

# Electrochemical treatment of anionic surfactants in synthetic wastewater with three-dimensional electrodes

Wuping Kong, Bo Wang\*, Hongzhu Ma, Lin Gu

*Institute of Energy Chemistry, College of Chemistry and Materials Science, Shaanxi Normal University, Xi'An 710062, China*

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## Abstract

The electrochemical oxidation of anionic surfactants (sodium dodecyl benzene sulfonate, DBS) contained in simulated wastewater treated by three-dimensional electrode system with combined modified kaolin served as packed bed particle electrodes and Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode was studied, the chemical oxygen demand (COD) removal of pollutants in the solutions was also investigated. The results showed that the three-dimensional electrodes in combined process could effectively decompose anionic surfactants. The COD removal efficiency can reach 86%, much higher than that of Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrodes used singly or modified kaolin employed singly (graphite as anode and cathode) on the same condition of pH 3 and 38.1 mA/cm<sup>2</sup> current density. The current efficiency and kinetic constant were calculated and energy consumption was studied. At the same time the influence of pH and current density on COD removal efficiency with combined three-dimensional electrodes was also investigated, respectively. The optimal initial pH value of degradation is 3 (acid condition), and a minor COD removal increase follows higher current density.

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**Keywords:** Modified kaolin particles; Three-dimensional electrode; Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode; COD removal

## 1. Introduction

Surfactants are made up of water-soluble and water-insoluble components. They can be classified according to functional ions in the solution: anionic, cationic, non-ionic and amphoteric. Owing to their special properties, surfactants are widely used in industrial production and family washing and are discharged as wastes after employed in factory and household. With the development of industrial economy and population increase, a large amount of the surfactants has been consumed, resulting in a serious environmental pollution problem [1].

The method of electrochemical oxidation for treatment of the organic contaminants contained in wastewater has become a hot focus in recent years because of its better effects than traditional chemical, physical and biological methods [2,3]. The three-dimensional electrode technology based on electrochemical oxidation has been attracting much more attention due to

that the rate of conversion within an electrochemical reactor can be increased substantially with its extensive specific surface area in comparison to conventional two-dimensional electrodes [4,5]. This is because that many small particles put into the three-dimensional electrode system form charged microelectrodes which are called particle electrodes under the influence of electric field. The three-dimensional electrode technology has been successfully used to remove metal ions from wastewater in the past. However, their application to eliminating organic pollutants from wastewater has just begun recently. In the oxidation process, the organics such as phenol and formic acids are ultimately mineralized using three-dimensional electrodes [6–8]. However, little attention has been paid to the possibility of applying electrochemical technology to the degradation of anionic surfactants.

Some researchers showed that titanium-based stannic oxide–antimony (III) anode materials had good effect on electrochemical oxidation on organics and wastewater treatment [9]. However, their poor stability led to that they could not apply to industry. According to the references [9,10], inter layer added between stannic oxide paint-coat and titanium matrix could enhance the stability and prolong the lifetime, though their cat-

\* Corresponding author. Tel.: +86 29 85308442; fax: +86 29 85307774.  
E-mail address: wangbo@snnu.edu.cn (B. Wang).

alytic effect were not good relative to titanium-based stannic oxide–antimony (III) electrodes [9].

As part of our systematic investigation on wastewater treatment with modified kaolin, the present study describes sodium dodecyl benzene sulfonate (DBS) taken, for example, of anionic surfactants as the target substance and modified kaolin particles that have a kind of absorption reaction on anionic surfactants were used and served as particle electrodes, along with titanium-based stannic oxide–antimony (III) as anode with cobalt inter layer.

In this work, we examined the properties of modified kaolin particles through SEM and XRD briefly and investigated the impact of pH value and current density on chemical oxygen demand (COD) removal efficiency of anionic surfactants in solutions in order to find the optimal conditions for electrolysis at the same time. It can be found that the effect of modified kaolin used was satisfactory.

## 2. Materials and experimental methods

### 2.1. Reagent

Kaolin used was analytical grade with the composition of  $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$  (surface area:  $20\text{ m}^2/\text{g}$ , pore volume:  $0.5\text{ cm}^3/\text{g}$ ). All chemical materials employed were of analytical purity grade. Distilled water was used as solvent.

