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## Electrochemical Treatment Of Anionic Surfactants In Synthetic Wastewater With Three-Dimensional Electrodes



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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 could effectively remove anionic surfactants. Its COD removal efficiency was 86% much higher than those of Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode used singly and modified kaolin employed singly at the same condition of pH 3 and 38.1 mA/cm<sup>2</sup> current density. At the same time the influence of pH and current density on COD removal efficiency with three-dimensional electrodes was also investigated, respectively.

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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.

### INTRODUCTION

Surfactants are made up of water-soluble and water-insoluble component. 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 in-

dustrial production and family washing. After employed in factory and household, they are discharged as wastes. With the development of industrial economy and increasing of population, large number of the surfactants has been consumed, resulting in a serious environmental pollution problem<sup>[1]</sup>.

The method of electrochemical oxidation for

treatment of the organic contaminants contained in wastewater has become a hot focus in recent years because of better effects than traditional chemical, physical and biological methods<sup>[2-4]</sup>, including three-dimensional electrodes. In the oxidation process, the compounds such as phenol and formic acid, are ultimately achieved to mineralize using three-dimensional electrodes<sup>[5-8]</sup>. However, little attention has been paid to the possibility of applying electrochemical technology to the degradation of anionic surfactants. It has also not been reported that anionic surfactants were treated with three-dimension electrodes.

In our experiments, we took sodium dodecyl benzene sulfonate (DBS) for example of anionic surfactants as target and used modified kaolin that had a good absorption effect on anionic surfactants and served as particle electrodes and titanium-based stannic oxide-antimony(III)oxide anode with cobalt inter layer. Some researches showed that titanium-based stannic oxide-antimony(III)oxide anode materials had good effect on electrochemical oxidation on organics and wastewater treatment<sup>[9-10]</sup>. However, their poor stability led to that they could not apply to industry. According to some reports, inter layer added between stannic oxide paint-coat and titanium matrix could enhance the stability and prolong the lifetime, though their catalytic effect were not good relative to titanium-based stannic oxide-antimony(III)oxide electrodes<sup>[9]</sup>. So  $\text{MnO}_x\text{-NiO}_y\text{-PO}_4^{3-}$ -modified kaolin was used in electrolytic apparatus to improve the effect of degradation of compounds. Modified kaolin was a kind of complex solid-phase system constituted of kaolin and containing mainly  $\text{Mn}^{2+}$  metal ions. It possessed big surface to absorb pollutants and served as particle electrodes to oxidize them. In this work, we discussed 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.

## MATERIALS AND METHODS

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

### kaolin

45g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , 20g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 50g  $\text{NaH}_2\text{PO}_4$  were mixed and dissolved in 250 ml distilled water solution sufficiently with beaker, then 10ml  $\text{H}_3\text{PO}_4$  was added to solution. The solution pH was adjusted properly with NaOH in order to produce deposits. Then 200g kaolin was put into beaker, and whisked mechanically 4 h at 50 °C. Clear liquid above deposits was poured out and deposits were washed with distilled water. As a moment went on, clear liquid was poured out again and did it in this way three times, filtrated. 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°C for 4 h.

### 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) (D/Max-3c, Rigalcu, Japan). 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. Ultra-absorbance of the samples was monitored using a double beam UV-Vis spectrophotometer (UV-7504, China). COD content and pH of all solutions and samples were determined according to standard methods for the examination of water and wastewater<sup>[11]</sup>. The COD removal ratio was calculated as follows:

$$\% \text{ COD removal} = (\text{COD}_0 - \text{COD}) / \text{COD}_0 \times 100\%$$

( $\text{COD}_0$ : COD value before electrolysis and COD: COD value after electrolysis).

