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Multi-Phase Electrochemical Catalytic Oxidation Of Wastewater With Anionic Surfactants



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ABSTRACT

A new multi-phase electrochemical catalytic oxidation 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 minutes. 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 that produced on the surface of catalyst activated by the electro field. The result indicates that the multi-phase catalytic electrochemical oxidation process is a promising wastewater treatment technique.

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KEYWORDS

Electrochemical catalytic
oxidation;
Anionic surfactant;
Kaolin;
Wastewater treatment.

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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 0.05M NaCl at a current density of 16.8 Am/cm² applying an electrochemical oxidation process in conjunction with chemical coagulation^[12]. Geert^[13] also performed a 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. Panizza 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 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.^[18] 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^[19].

In this work, the multi-functional CuO-Co₂O₃-PO₄³⁻ 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.

MATERIALS AND METHODS

Reagent

All chemicals used in the experiment were analytically pure reagent.

The synthetic solution was prepared dissolving about 0.75g dm⁻³ of sodium dodecyl benzene sulfonate (molar weight $M = 348.48\text{kg}\cdot\text{mol}^{-1}$), representing the anionic surfactants, in distilled water in 0.5 N Na₂SO₄. 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 Al₄[Si₄O₁₀](OH)₈ (surface area: 20m²/g and pore volume: 0.5cm³/g). Cu(NO₃)₂, Co(NO₃)₂, H₃PO₃ and Na₃PO₄ were obtained from Xi'an Reagent Co.

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and used without further purification.

Catalyst preparation

The catalyst was prepared as follows: adding 50g $\text{Cu}(\text{NO}_3)_2$, 20g $\text{Co}(\text{NO}_3)_2$ and 50g Na_3PO_4 into 250ml distilled water (PH = 7.1), 10ml H_3PO_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 200g kaolin was impregnated into the solution with stirring in a water bath at 50°C for 4h.. Then the solution was aged at room temperature for 48h and filtrated, washing, the deposit was dried at 100°C for 4h, then calcined at 600°C for 4h.

Set-up of waster water treatment

Figure1 shows the schematic diagram of the electrochemical oxidation. 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 cm, 1.0 cm 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 true graphite surface of working electrode (3.2 cm x 6 cm) was 19.2 cm². The 30g 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 35V.

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^[20]. The COD removal efficiency is determined as below:

$$\eta(\%) = \frac{c_0 - c}{c_0} \times 100\% \quad (1)$$

Where, c_0 and c denote the COD concentration at initial time and given time t , respectively.

