

Catalytic oxidation of anionic surfactants by electrochemical oxidation with $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin

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Received 16 December 2005; received in revised form 4 February 2006; accepted 2 March 2006

Available online 18 April 2006

Abstract

A new catalytic oxidation of anionic surfactants by electrochemistry method was designed and used to investigate the removal of anionic surfactant from simulated wastewater. Synergetic effect on COD removal was studied when integrating the electrochemical reactor, using porous graphite as anode and cathode, with the effective $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin catalyst in a single undivided cell. The result showed that this combined process could effectively remove anionic surfactant. Its COD removal efficiency was much higher than those individual processes and could reach up to 90% in 60 min. The operating parameters such as initial pH, cell voltage, and current intensity were also investigated. Possible theory for COD removal was also proposed to predict the role of modified kaolin, electro-catalysis and oxidation in the combined process. The pollutants in wastewater could be decreased by the high reactive OH^\bullet that produced on the surface of catalyst by the decomposition of electrochemical generated H_2O_2 . The result indicates that the catalytic oxidation by electrochemistry method is a promising wastewater treatment technique.
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Keywords: Electrochemical catalytic oxidation; Anionic surfactant; Kaolin; Wastewater treatment

1. Introduction

Surfactants are the active cleaning ingredients in synthetic detergents used for all kinds of washing [1]. Household surfactants account for the majority of the chemical oxygen demand (COD) present in washing wastewater (e.g. laundry water, detergents in car washing). The most common surfactants present in household water are the negative charged linear alkyl surfactants (LAS). Others includes cationic (positive charge), non-ionic (no charge) and amphoteric (positive or negative charge). For that anionic types are widely used in industrial and household detergents, as a result, their fate in the environment have been studied extensively [2–4]. With increasing use of surfactants products nowadays, more and more attentions have been paid on the elimination of these pollution dangers.

Many researches have demonstrated that electrochemical technologies can be efficiently applied to the treatment of wastewater containing organic pollutants [5–7] besides the traditional chemical, physical and biological methods. 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 [8], carbon felt [9], Pt/Ti [10] and graphite [11]. The complete indirect oxidation of linear alkyl surfactants (LAS) and alkyl benzene surfactants (ABS) at bipolar dimensional stable anodes (DSA) was also studied. These authors achieve a complete surfactant removal with an electrolyte addition of 0.05 M NaCl at a current density of 16.8 mA cm^{-2} applying an electrochemical oxidation process in conjunction with chemical coagulation [12]. Bidga [13] also performed an electrochemical degradation process with carbon electrodes and achieved 82% surfactant removal on total organic carbon (TOC) basis. However, the main drawback of the indirect electrochemical degradation process is the formation of chlorinated compounds. Lin et al. [14] had found the formation of chlorinated organic compounds using chromatograph while treating the anionic surfactants.

Nowadays a single process alone may not be adequate for the treatment of all various organic compounds. Hence, the researchers attempt to combine two or more treatment methods for the complete and successful removal. The combinations of electrochemical oxidation and Fenton reaction [15], ozonation [16], or photocatalysis [17], have been extensively studied

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as the pretreatment or mineralization process for the treatment of wastewater. Although the high oxygen over-potential anodes have demonstrated a good performance on wastewater treatment, the high costs of these electrodes also limit their application in industrial and household wastewater treatment. Farmer et al. [16] proposed another kind of electro-oxidation, mediated electro-oxidation, in treating mixed and hazardous materials. In their works, metal ions, usually called mediators, are oxidized to a active, high valence state in the presence of electric field, which in turn attack organic pollutants directly and may also produce hydroxyl free radicals that promote destruction of organic pollutants. However, the addition of heavy metals may give rise to a secondary pollution and limit its applications [18].

In this work, the multi-functional $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin was applied to treat anionic surfactants, along with a pilot electrochemical cell (200 ml volume). The objective of our work was to investigate the conjunctive function of modified kaolin used in electrochemical cell and to study the influence of several process parameters such as initial pH, temperature, current density, electrode distance and cell voltage.

