperature obviously rose, so the best condition for the EC process is 50 mA cm^{-2} .

3.3. IR spectral studies of Acid Red 3R

Fig. 8 showed the IR spectral of the solution before and after the EC treatment. It can be seen that some structure changes might have occurred during the EC process. After treatment with EC process, absorption at 1128.26 cm^{-1} assigned to $-\text{SO}_3$ group almost disappeared. In addition, the peaks at $1500\text{--}1900 \text{ cm}^{-1}$ assigned to $\text{N}=\text{N}$ also weakened, indicating that the $\text{N}=\text{N}$ group involved in the reaction. The peaks at $2100\text{--}2400 \text{ cm}^{-1}$ and

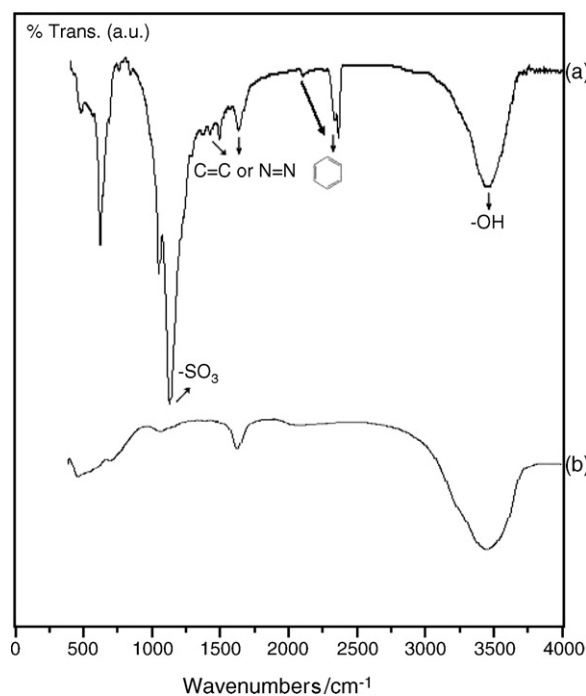


Fig. 8. Infrared absorption of Acid Red 3R [(a) before treatment and (b) after treatment] (initial pH 10; electrolyte: Na_2SO_4 0.75 mol l^{-1} ; room temperature; current density: 50 mA cm^{-2}).

1500–1675 assigned to aromatic compound almost disappeared after EC process, showing that the EC was indeed an effective method in the treatment of wastewater containing the dye-stuff.

3.4. Characteristics of CoPM catalyst

3.4.1. FT-IR analysis

Infrared spectrum for CoPM was shown in Fig. 9. Bands at 630, 750 and 880 cm^{-1} can be attributed to $\nu_{\text{as}}(\text{Mo-O-Mo})$, $\nu_3(\text{MoO}_4)$ and $\nu_1(\text{MoO}_4)$, respectively, which suggest the presence of $[\text{MoO}_4]$ tetrahedral species. The bands located in 980–1005 cm^{-1} can be attributed to orthophosphate species [19]. Band at 1100 cm^{-1} corresponding to symmetric and asymmetric vibration modes of terminal PO_3^{2-} was intense enough to show that cobalt introduction favors the phosphite group formation.

3.4.2. XRD analysis

The XRD patterns of the materials were shown in Fig. 10. For the graph (a), the peaks at $2\theta = 35\text{--}40^\circ$ were the typical diffraction peaks of kaolin. It also exhibited a sharp peak at $2\theta = 26.58^\circ$ for SiO_2 ($d = 0.3342$). But in the graph (c), the peak of SiO_2 was located at $2\theta = 27.285^\circ$, which indicated that CoPM had been loaded on the kaolin, leading to the excursion of peak. In the graph (b), the very weak peak at $2\theta = 43.45^\circ$, the characteristic peak for CoO (200), was influenced by the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$