The synthetic solution was prepared dissolving about  $0.75\text{ g}$  of sodium dodecyl benzene sulfonate (molar weight  $M = 348.48\text{ kg mol}^{-1}$ ), representing the anionic surfactants, in distilled water with  $15\text{ g/L Na}_2\text{SO}_4$ .

### 2.2. Preparation of the $\text{MnO}_x\text{--NiO}_y\text{--PO}_4^{3-}$ -modified kaolin

Forty-five grams  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ ,  $20\text{ g NiCl}_2\cdot 6\text{H}_2\text{O}$  and  $50\text{ g NaH}_2\text{PO}_4$  were mixed and dissolved in  $250\text{ mL}$  distilled water solution sufficiently in a beaker, then  $10\text{ mL H}_3\text{PO}_4$  was added to the solution. The solution pH was adjusted properly with  $\text{NaOH}$  in order to produce precipitates. Then  $200\text{ g}$  kaolin was put into beaker, and whisked mechanically  $4\text{ h}$  at  $50^\circ\text{C}$ . Clear liquid above deposits was poured out and deposits washed with distilled water. This procedure was repeated three times, filtered.

The metal complex materials after filtration were dehydrated in the drier, and molded into many small amorphous particles which were decomposed in the furnace at  $750^\circ\text{C}$  for  $4\text{ h}$ .

### 2.3. Preparation of $\text{Ti/Co/SnO}_2\text{--Sb}_2\text{O}_3$ anode

The titanium plates were subjected to surface pre-treatment with corundum sandblasting and hot hydrochloric acid pickling. The propanol–HCl solution dissolving the mixture of  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{TiCl}_4$  were used as the coating solutions for the inter layer and painted uniformly on the titanium plates, then the liquid coated on the plates was evaporated at  $85^\circ\text{C}$  and repeated several times. The materials of the inter layer were thermally annealed at  $500^\circ\text{C}$  for  $1.5\text{ h}$ . The outer layer prepared by mixing  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  proportionally dissolved in propanol–HCl mixture was painted uniformly on the inter layer of the electrode, afterwards the solvent was evaporated in air at  $85^\circ\text{C}$  and repeated several times, then outer layer were annealed at  $500^\circ\text{C}$  for  $2\text{ h}$ . This procedure was repeated until the coating thickness was  $50\text{ }\mu\text{m}$ .

### 2.4. Experimental setup

The experiments of the electrochemical oxidation of sodium dodecyl benzene sulfonate were carried out in a reactor made of Pyrex glass with volume of  $0.25\text{ dm}^3$  and filled with  $0.15\text{ dm}^3$  solutions containing dissolved DBS and  $15\text{ g/L Na}_2\text{SO}_4$  as the electrolyte (Fig. 1) [1]. There is a support layer attached to the reactor and used to load up with modified kaolin near the bottom. The  $\text{Ti/Co/SnO}_2$  electrode ( $60\text{ mm} \times 110\text{ mm} \times 2\text{ mm}$ ) was used as anode and graphite plate ( $600\text{ mm} \times 110\text{ mm} \times 2\text{ mm}$ ) was employed as cathode. A stirrer was driven by magnetic stirrer apparatus. The reaction temperature was monitored with a glass thermometer and was kept constant through pre-adjusting magnetic stirrer apparatus before experimentation.

### 2.5. Analysis and calculation

Scanning electron micrographs (SEM) were obtained with a scanning electron microscope (Quanta 2000, Philips-FEI Corporation, Holland). The crystallinity of the modified kaolin particles was determined by powder X-ray diffraction (XRD)

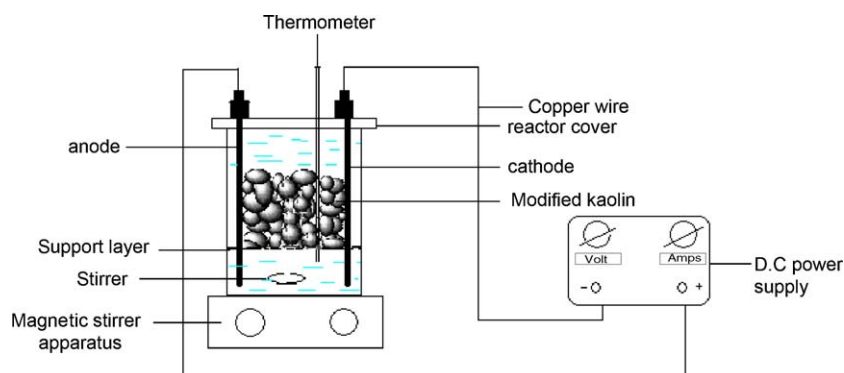


Fig. 1. Experimental setup.