2. Materials and methods

2.1. Reagent

All chemicals used in the experiment were analytically pure reagent.

The synthetic solution was prepared dissolving about 0.75 g dm^{-3} of sodium dodecyl benzene sulfonate (molar weight $M = 348.48 \text{ kg mol}^{-1}$), representing the anionic surfactants, in distilled water in $0.5 \text{ N Na}_2\text{SO}_4$. Surfactant solutions were made alkaline or acid by means of sodium hydroxide and sulphuric acid addition, respectively. 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: $0.5 \text{ cm}^3 \text{ g}^{-1}$). $30\% \text{ H}_2\text{O}_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, H_3PO_3 and Na_3PO_4 were obtained from Xi'an Reagent Co. and used without further purification.

2.2. Catalyst preparation

The catalyst was prepared as follows: adding $50 \text{ g Cu}(\text{NO}_3)_2$, $20 \text{ g Co}(\text{NO}_3)_2$ and $50 \text{ g Na}_3\text{PO}_4$ into 250 ml distilled water (pH 7.1), $10 \text{ ml H}_3\text{PO}_4$ was added to dissolve the nitrate of metal (Cu, Co), then the solution pH was adjusted with NaOH solution to a neutral conditions. Then 200 g kaolin was impregnated into the solution with stirring in a water bath at 50° for 4 h . Then the solution was aged at room temperature for 48 h and filtrated, washing, the deposit was dried at 100°C for 4 h , then calcined at 600°C for 4 h .

2.3. Set-up of waster water treatment

The experiments were conducted by batch process using undivided cell of 0.15 l capacity under constant temperature conditions. The anode and cathode were positioned vertically and parallel to each other with an inter gap of 0.5 , 1.0 and 1.5 cm , respectively. The material used as the anode and cathode are both

porous graphite (Supplied by Spring Chemical Industrial Company Limited, Shaanxi, China). The superficial graphite surface of working electrode ($3.2 \text{ cm} \times 6 \text{ cm}$) was 19.2 cm^2 . The 30 g catalyst was packed around the working electrode, forming a multi-phase electrochemical oxidation packed bed. The solution was constantly stirred at 200 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, WYK302b, Xi'an, China. The current and voltage were adjustable between 0 and 2.5 A and between 0 and 35 V .

2.4. Analysis techniques

All the experiments runs were carried out in duplicate and analysis of each parameter was done in triplicate for each run. The coefficient of variation obtained was not more than 5% for the three determinations and for the experiment runs carried out in duplicate. The initial pH of the solution was measured using an Orion 290 pH meter. The chemical oxygen demand (COD) was chosen as parameter in order to evaluate the process of oxidation and was determined according to standard methods for the examination of water and wastewater [19]. Ultra-absorbance of the samples was monitored using a double beam UV-vis spectrophotometer (UV-7504, China). An IR spectrometer, model IR Eouinx55 (Germany) was used for sample IR spectrometer analysis. After electrolysis, the sample was filtrated, and the filtrate was air-dried to a constant weight for IR analysis. The crystallinity of the catalyst was determined by powder X-ray diffraction (XRD) D/Max-3c model (Rigaluc, Jp) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). Solid morphology and average crystal size were determined by scanning electron microscopy (SEM, Quanta 200, Holland) and a gold film was sputtered onto the sample prior to observation (ISI DS-130). Co^{3+} , Cu^{2+} that leaching from the catalyst were measured using Perkin-Elmer inductively coupled plasma-atomic emission spectroscopy (ICPAES).

3. Results and discussion

3.1. Characteristics of catalyst

The XRD of $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin before and after electrolysis was shown in Fig. 1. It can be seen that amorphous component of crystallinity $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin was rather high, and the crystallinity structure of each samples had little changes before and after electrolysis, the difference only occurred on the intensity of each spectra, indicating that the catalyst structure was almost unchanged and it was stable in the electrolysis process, moreover, less than 2 ppm of Cu^{2+} or Co^{3+} was detected in the final treated water.