### Experimental setup

The experiments of the electrochemical oxidation of sodium dodecyl benzene sulfonate was carried out in a reactor made of Pyrex glass with volume of 0.25 dm<sup>3</sup> and filled with 0.15 dm<sup>3</sup> solutions containing dissolved DBS and 15g/L  $\text{Na}_2\text{SO}_4$  electrolyte (Figure 1). There is a support layer attached to the reactor and used to load up with modified

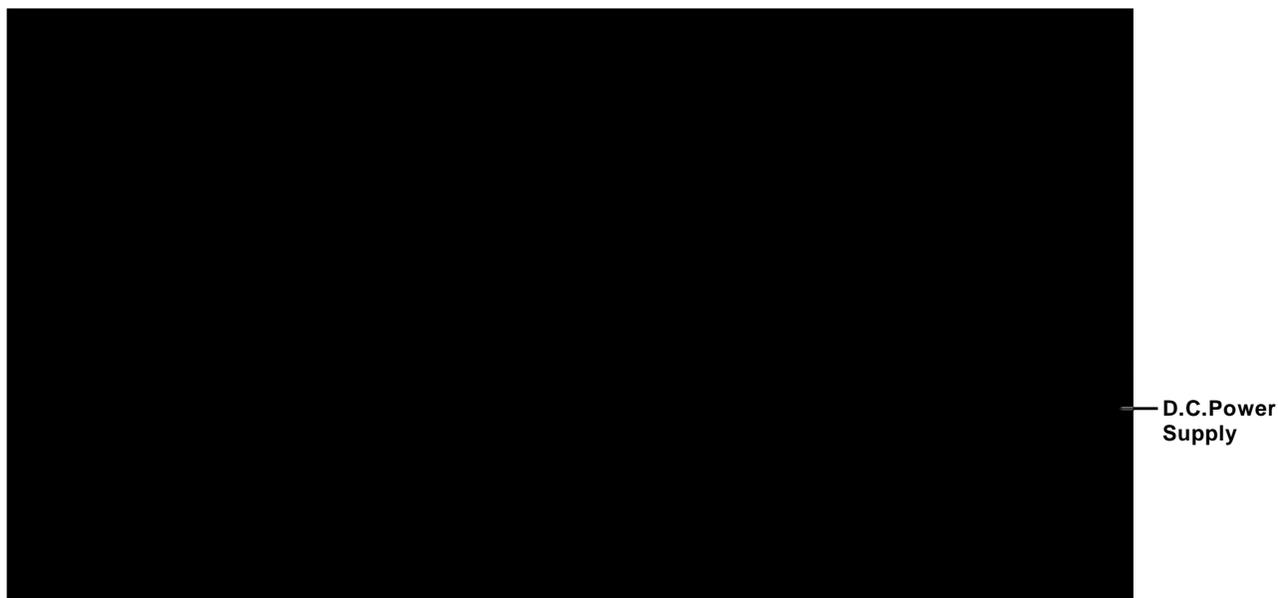


Figure1: Experimental setup

kaolin near the bottom. The Ti/Co/SnO<sub>2</sub> electrode (60mm × 110mm × 2mm) was used as an anode and graphite plate (600mm × 110mm × 2mm) was employed as a cathode. A stirrer was driven by magnetic stirrer apparatus. The reaction temperature was monitored with a glass thermometer.

All chemical materials employed are of analytical purity grade. Solvents in all solutions used are distilled water.

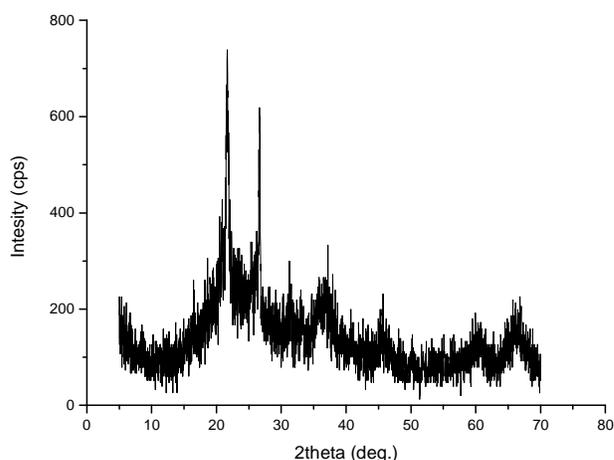
#### Preparation of Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode