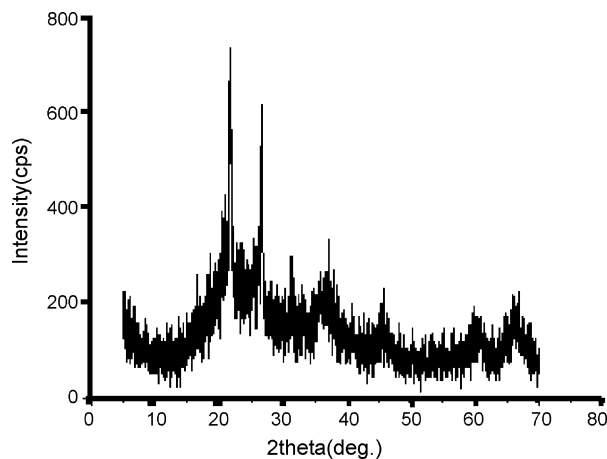


Fig. 2. XRD pattern of  $\text{MnO}_x\text{-NiO}_y\text{-PO}_4^{3-}$ -modified kaolin.

(D/Max-3c, Rigalco, Japan). An IR spectrometer, model IR Eouinx55 (Germany) was used for sample IR spectrometric analysis. After electrolysis, the sample was filtrated, and the filtrate was air-dried to a constant weight for IR analysis. Ultra-absorbance of the samples was monitored using a double beam UV-vis spectrophotometer (UV-7504, China). COD and pH value of all solutions and samples were determined according to standard methods for the examination of water and wastewater [11,12].

The current efficiency (CE) for the oxidation of the DBS was calculated from the values of the COD using Eq. (1):

$$\text{CE} = \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}]FV}{8I\Delta t} \quad (1)$$

where  $(\text{COD})_t$  and  $(\text{COD})_{t+\Delta t}$  are the chemical oxygen demands at  $t$  and  $t + \Delta t$  ( $\text{gO}_2 \text{ dm}^{-3}$ ), respectively,  $I$  the current density (A),  $F$  the Faraday constant ( $96,487 \text{ C mol}^{-1}$ ),  $V$  the volume of the electrolyte ( $\text{dm}^{-3}$ ) and 8 is a dimensional factor for unit consistence.

### 3. Results and discussion

#### 3.1. Characterization of modified kaolin

The XRD pattern of  $\text{MnO}_x\text{-NiO}_y\text{-PO}_4^{3-}$ -modified kaolin complex system is shown in Fig. 2. It was found that the

$\text{MnO}_x\text{-NiO}_y\text{-PO}_4^{3-}$ -modified material consisted primarily of original kaolin and a little amorphous component, which indicated the formation of the  $\text{MnO}_x\text{-NiO}_y\text{-PO}_4^{3-}$ -modified material. The crystallinity of the modified product was relatively high and it can be attributed to the structure formed with respect to the original kaolin. The intensity of each peak was relatively low, maybe due to that  $\text{MnO}_x$  and  $\text{NiO}_y$  were both dispersed into the inner structure of kaolin.

SEM of the product had been obtained to study the morphology of prepared amorphous particles. Dense surface could be seen in Fig. 3(a) and the porous structures were formed that had absorption effect and functioned as packed bed electrodes in Fig. 3(b).

#### 3.2. Study of the degradation of DBS

As could be seen from Fig. 4, the COD removal using  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  electrode solely was 56% at the end of 60 min at pH 3 and applied current density  $38.1 \text{ mA/cm}^2$ . When the modified kaolin particles (graphite as anode and cathode) employed singly, the COD removal efficiency on DBS can reach 72%, which indicates that the effect of using the modified kaolin particles is better than that of  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  used singly. It is probably because that the  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  anode could produce  $\text{O}_2$  and  $\text{OH}^\bullet$  simultaneously, while the generated  $\text{O}_2$  would reduce the hydroxyl radical electro-generated from water which could improve the DBS degradation effect. While the result of degradation by combining the modified kaolin particles with  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  electrode was best of all, and the COD removal reached 86% under the same condition. With extended electrochemical oxidation, the COD removal would be further improved. So the better effect was acquired than using them singly, respectively.