The morphology of $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin examined by SEM and representative micrographs were shown in Fig. 2. It was observed that a micro-sized and pored structure with bigger surface had formed during the calcinations of modified kaolin.

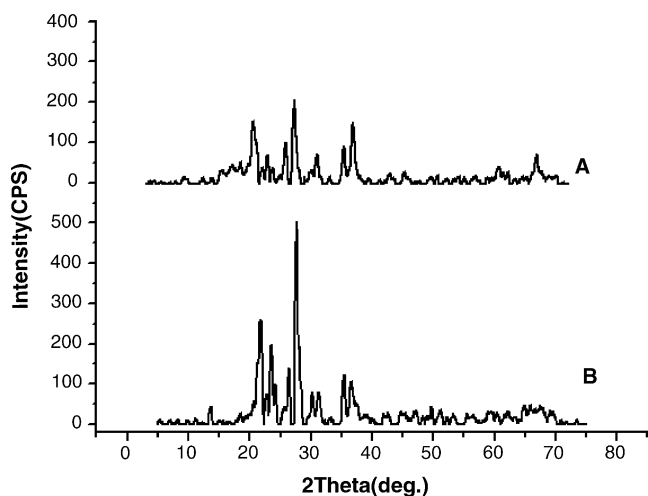


Fig. 1. XRD patterns of $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin before and after electrolysis: (A) after treatment; (B) before treatment.

3.2. Synergetic effect on COD removal

In the presence of catalyst ($\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin), organic pollutants can be degraded both by electrolysis and adsorption (or adsorption by catalysis). To evaluate the feasibility of adding catalyst into the electro-catalysis process, the efficiencies of COD removal by only modified kaolin, electro-catalysis and their combined process were compared in the same reactor, respectively. Effect of kaolin's adsorption was performed at the same conditions except the absence of current. The tendency of COD value variation during the whole electrolysis, adsorption process and combined processes in the first 60 min was shown in Fig. 3. It can be seen that COD was removed by catalyst adsorption more rapidly than by electro-catalysis. However, the two processes were not environmentally equivalent due to the accumulation of unconverted contaminants on the solid phase by adsorption. Moreover, the whole combined process is a mass transfer process and its COD decreasing rate may depend on the stirring speed, particle size and also the solution conditions.

Such a combined process obviously possesses advantages over electro-catalysis or adsorption alone in the process of eliminating organic compounds. Therefore, it is of our inter-

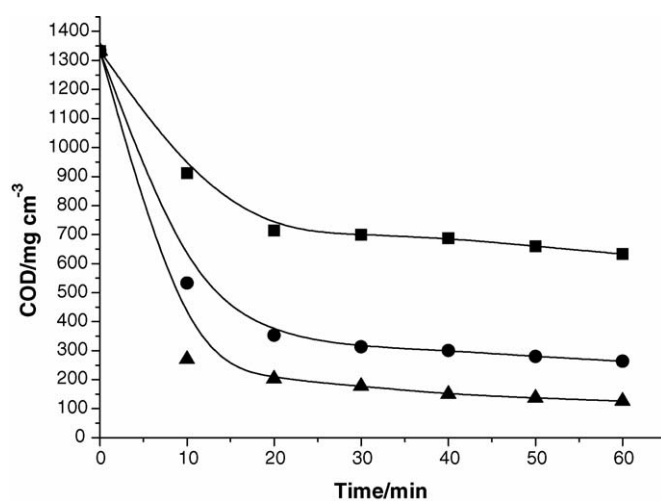


Fig. 3. The synergetic effects on COD removal in the combined process. (■) Electrochemical process; (●) catalyst adsorption process; (▲) catalyst-electro combined process (cell voltage: 10 V; current intensity: 30 mA cm^{-2} ; electrode distance: 10 mm; initial pH: 3).

est to study the roles of some operational conditions on COD removal. The main parameters examined included the initial pH of electrolyte, cell voltage, the current density and the electrode distance on COD removal.