The titanium plates were subjected to surface pre-treatment with corundum sandblasting and hot hydrochloric acid pickling. Inter layer liquid constituted of a mixture of SnCl<sub>4</sub>·5H<sub>2</sub>O, Sb<sub>2</sub>O<sub>3</sub>, COCl<sub>2</sub>·6H<sub>2</sub>O and TiCl<sub>4</sub> proportionally dissolved in propanol-HCl mixture was painted averagely on the titanium plated. Then the solvent was evaporated in air at 85°C and do it repeatedly ten times. Then the inter layer materials were decomposed at 500°C for 1.5 h. Outer layer prepared by a mixture SnCl<sub>4</sub>·5H<sub>2</sub>O, Sb<sub>2</sub>O<sub>3</sub> and COCl<sub>2</sub>·6H<sub>2</sub>O proportionally dissolved in propanol-HCl mixture was painted averagely on the inter layer of the electrode, afterwards the solvent was evaporated in air at 85°C and operated it three times. Then out layer were decomposed at 500°C for 2 h. There after this procedure was repeated until the coating thickness was 50μm.

## RESULTS AND DISCUSSION

### Characterization of modified kaolin

The XRD pattern of MnO<sub>x</sub>-NiO<sub>y</sub>-PO<sub>4</sub><sup>3-</sup>-modified kaolin complex system was shown in figure 2. It was found that materials mainly contained the silicon dioxide which was one of components of kaolin and a few manganese oxides and nickel oxides and few phosphate radicals. Their intensities of peak were weak relative to silicon dioxide as a result of amount of manganese chloride, nickel chloride and phos-

Figure 2: XRD pattern of MnO<sub>x</sub>-NiO<sub>y</sub>-PO<sub>4</sub><sup>3-</sup>-modified kaolin

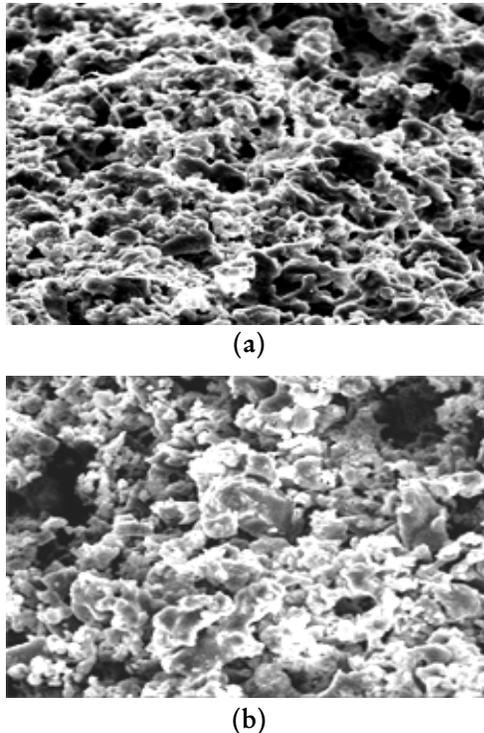


Figure 3: Scanning electron micrographs of the surface of typical modified kaolin (a): magnification 1000 $\times$ ; (b): magnification 5000 $\times$ .

phate radicals compounds added to the complex system were much lower than of silicon dioxide which loaded up with them.

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

### Study of degradation of DBS

As could be seen from figure 4, the COD removal using Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode solely was 56% at the end of 60min at pH 3 and applied current density 38.1mA/cm<sup>2</sup>, this was because that Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode could produce oxygen evolution. But COD removal efficiency on DBS by combined modified kaolin particles with Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode 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 was probably because modified kaolin particulates had a big surface that could absorb pollutants and served as particle electrodes on which organics could be removed. At the same time sodium dodecyl benzene sulfonate was incinerate by reaction with hydroxyl radical electro-generated by water discharge (Reaction 1 and Reaction 2)<sup>[1,9]</sup>:

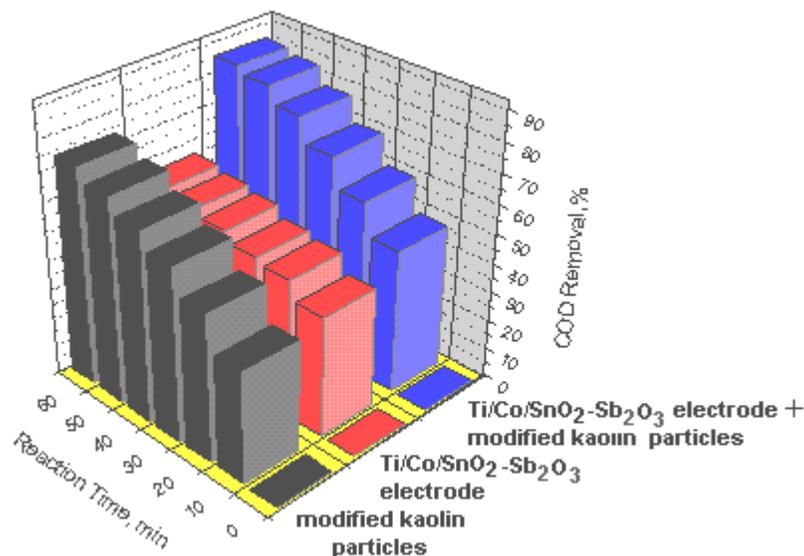
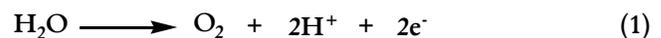
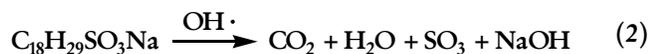


Figure 4: Evolution of the COD removal during the treatment of synthetic DBS wastewater using 15 g/L Na<sub>2</sub>SO<sub>4</sub> as supporting electrolytes. Condition: agitation speed = 300 rpm, T = 20°C, pH = 3, applied current density = 38.1 mA/cm<sup>2</sup>.

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It can also be found that the COD removal efficiency by combined modified kaolin particles and Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode is not simply equal to the sum of the individual removal efficiencies by combined modified kaolin particles and by Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode. This is 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

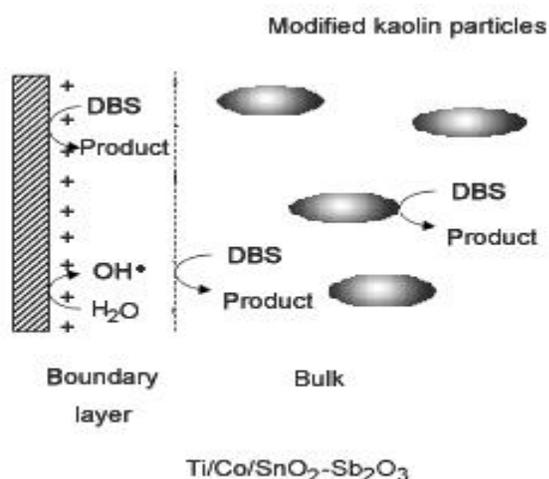


Figure 5: Processes of degradation of DBS compounds

than the individual ones and hence the additive law of the individual system performances would be invalid<sup>[12]</sup>.

Figure 5 shows that assumable mechanism of electrochemical abatement process of sodium dodecyl benzene sulfonate which was degraded through direct and indirect oxidation. Hydroxyl radicals were generated at Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode in the course of electrolysis that could oxidize organic compounds<sup>[13]</sup>. This was indirect process. At the same time sodium dodecyl benzene sulfonate could be either oxidized at Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> anode directly or at modified particle electrodes.

Figure 6 shows the IR spectral 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. After electrolysis, peaks at 2957 cm<sup>-1</sup> 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.