It is probably because modified kaolin particles have a kind of absorption reaction on pollutants and can serve as particle electrodes on which organics could be removed. Moreover, it can also be found from the Fig. 4 that the COD removal efficiency was only 25% of the modified kaolin particles (only absorption reaction occurred) without electrolysis, which indicates that the electrochemical oxidation of particle electrodes is more important than absorption. At the same time sodium dodecyl benzene sulfonate is incinerated by reaction with hydroxyl radical electro-generated from water discharge (Eqs. (2) and (3))

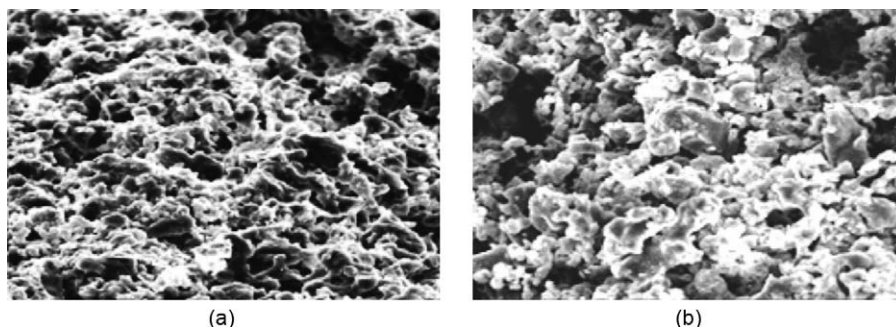


Fig. 3. Scanning electron micrographs of the surface of typical modified kaolin. Magnification: (a)  $1000\times$  and (b)  $5000\times$ .

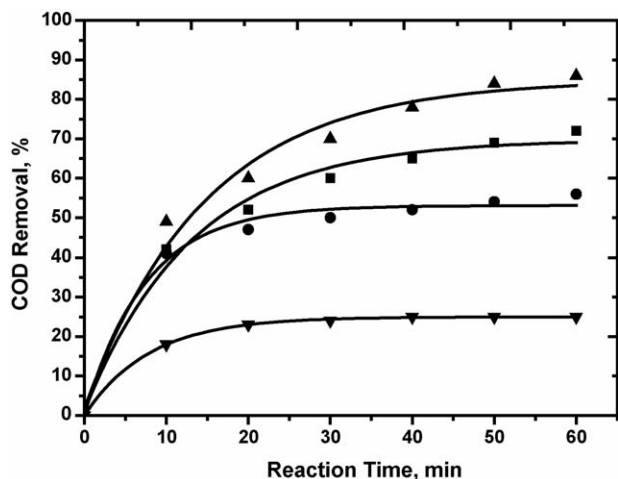
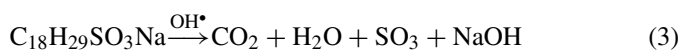


Fig. 4. Evolution of the COD removal with 15 g/L Na<sub>2</sub>SO<sub>4</sub> as electrolytes (condition: agitation speed = 300 rpm,  $T = 20^\circ\text{C}$ , pH 3, applied current density = 38.1 mA/cm<sup>2</sup>, (●) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>; (■) modified kaolin particles; (▲) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> + modified kaolin particles; (▼) modified kaolin particles (only absorption reaction)).

[1,9]:



It can also be found that the COD removal efficiency with three-dimensional electrodes of combined process is not simply equal to the sum of the individual removal efficiencies of modified kaolin particles and Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode, maybe due to the fact that the combined modified kaolin particles and Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode are more complex processes than the individual ones and hence the additive law of the individual system performances would be invalid [13].