3.3. Effect of operating variables on COD removal

3.3.1. Effect of initial pH values on COD removal

Fig. 4 shows the influence of the initial pH on the COD removal rate during the oxidation of sodium dodecyl benzene sulfonate in the combined electrolysis batch. The results were compared in terms of the time required for COD changes. A significant difference in surfactant degradation was noted between electrolysis with an electrolyte under initially neutral, acid (pH 4, 5) or alkaline (pH 9, 12) conditions. While almost little degradation took place at an initial pH of 9, acid conditions clearly promoted the adsorption–electrocatalytic oxidation of surfactant. It can also be seen from Fig. 4 that the COD removal efficiency increased from 39.5 to 89.8% when the initial pH varied from 9 to 3, it can be concluded that an initial pH of 5 or lower is optimal for the adsorption–electrocatalytic oxidation

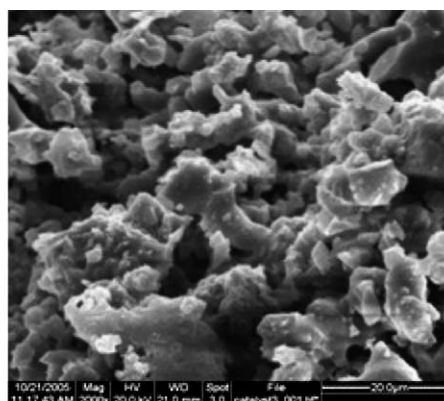
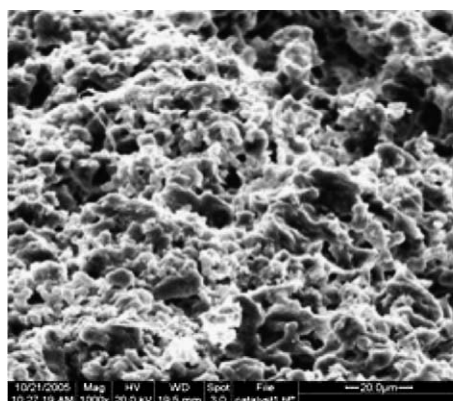


Fig. 2. Solid morphology of catalyst by SEM.

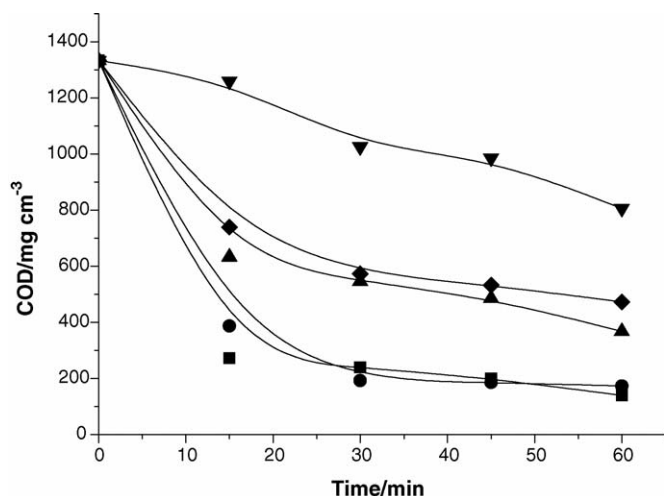


Fig. 4. Influence of initial pH on the evolution of COD with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na_2SO_4 0.5 N; T: room temperature; initial pH: (■) 3; (●) 5; (▲) 7; (▼) 9; (◆) 12.

of surfactant, which maybe due to that the $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin catalyst has higher catalytic activity in the lower initial pH conditions and consistent with the reference reported [20].