The changes in UV-Vis absorbance characteris-

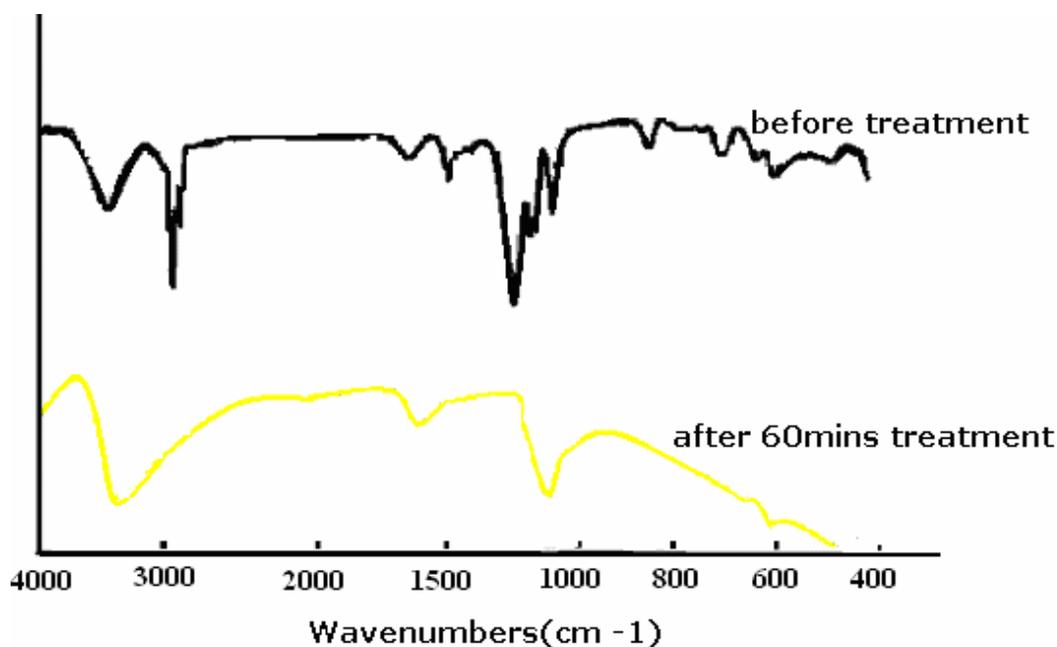


Figure 6: Changes of infrared absorption bands of anionic surfactant

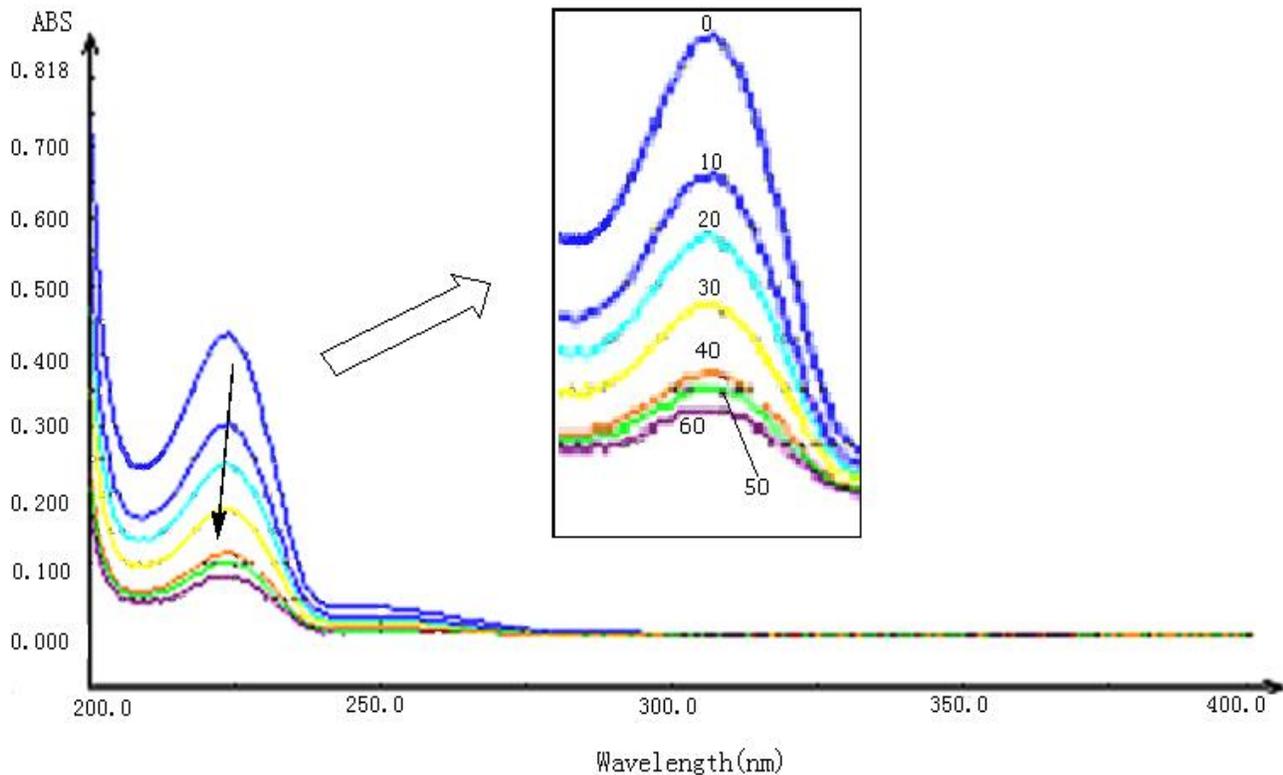


Figure 7: UV-Vis spectra of treated surfactant with three dimensional electrodes

tics of sodium dodecyl benzene sulfonate were investigated from 200 to 400nm during the electrochemical degradation process and the results are shown in figure 7. It can be seen that a maximum absorbance peak at 224nm 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.

#### Influence of pH on the COD removal

Figure 8 shows the influence of initial pH on the variation of the COD during the electrochemical oxidation. As can be seen from this figure that there was significant difference in COD removal on DBS used combined Ti/Co/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> electrode with modified kaolin particles between electrolysis with an electrolyte under initial acid (pH 3), close to neutral (pH 6.5) and alkaline (pH 10) conditions. It seemed that the optimal pH value was 3 relative to 6.5 and 10 and three dimensional electrodes ran more efficiently at lower pH value. Moreover, when the

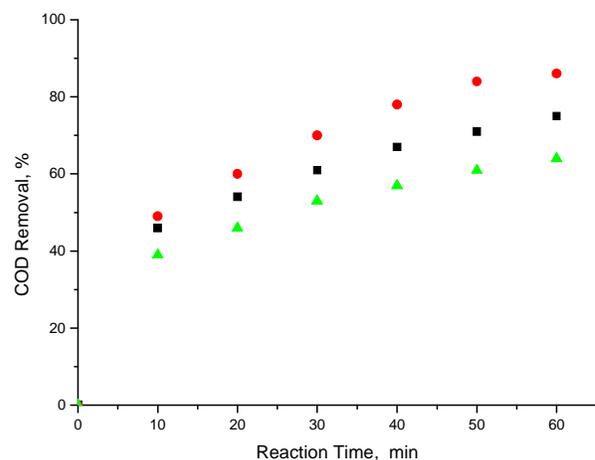


Figure 8: Influence of initial pH on evolution of the COD removal during the treatment of synthetic DBS wastewater using 15 g/L Na<sub>2</sub>SO<sub>4</sub> as supporting electrolytes. Condition: agitation speed = 300 rpm, T = 20°C, applied current density = 38.1 mA/cm<sup>2</sup>, initial pH = (●) 3; (■) 6.5; (▲) 10.

pH of the solutions was adjusted 10, more hydroxyl in the system were gathered at anode and competed with anode materials to react to produce oxygen, hence caused bad degradation effect. The result was

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not observed in some other papers<sup>[14-16]</sup>. 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 work.

### Influence of current density on the COD removal

The influence of the current density on the COD evolution as a function of time during the electrolysis with the three-dimensional electrodes is reported in figure 8. The COD removal under the condition of current density 38.1, 57.1 and 71.4 mA/cm<sup>2</sup> 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.

### CONCLUSIONS

This study presents that electrochemical oxidation combined modified kaolin with  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  electrode in three-dimensional system can be successfully carried out for treating sodium dodecyl benzene sulfonate anionic surfactants contained in synthetic wastewater with  $\text{Na}_2\text{SO}_4$  electrolyte due to that modified kaolin particles have absorption effect and serve as particle electrodes. Comparing to three-dimensional electrodes method, the degradation effect of sodium dodecyl benzene sulfonate using  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  anode singly is not good, because it can produce oxygen evolution. The pH value has significant impact on the COD removal. The optimal initial pH value of the degradation is at 3 (acid condition). But a minor COD removal increase follows higher current density.

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