The trend of CE with reaction time during the electrochemical process is shown in Fig. 5. It can be found that the CE of the electrochemical degradation with modified kaolin particles is much higher than that without it, which maybe due to that the

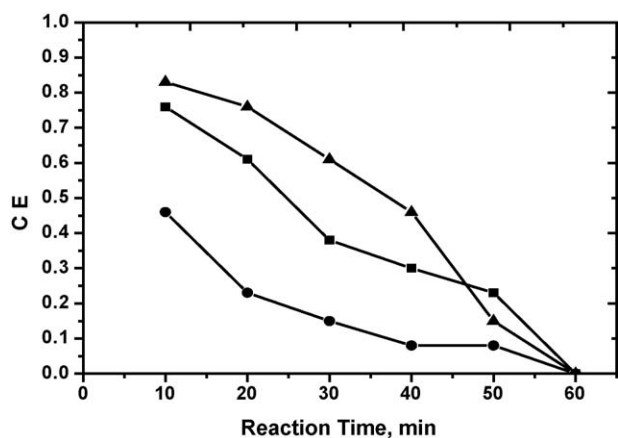


Fig. 5. Evolution of CE with 15 g/L Na<sub>2</sub>SO<sub>4</sub> as electrolytes (condition: agitation speed = 300 rpm,  $T = 20^\circ\text{C}$ , pH 3, applied current density = 38.1 mA/cm<sup>2</sup>, (●) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>; (■) modified kaolin particles; (▲) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> + modified kaolin particles).

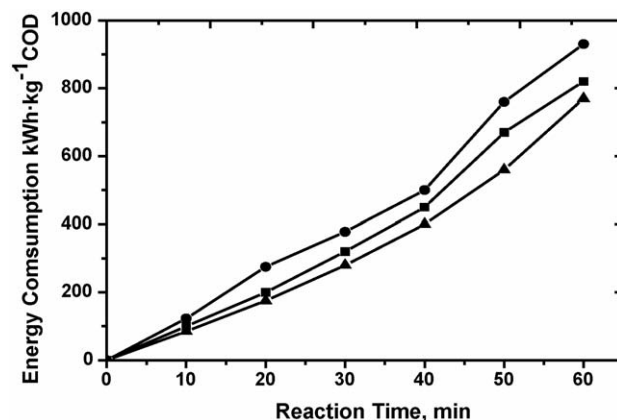


Fig. 6. Evolution of the energy consumption (condition: agitation speed = 300 rpm,  $T = 20^\circ\text{C}$ , pH 3, applied current density = 38.1 mA/cm<sup>2</sup>, (●) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>; (■) modified kaolin particles; (▲) Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> + modified kaolin particles).

kaolin particles serve as particle electrodes so that degradation of DBS not only take place at the anode, but also carried out on the surface of the kaolin particles. Moreover, the CE values in the first 30 min of treatment are higher than the last 30 min during all processes, which indicates that degradation of the first 30 min of treatment mainly contributes to the whole process.

Fig. 6 shows the evolution of energy consumption which is measured in kWh kg<sup>-1</sup> COD during the electrochemical process. The energy consumption of the combined process is less than that of the other individual processes, maybe due to that the COD removal in the combined process is the most quick.

The IR spectra of the dried solution residual before and after the three-dimensional electrochemical process combined modified kaolin particles with Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode are shown in Fig. 7. After electrolysis, peaks at 2957 and 2856 cm<sup>-1</sup> assigned to -CH<sub>3</sub> and -CH<sub>2</sub>, respectively, almost disappeared, in addition, the peak at about 1191 cm<sup>-1</sup> assigned to -SO<sub>3</sub> also weakened after the treatment, which may be due to that benzene sulfonate was oxidized to SO<sub>4</sub><sup>2-</sup>. It can be concluded that some structure changes might have occurred during the electrochemical process [14].

The changes in UV-vis absorbance characteristics of sodium dodecyl benzene sulfonate were investigated from 200 to 400 nm during the electrochemical degradation process and the results

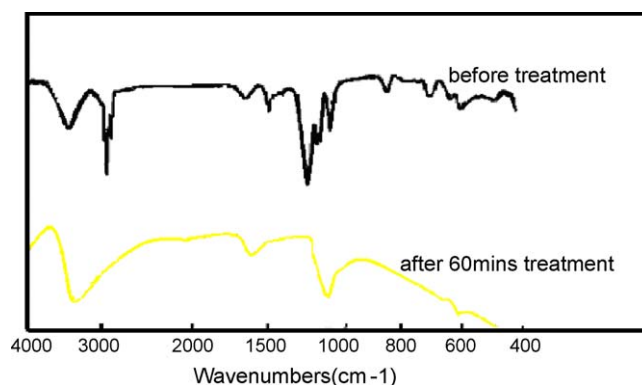


Fig. 7. Infrared spectra of anionic surfactant.