However, it is interesting to observe from Fig. 4 that the increasing in pH from 9 to 12 also resulted in an increasing in COD removal, which can be explained that the reaction no longer occurred directly on the surface of catalyst but in the suspended solution, which involved a flocculation process. When in strong alkaline solutions, some dissolved kaolin can flocculate with pollutants forming a suspended particle solution. These leaching suspended particles are micro-sized and can easily interact with pollutants. This process would decrease the COD value but could not completely convert all organics into water and carbon dioxide.

3.3.2. Effect of cell voltage on COD removal

Potential is a major driving force for respective phenomena of interest in electrochemical reactors, the cell voltage significantly influences both the electro-catalysis and adsorption-catalysis process. Fig. 5 shows the COD removal under four different cell voltages. It is evident that COD decreased rapidly with the increasing of cell voltage, COD efficiency increased from 71 to 94.5% with increasing the applied cell voltage from 5.0 to 20.0 V, indicating that the surfactant can be catalytic destroyed at the surface of catalyst activated by high voltage electric field. However, when the applied cell voltage was higher than 15.0 V, there was only a moderate increase on COD removal efficiency.

3.3.3. Effect of current density on COD removal

The influences of the applied current density on the trend of COD removal versus specific charge passed were shown in Fig. 6. In the range of current density ($10\text{--}70 \text{ mA cm}^{-2}$) studied, COD abatement was dependent of this parameter. Although the oxidation of the surfactant did not occur directly on the electrode surface but in the bulk solution where modified kaolin existed,

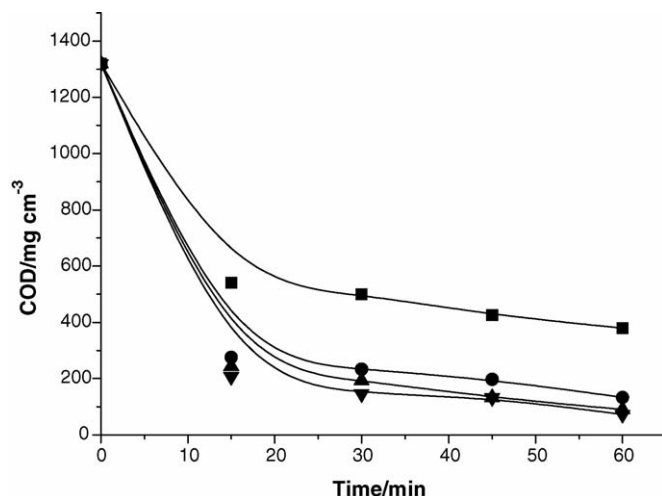


Fig. 5. Influence of applied cell voltage on the COD removal with the specific current density during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na_2SO_4 0.5 N; T: room temperature; initial pH: 3; cell voltage: (■) 5.0 V; (●) 10.0 V; (▲) 15.0 V; (▼) 20.0 V.

hydroxyl radicals can be formed when more active oxygen and hydrogen, which produced on the active site of the electrode surface, interacted through the catalysis of modified kaolin with the increasing of applied current density. When operating at higher current densities, there was a better reactor performance and lower operating cost. However, when the applied current was higher than 50 mA cm^{-2} , there was a sharp decreasing on COD removal, which can be explained that increased current density can lead to the increase of cell temperature, and the adsorption of pollutants on the surface of catalyst will be hindered at high temperature, and more energy will be consumed at higher current density applied. So the best condition for the successive is 50 mA cm^{-2} .