Ultra-absorbance of the samples was monitored

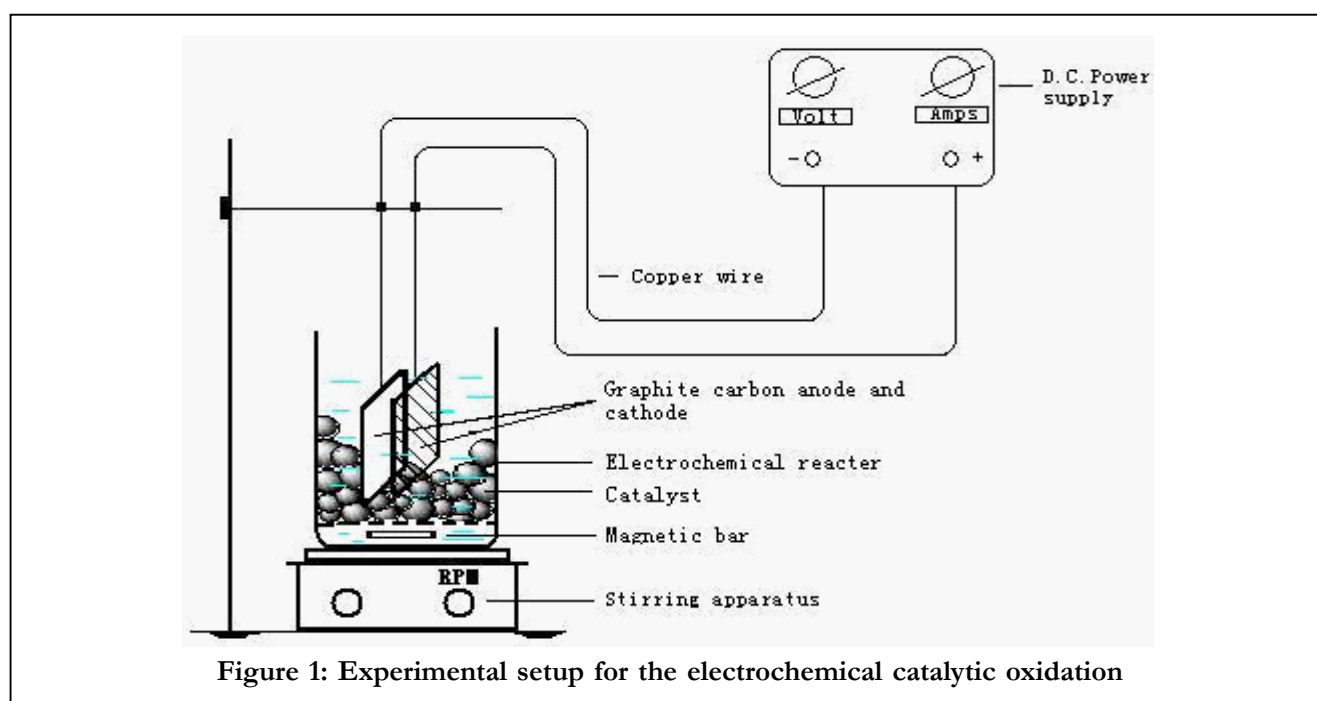


Figure 1: Experimental setup for the electrochemical catalytic oxidation

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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 CuK_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).

RESULT AND DISCUSSION

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 figure 2. 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 in the electrolysis process.

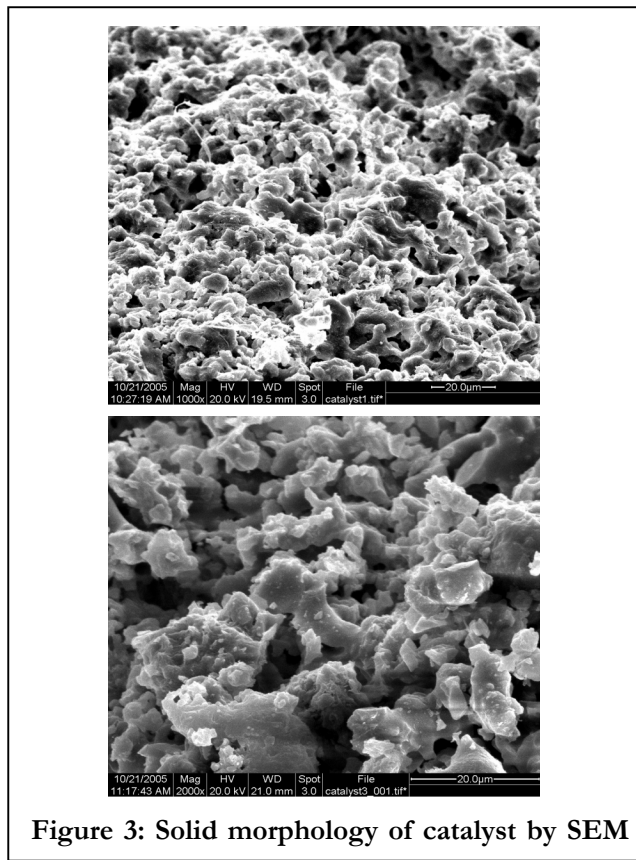


Figure 3: Solid morphology of catalyst by SEM

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 figure 3. It was observed that a micro-sized and pored structure with bigger sur-