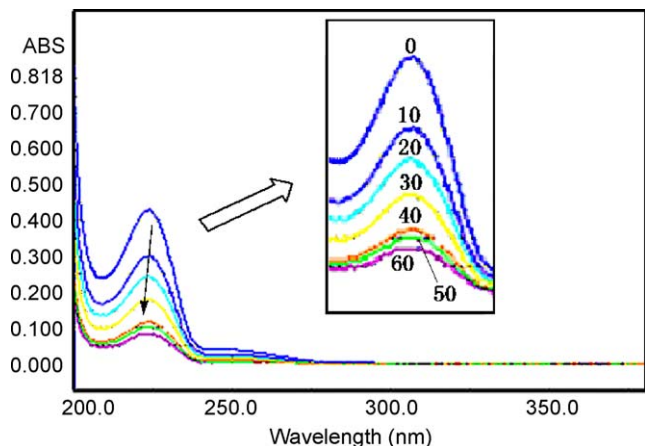


Fig. 8. UV-vis spectra of treated surfactant with three-dimensional electrodes.

are shown in Fig. 8. It can be seen that a maximum absorbance peak at 224 nm which represents the sodium dodecyl benzene sulfonate and disappears gradually during the electrochemical oxidation process. It can be concluded that the surfactant concentration decreases when three-dimensional electrochemical electrodes were applied.

### 3.3. Influence of pH on the COD removal

Fig. 9 shows the influence of initial pH on the variation of the COD during the electrochemical oxidation. As can be seen from this figure, there was a significant difference on COD removal of DBS when using three-dimensional electrodes under the combining process at different initial pH conditions: acid (pH 3), close to neutral (pH 6.5) and alkaline (pH 10). It seemed that the optimal pH value was 3 relative to 6.5 and 10 and three-dimensional electrodes ran more efficiently at a lower pH value. Moreover, when the pH of the solutions was adjusted to 10, more hydroxyl in the system was gathered at anode and competed with anode materials to produce oxygen, hence the degradation effect decreased and this result was not observed in some other

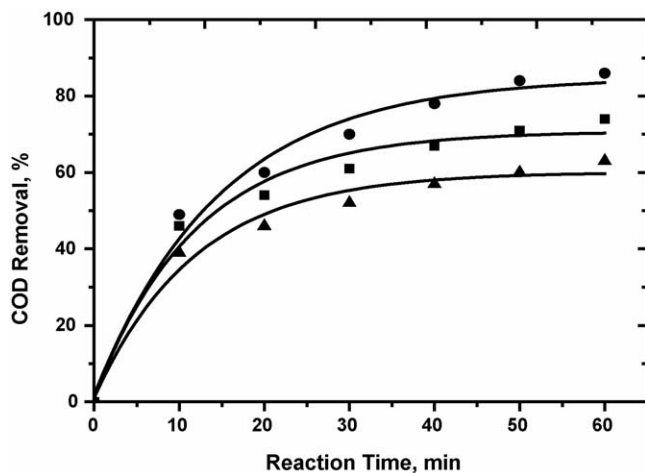


Fig. 9. Influence of initial pH on COD removal (condition: agitation speed = 300 rpm,  $T = 20^\circ\text{C}$ , applied current density =  $38.1\text{ mA/cm}^2$ , initial pH: (●) 3; (■) 6.5; (▲) 10).

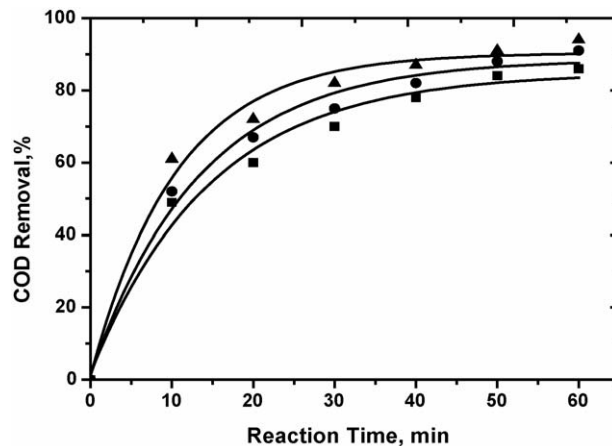


Fig. 10. Influence of applied current density on COD removal (condition: agitation speed = 300 rpm,  $T = 20^\circ\text{C}$ , pH 3, applied current density ( $\text{mA/cm}^2$ ) = (■) 38.1; (●) 57.1; (▲) 71.4).

papers [15–18]. The discrepancy may be attributed to the different electrolytes employed. The removal of sodium dodecyl benzene sulfonate in the present research was based on  $\text{Na}_2\text{SO}_4$  electrolyte while  $\text{NaCl}$  electrolyte was used in their works.