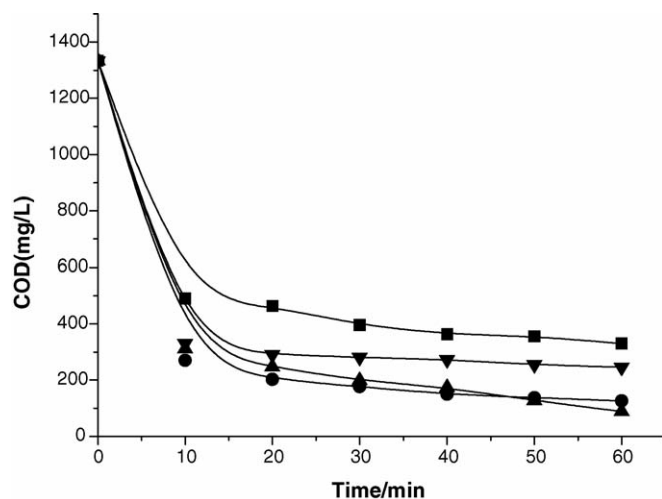


Fig. 6. Influence of applied current density on the evolution of COD with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na_2SO_4 0.5 N; T: room temperature; initial pH: 3; current density: (■) 10.0 mA cm^{-2} ; (●) 30.0 mA cm^{-2} ; (▲) 50 mA cm^{-2} ; (▼) 70.0 mA cm^{-2} .

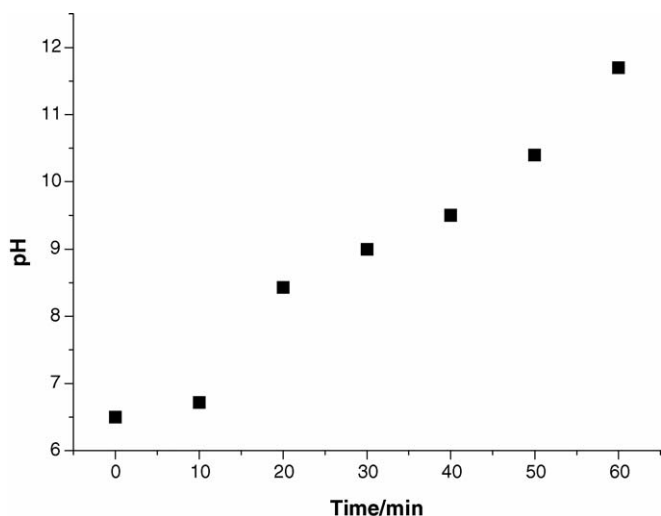


Fig. 7. The changing of pH value in the electrochemical oxidation process. (Operating conditions: applied cell voltage: 15 V; initial pH: 6.5; electrolyte: Na_2SO_4 0.5 N; T : room temperature; current density: 50 mA cm^{-2}).

3.4. The changes of pH value under neutral conditions

The changes of pH value in the process are given in Fig. 7. The starting pH value is 6.5, with time longer the pH elevated and the end pH value is about 12 after 60 min, which may be due to that H_2 produced and resulting in a shift of pH to the alkaline region.

3.5. UV–vis spectrophotometric investigations

The changes in absorbance characteristics of sodium dodecyl benzene sulfonate in 223 nm were investigated during the electrochemical oxidation process and shown in Fig. 8. It can be seen the concentration of sodium dodecyl benzene sulfonate decreased gradually during the absorption electrochemical oxidation process.

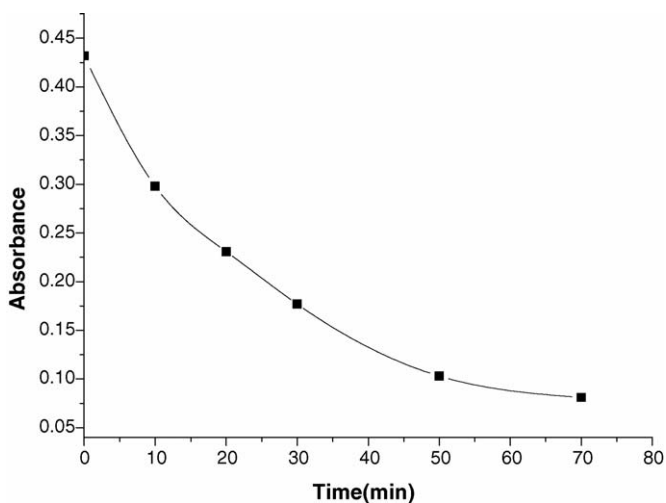


Fig. 8. UV–vis spectra of treated solution of sodium dodecyl benzene sulfonate in 223 nm with a 1000-fold dilution. (Applied cell voltage: 15 V; initial pH: 3; electrolyte: Na_2SO_4 0.5 N; T : room temperature; current density: 50 mA cm^{-2}).