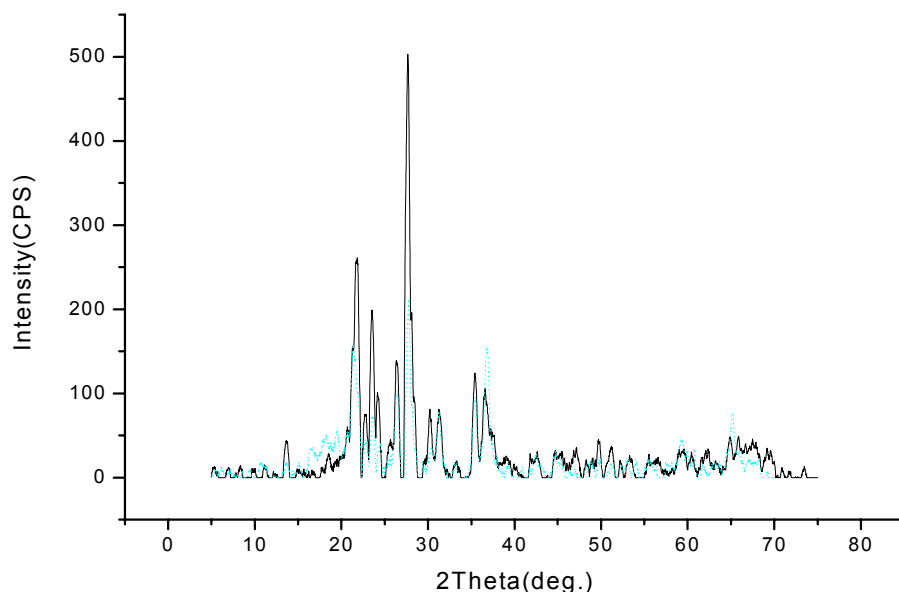


Figure 2: XRD patterns of $\text{CuO-Co}_2\text{O}_3\text{-PO}_4^{3-}$ modified Kaolin before and after electrolysis (Solid curve: before treatment, Dot curve: after treatment)

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face had formed during the calcinations of modified kaolin.

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-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-catalysis was performed at the same conditions except the absence of current. The tendency of COD concentration during the whole electrolysis, adsorption-catalysis process and combined processes in the first 60 min was tried by the following apparent first-order kinetics:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (2)$$

where, k is the first-order reaction rate constant, it fits the experimental data well as shown in figure 4. The fitted values of k in the three different processes were listed in TABLE 1. It can be seen that COD was removed by adsorption-catalysis 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-catalysis. The reaction

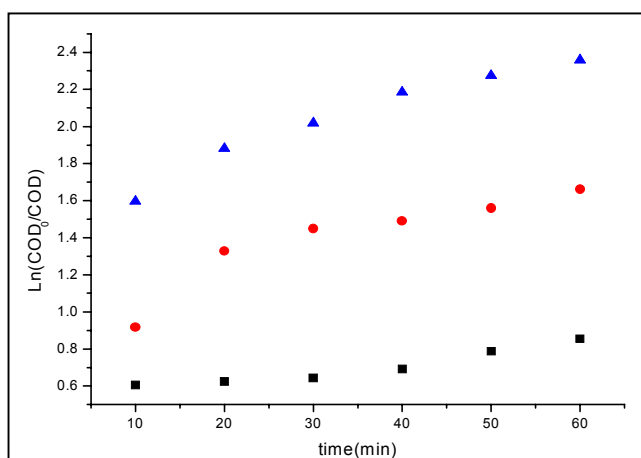


Figure 4: The synergetic effects on COD removal in the combined process (cell voltage: 10V; current intensity: 30mA/cm²; electrode distance: 10mm; initial pH=3)

TABLE 1: First-order reaction rate constant under three processes

Process	k (per min)
Electro-catalysis	0.00507
Adsorption-catalysis	0.01275
Combined process	0.06901

rate constants in the combined process were found larger than that of the sum of two individual processes, i.e. there existed synergetic effects in the combined process.

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

Effect of operating variables on COD removal

1. Effect of Initial pH values on COD removal

Figure 5 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

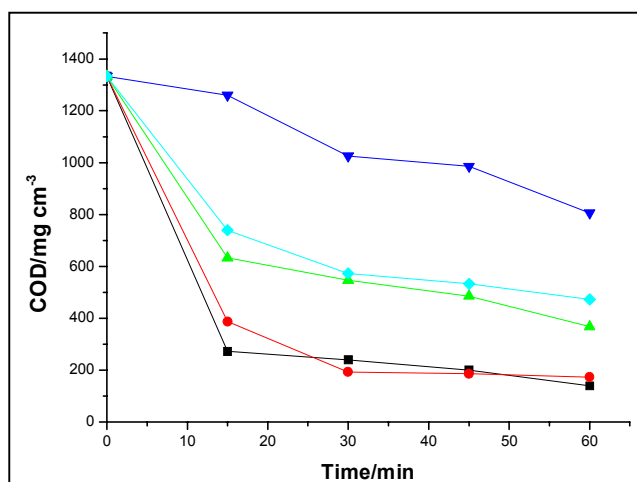


Figure 5: Influence of initial pH on the evolution of COD with the specific electrical charge passed during the electrolyses of 750mg dm⁻³ of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na₂SO₄ 0.5N; T: room temperature; initial pH: (■) 3; (●) 5; (▲) 7; (▼) 9; (◆) 12.