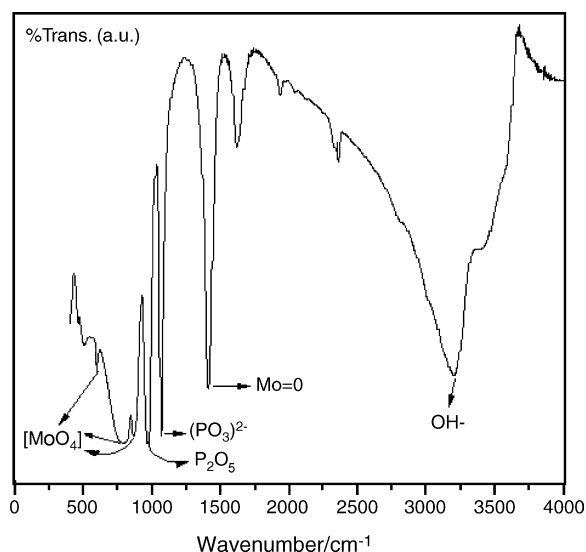


Fig. 9. FT-IR spectra of the CoPM.

and shifted to $2\theta = 42.72^\circ$. The patterns of the CoPM/kaolin(a) and CoPM(b) showed the characteristic peaks of heteropolyanion with the kegin structure [20]. For diffraction patterns, the graph (a) was somewhat different from (b). Some peaks became excursion, weak and sharp, which demonstrated that the strong interaction between CoPM and the support. And XRD patterns

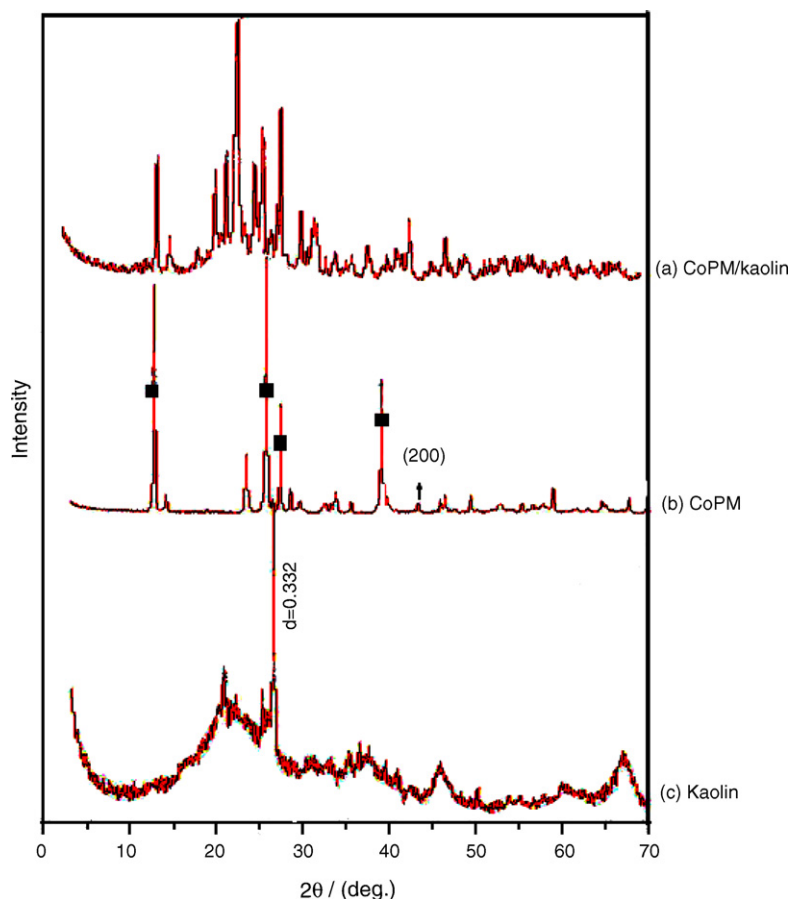


Fig. 10. X-ray diffraction patterns of (a) CoPM/kaolin, (b) CoPM and (c) kaolin.