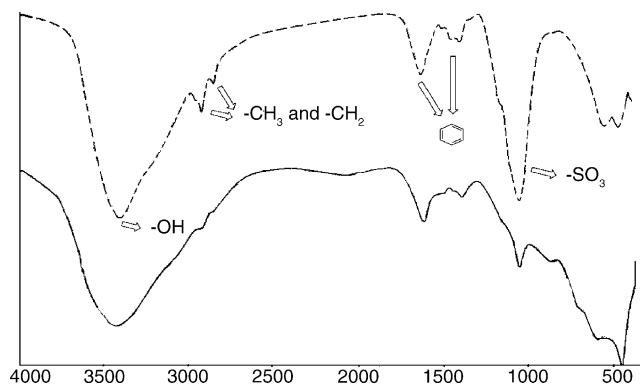


Fig. 9. Infrared absorption of sodium dodecyl benzene sulfonate. (Dot line: before treatment; normal curve: after treatment; operating conditions: applied cell voltage: 15 V; initial pH: 3; electrolyte: Na_2SO_4 0.5 N; T : room temperature; current density: 50 mA cm^{-2}).

3.6. IR spectral studies

Fig. 9 shows the IR spectral of the dried solution residual before and after the multi-phase electrochemical treatment. It can be seen that some structure changes might have occurred during the electrochemical process. After electrolysis, absorptions at 2957 and 2856 cm^{-1} assigned to $-\text{CH}_3$ and $-\text{CH}_2$ almost disappeared, indicating that active hydroxyl radicals produced destroyed this bond, and the surfactant were finally degraded to H_2O and CO_2 . In addition, the peak at about 1191 cm^{-1} assigned to $-\text{SO}_3$ group also weakened after the treatment, indicating the benzene-sulfonate group was oxidized to SO_4^{2-} .

3.7. Possible mechanism

Multi-phase electrochemical oxidation of anionic surfactants with $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin was dependent on both the role of the electro-catalysis and adsorption. It is necessary to discuss the role that electro-catalysis and adsorption played in the combined process. The degradation of organics by combined electrolysis was assumed due to the hydroxyl radicals produced by electro-catalysis and catalysis of modified kaolin:



The process involve the following four steps: (i) mass transfer of O_2 formed from anode toward the surface of the cathode, some OH^\bullet also produced form the anode, (ii) in the acid solutions, O_2 easily obtain electrons on the cathode and meanwhile reacted with hydrogen ion to form hydrogen peroxide



(iii) hydrogen peroxide were decomposed and also produced highly reactive hydroxyl radicals in the presence of heterogeneous catalyst $\text{CuO-CO}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin, (iv) the reaction between hydroxyl radicals and organic pollutants adsorbed on the surface of catalyst. The role of the catalyst is

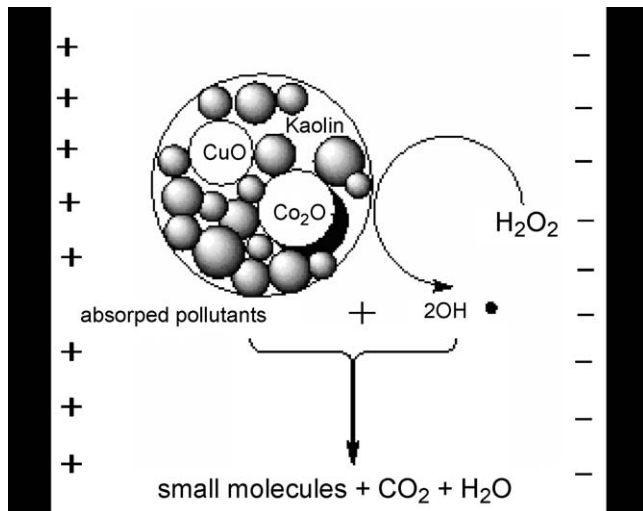


Fig. 10. The main reaction mechanism of multi-phase electrochemical oxidation.