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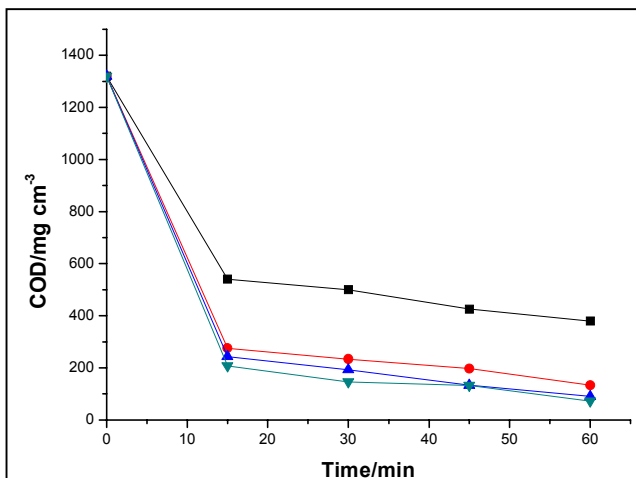


Figure 6: Influence of applied cell voltage on the COD removal with the specific current density during the electrolyses of 750mg dm^{-3} of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na_2SO_4 0.5N; T: room temperature; Initial pH: 3; Cell voltage: (■) 5.0 V; (●) 10.0 V; (▲) 15.0 V; (▼) 20.0 V.

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 figure 6 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 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^[21-22].

However, it is interesting to observe from figure 5 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 on the electrodes, which involved electro-coagulation process. Leu et al.^[12] found that an initial pH of 7 or higher is optimal for the electro-coagulation of surfactants with addition of H_2O_2 , which indicated that the initial pH value at modified kaolin in electro-catalytic ex-

periments was somewhat different from only electrocatalytic experiments.

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 electrocatalysis and adsorption-catalysis process. Figure 6 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. 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 figure 7. In the range of current density ($10\sim 70\text{ mA cm}^{-2}$) studied, COD abatement was dependent of this parameter. Although the

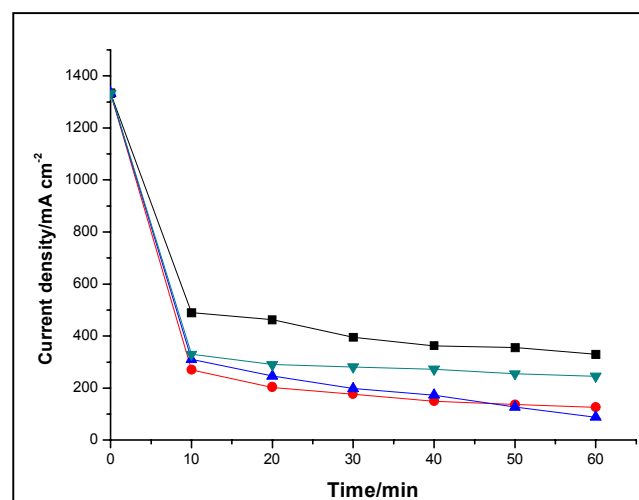


Figure 7: Influence of applied current density on the evolution of COD with the specific electrical charge passed during the electrolyses of 750mg dm^{-3} of sodium dodecyl benzene sulfonate on the porous graphite anode. Electrolyte: Na_2SO_4 0.5N; T: room temperature; Initial pH: 3; Current density: (■) 10.0 mA cm^{-2} ; (●) 30.0 mA cm^{-2} ; (▲) 50 mA cm^{-2} ; (▼) 70.0 mA cm^{-2} .

oxidation of the surfactant did not occur directly on the electrode surface but in the bulk solution where modified kaolin existed, 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 varied above 50mA cm^{-2} , there was a sharp decreasing on COD removal and the cell temperature obviously rose, so the best condition for the successive is 50mA cm^{-2} .