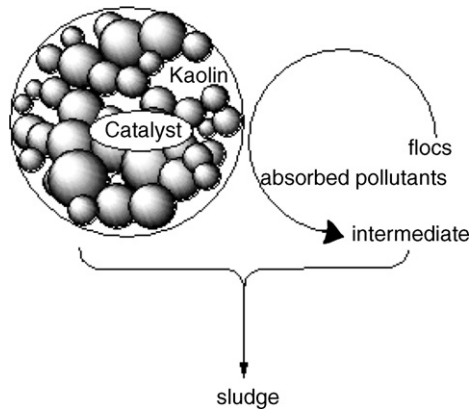


Fig. 11. The main multiphase catalytic decoloration reaction mechanism.

of (a) in Fig. 10 also demonstrated crystallinity starting at the sample treated at 650 °C.

3.5. Possible mechanism

Based on the experimental results and above discussions, the following mechanism maybe proposed and the decolorization process of C.I. Acid Red 3R can be described as Fig. 11. Ferric hydroxide flocs are characterized by adsorption. Organics as well as catalyst near the surface of ferric hydroxide are transported to the surface and then react with ferric hydroxide, forming intermediate, which then decomposes in the rate-determining step giving the final products. And the last step is slow reaction. If catalyst was introduced into this process, the rate of reaction will be faster.



where R is the C.I. Acid Red 3R, ML_n the ferric hydroxide, I the active intermediate, and P is the sludge. Applying the steady-state approximation theory to determine the concentration of the intermediate as follow:

$$\frac{d[I]}{dt} = k_1[R]([ML_n]_0 - [I]) - k_{-1}[I] - k_2[I] = 0 \quad (3)$$

Intermediate concentration can be expressed as follows:

$$[I] = \frac{k_1[R][ML_n]_0}{k_1[R] + k_{-1} + k_2} \quad (4)$$

The rate-determining step, Eq. (2), expresses the rate equation and is given by:

$$\text{rate} = k_2[I] \quad (5)$$

Thus, substitution Eq. (4) can get:

$$\text{rate} = \frac{k_1 k_2 [ML_n]_0 [R]}{k_1 [R] + k_{-1} + k_2} \quad (6)$$

expressing the initial concentration of reactant, $[R]_0$:

$$[R]_0 = [R] + [I] \quad (7)$$

Thus, substitution from Eq. (4) and assuming that:

$$k_1[R] \ll k_{-1} + k_2, \quad [R] = \frac{[k_{-1} + k_2][R]_0}{k_{-1} + k_2 + k_1[ML_n]_0} \quad (8)$$

From Eqs. (6) and (8), the rate can be expressed as:

$$\text{rate} = \frac{k_1 k_2 [ML_n]_0 [R]_0}{k_1 [R]_0 + k_{-1} + k_2 + k_1 [ML_n]_0} \quad (9)$$

It can be found from Eq. (9) that at lower $[R]_0$, the first term in the denominator becomes very small compared to the others and can be neglected. Therefore, the rate attains a first-order dependence on $[R]_0$. However, with increasing $[R]_0$, the rate decreases and reaches a limiting rate at higher concentration, which is consistent with the result of Fig. 5, so it can be concluded that the assumed mechanism is suitable for this electro-coagulation process.

4. Conclusion

The multiphase catalytic decolorization of Acid Red 3R using EC method assisted by CoPM/kaolin has been successfully investigated. In addition to a prompt removal of the color, the EC method assisted by modified kaolin can lead simultaneously to the decolorization of the dye with almost complete mineralization of carbon, nitrogen, and sulfur heteroatoms.

The effect of various operational parameters on color removal efficiency was also investigated and optimized. The dye solutions decolorized more efficiently when the initial pH values of the solution ranged from 8.0 to 10. It can also be found that the decolorization can be reached up to 98.3% within 7 min when the optimum current density was 65 mA cm⁻². The ensemble of these results clearly suggests that this multiphase catalytic reaction may be envisaged as a method for treatment of colored wastewater in textile industries with the mild conditions.

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