### 3.4. Influence of current density on the COD removal

The influence of the current density on the COD evolution during the electrolysis with the three-dimensional electrodes is reported in Fig. 10. The values of COD removal under the condition of current density 38.1, 57.1 and  $71.4\text{ mA/cm}^2$  at 60 min were 86, 90 and 93%, respectively. So the higher current density caused a faster COD removal. It was further noted that there were minor differences in the COD removal at the different current densities. This result could be explained that the more hydroxyl radical electro-generated by water discharge to oxidize sodium dodecyl benzene sulfonate and more oxygen evolution produced at  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  anode simultaneously with the increase of current density.

### 3.5. Possible mechanism and kinetic of degradation of DBS

The kinetics of the treatment on DBS at certain conditions, including reaction temperature and applied current density, could be expressed as Eq. (4):

$$\frac{-d[\text{DBS}]}{dt} = k[\text{DBS}] \quad (4)$$

where  $k$  is the apparent pseudo-first order kinetic constant for the electrochemical process of DBS degradation. Because the concentration of DBS is in proportion to quantity of COD, Eq. (4) can be transformed into Eq. (5):

$$\frac{-d[\text{COD}]}{dt} = k[\text{COD}] \quad (5)$$

With Eq. (5) above, the values of kinetic constant  $k$  in the electrolysis with modified kaolin and  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  electrode (combined process) and employed singly are calculated in Table 1.

Table 1  
Calculation of kinetic constant in the electrochemical processes

Process	Kinetic constant, $k$ ( $\text{min}^{-1}$ )	Coefficient
Modified kaolin	0.032	0.9875
Ti/Co/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>3</sub>	0.025	0.9954
Combining process	0.044	0.9846

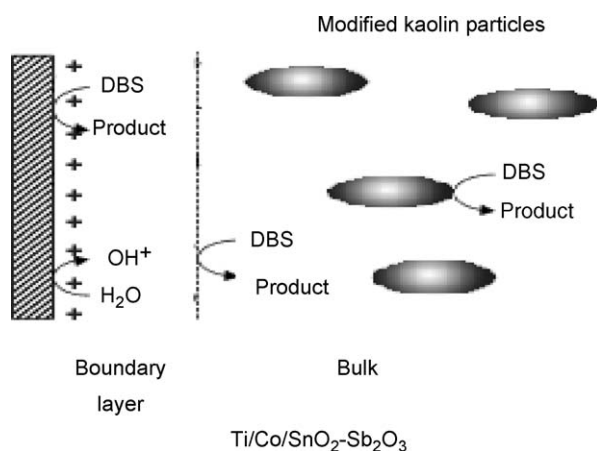


Fig. 11. Possible processes of degradation of DBS compounds.

Fig. 11 shows that the possible mechanism of electrochemical abatement process of sodium dodecyl benzene sulfonate which was degraded through direct and indirect oxidation. Hydroxyl radicals generated at Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode in the course of electrolysis could oxidize organic compounds [19–23]. At the same time sodium dodecyl benzene sulfonate could be either absorbed on the surface of the modified kaolin particles, then are oxidized at particle electrodes, or oxidized at Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode directly.

#### 4. Conclusions

The electrochemical oxidation combining modified kaolin with Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode in the three-dimensional electrode system can be successfully carried out for treating the sodium dodecyl benzene sulfonate anionic surfactants contained in synthetic wastewater with Na<sub>2</sub>SO<sub>4</sub> electrolyte. From the results, it can be concluded that the degradation effect of the combining process is better than that of employing modified kaolin singly and using Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode singly, respectively. The influence of pH and current density on COD removal efficiency under the combining electrolysis was also investigated. It was found that the pH value has a significant impact on the COD removal in the course of the electrochemical treatment.

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