UV-Vis spectrophotometric investigations

The Changes in absorbance characteristics of sodium dodecyl benzene sulfonate were investigated from 200 to 400nm during the absorption electrochemical oxidation process, and the results were shown in figure 8. It can be seen that there was a maximum absorbance at 223nm attributed to sodium dodecyl benzene sulfonate in the ultraviolet region. This peak disappeared gradually during the absorption electro-chemical oxidation process. The concentration of sodium dodecyl benzene sulfonate was

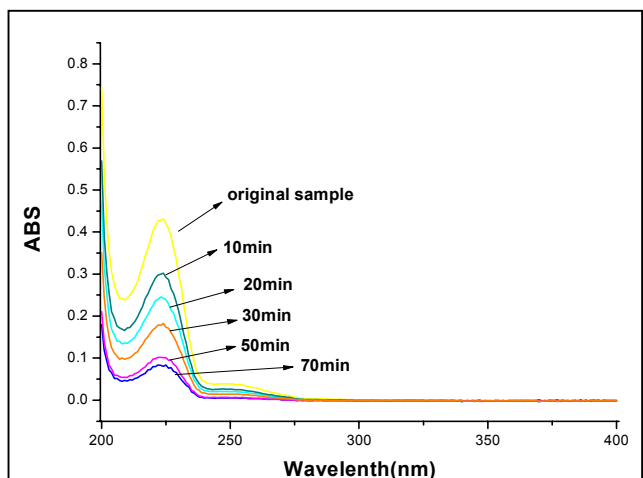
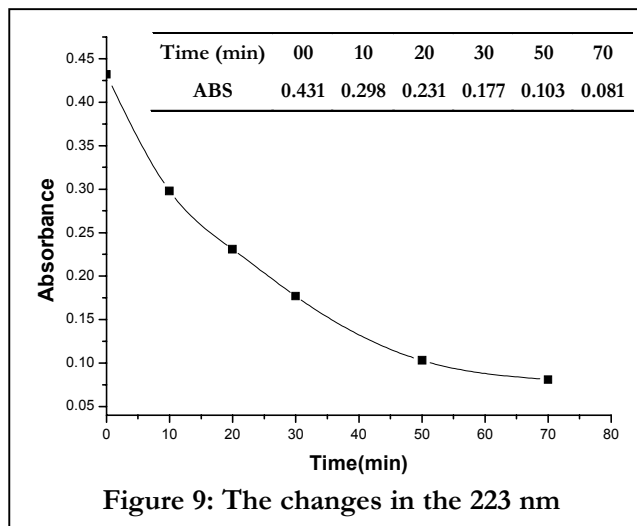


Figure 8: UV-Vis spectra of treated solution of sodium dodecyl benzene sulfonate with a 1000-fold dilution (operating conditions: applied cell voltage: 15V; Initial pH: 3; Electrolyte: Na_2SO_4 0.5N; T: room temperature; Current density: 50mA cm^{-2}). The times (in minutes) of the samples taken from the reactor are shown on the curves.



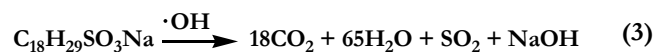
removed rapidly in the first 10min, the removal rate reached near 30%, which can also be seen clearly from the figure 9.

IR spectral studies

Figure 10 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 cm^{-1} 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-} .