not only participating the reactions of decomposition of H₂O₂ but also catalyze the formation of H₂O₂, they also adsorb the pollutants made the further degradation easily occur on the surface of them. Moreover, for all the parameter effect tested, the rate of COD removal almost varies in the first 10–15 min, this is attributed to the great porous structure of the fresh catalyst, when the catalyst was added to the system, the pollutants was immediately absorbed and concentrated, thus the COD rapidly decreased in the first 10–15 min. The main reaction mechanism of catalytic oxidation of pollutant by electrochemical generated H₂O₂ can be summarized as Fig. 10.

3.8. Comparison with H₂O₂-catalyst system

To prove the possible mechanism proposed, the experiments using H₂O₂-catalyst system have been carried out to com-

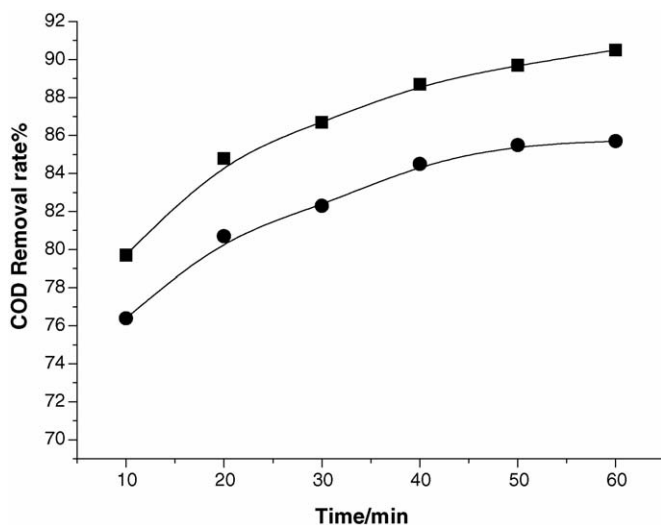


Fig. 11. Comparison of COD removal rate with two different systems. (■) Electrochemical combined system, operating conditions: applied cell voltage: 15 V; initial pH: 3; electrolyte: Na₂SO₄ 0.5 N; T: room temperature; current density: 50 mA cm⁻²; (●) H₂O₂-catalyst system.

pare with that of combined electrochemical process. Fig. 11 showed the COD removal under two different systems. Two millilitres 30% H₂O₂ was added dropwise into the system per 10 min, it was observed that the COD removal rate could still reach 85% after 60 min treatment under H₂O₂-catalyst system, which should attributed to the decompositions of H₂O₂ in presence of CuO–Co₂O₃–PO₄³⁻ modified kaolin. However, it could be seen from Fig. 11 that the decay of COD removal under H₂O₂-catalyst system was somewhat slower than that of electrochemical combined process, which indicated that the reactions occurred in electrochemical combined system was not only the decomposition of H₂O₂ generated by electrochemistry but also other reactions (e.g. direct oxidation on electrodes).

4. Conclusion

The catalytic oxidation of wastewater containing anionic surfactants by electrochemistry with CuO–Co₂O₃–PO₄³⁻ modified kaolin on porous graphite anode and cathode has been carried out successfully over the individual process for anionic surfactant abatement. In the combined process, pollutants can be either directly oxidized by the electro-catalysis on the anode surface, or by adsorption on the surface of modified kaolin activated by electro field.

The modified catalyst with a pored and big surface structure and the effect of various operating parameters on COD removal were investigated. The removal of anionic surfactant may be contributed to a combination of many factors, such as direct oxidation, adsorption, electrochemical catalytic oxidation, etc. Further work was needed to test on industrial scale and other organic wastewater.

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