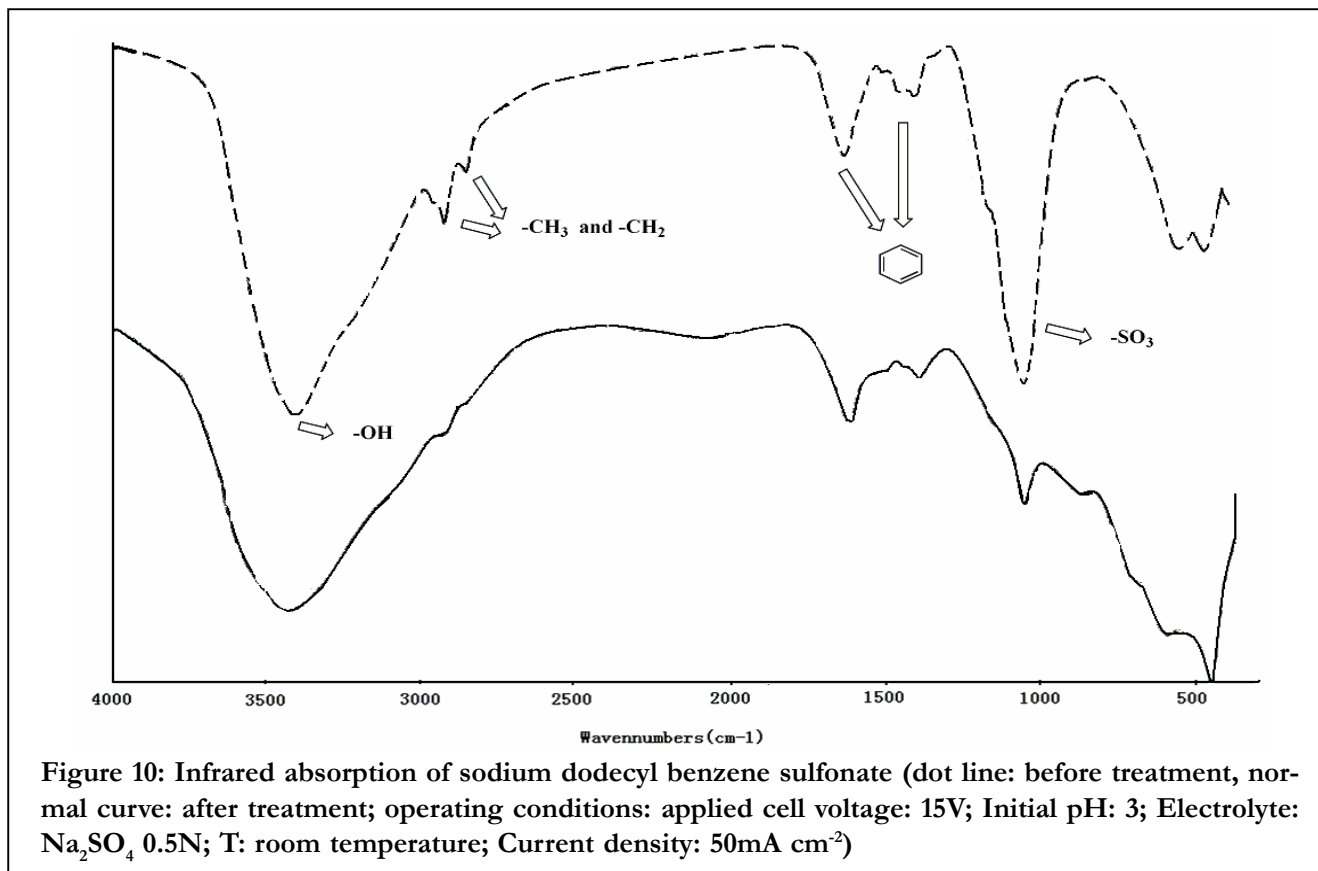
Possible mechanism

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 catalysis. It is necessary to discuss the role that electro-catalysis and adsorption catalysis 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:

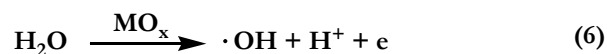


The process involve the following four steps: (i)

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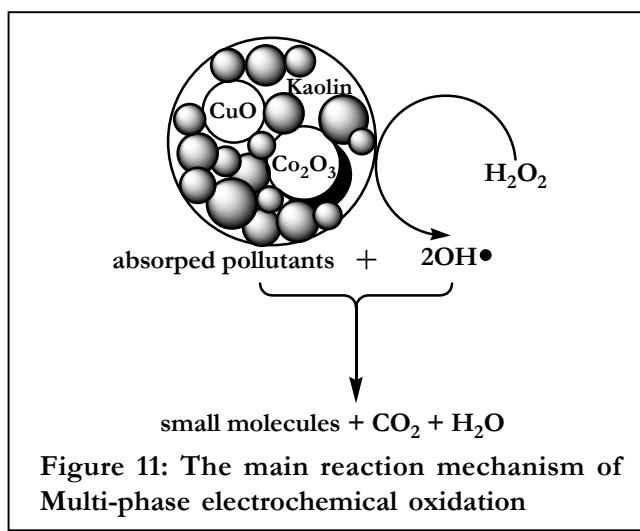
mass transfer of O₂ formed from anode toward the surface of the cathode, some OH· also produced from the anode, (ii) in the acid solutions, O₂ easily obtain electrons on the cathode and meanwhile reacted with hydrogen ion to form hydrogen peroxide.



(iii) hydrogen peroxide were decomposed and also produced highly reactive hydroxyl radicals in the presence of heterogeneous catalyst CuO-Co₂O₃-PO₄³⁻ modified Kaolin, (iv) the reaction between hydroxyl radicals and organic pollutants adsorbed on the surface of catalyst. The main reaction mechanism of multi-phase electrochemical oxidation can be summarized as figure 11.

CONCLUSION

The multi-phase electrochemical oxidation of wastewater containing anionic surfactants 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 electrocatalysis on the anode surface, or by adsorption catalysis on the surface of modified kaolin activated by electro field. The modified catalyst with a pored and big surface



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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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