

Electrochemical treatment of paper mill wastewater using three-dimensional electrodes with Ti/Co/SnO₂-Sb₂O₅ anode

Bo Wang*, Wuping Kong, Hongzhu Ma

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

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Abstract

The properties of the interlayer and outer layer of Ti/Co/SnO₂-Sb₂O₅ electrode were studied, and the electrochemical behavior was examined as well. As a result of unsatisfactory treatment using Ti/Co/SnO₂-Sb₂O₅ electrode, electrochemical disposal of paper mill wastewater employing three-dimensional electrodes, combining active carbon granules serving as packed bed particle electrodes, with Ti/Co/SnO₂-Sb₂O₅ anode, was performed. The outcome demonstrates that efficient degradation was achieved. The residual dimensionless chemical oxygen demand (COD) concentration reached 0.137, and color removal 75% applying 167 mA cm⁻² current density at pH 11 and 15 g l⁻¹ NaCl. The instant current efficiency, energy cost, electrochemical oxidation index (EOI) and kinetic constant of the reaction were calculated. At the same time, the influence of pH and current density on COD abatement and decolorization was also investigated, respectively. © 2006 Elsevier B.V. All rights reserved.

Keywords: Three-dimensional electrodes; Ti/Co/SnO₂-Sb₂O₅ electrode; Residual dimensionless COD concentration; Color removal

1. Introduction

With the development of industrial economy and the increase of population, enormous amounts of paper have been consumed so that large quantities of wastewater discharged by paper mills in natural water receptors have been causing severe environmental problem. This kind of paper mill wastewater, containing many toxic and intensely colored, mainly organic substances, is characterized by a high level of chemical oxygen demand (COD). Thus, it is necessary to be treated to reduce any possible impacts on the aquatic environment [1–4].

There are several conventional wastewater treatment methods, including physical, chemical and biological methods, and many treatment processes have been studied. The biological methods are very effective for the disposal of wastewater with a high value of biological oxygen demand (BOD), but they are ineffective if recalcitrant organic compounds are present because they must be supported by a physical-chemical treatment [5]. Up to now, great attention has been directed toward new techniques, based on chemical or physical processes [6–9].

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 convenience and effectiveness than traditional methods [10]. Since the discovery by Beer, about 30 years ago, a lot of work has been done on the dimensionally stable anode (DSA) of catalytic oxide electrode, which can generate an active hydroxyl radical and active chloride species to destroy refractory organic waste into carbon dioxide in the course of polluted water treatment [11]. Although tin- and antimony-oxide based electrodes (Ti/SnO₂-Sb₂O₅) are promising anodes for the electrochemical treatment of wastewater and ground water because of their high over-potential for oxygen evolution, their ability to generate hydroxyl radicals and the lower cost compared to that of precious metal oxides. The commercial application of Ti/SnO₂-Sb₂O₅ is hampered by its short lifetime [12]. Interlayer added between stannic oxide paint-coat and titanium matrix may enhance the stability and prolong the lifetime of these electrodes [13]. The voltametric behavior of Ti/SnO₂-Sb₂O₅ anode with Co interlayer has not been studied so far.

In the present study, the properties of Ti/Co/SnO₂-Sb₂O₅ anode were examined, including its morphology. Then, paper mill wastewater was treated through three-dimensional electrode reactor combining plenty of active carbon granules, serving as

* Corresponding author. Fax: +86 29 85307774.
E-mail address: wangbo@snnu.edu.cn (B. Wang).

particle electrodes, with the Ti/Co/SnO₂-Sb₂O₅ anode in order to attain the best degradation effect. The three-dimensional electrode technology based on electrochemical oxidation has been attracting much more attention due to the fact that the rate of conversion within an electrochemical reactor can be increased substantially with its large specific surface area in comparison to conventional two-dimensional electrodes [14–15]. This is because, the large number of the active carbon particles placed into the three-dimensional electrode system form charged microelectrodes, which are called particle electrodes, under the influence of electric field. The variation of the residual COD concentration and the wastewater decolorization was compared in the different experimental runs, employing Ti/Co/SnO₂-Sb₂O₅ anode alone or in combination with active carbon granules. At the same time, the instantaneous current efficiency (ICE) and energy consumption were calculated in the different electrochemical treatment processes. The impact of pH value and current density on the COD abatement effect and the decolorization of the wastewater solutions, were investigated.

2. Materials and experimental methods

2.1. Reagents and paper mill wastewater

Active carbon, with a particle size range from 0.22 to 1.48 mm was used. The mean particle size of active carbon was 0.84 mm. The surface area is 20 m² g⁻¹. All chemical materials employed are of analytical purity grade. Distilled water was used to prepare all the solutions. Throughout the experiment, the wastewater used, was taken from the same batch collected from the paper mill industry.

2.2. Ti/Co/SnO₂-Sb₂O₅ electrode preparation

The titanium plates were subjected to surface pre-treatment with corundum sandblasting and hot hydrochloric acid pickling. Interlayer liquid mixture constituted of SnCl₄·5H₂O, CoCl₂·6H₂O and TiCl₄ dissolved in propanol-HCl solution was painted on the titanium plated. Then the solvent was evaporated in air at 85 °C and the same procedure was repeatedly ten times. Then the interlayer materials were decomposed at 700 °C for 2 h. The outer layer was prepared by a mixture of SnCl₄·5H₂O, SbCl₃ dissolved in propanol-HCl painted on the surface of the interlayer of the electrode, afterwards the solvent was evaporated in air at 85 °C and the procedure was repeated three times. Then its materials were decomposed at 700 °C for 2 h. This procedure was repeated until the coating thickness became 50 μm.

3. Instruments

3.1. Procedure and set-up

The experiments were carried out by batch processes using undivided cell of 0.15 L capacity and 15 g L⁻¹ NaCl as electrolyte under constant temperature conditions (room temperature). The anode and cathode were positioned vertically and parallel to each other. The Ti/Co/SnO₂ electrode

(60 mm × 110 mm × 2 mm) was used as an anode and a porous graphite plate (60 mm × 110 mm × 2 mm) was employed as a cathode. A support layer was attached to the cell and was used to load up with active carbon particles near the bottom. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. A regulated DC power supply (WYK302b, Xi'an, China), was used while the current and voltage were adjustable between 0–2.5 A and 0–35 V, respectively. During the experiments, samples were drawn from the cell at every ten minutes and were analyzed.

3.2. Analysis and calculation

The initial pH of the solution was measured using an Orion 290 pH meter. The COD and decolorization were chosen as parameters in order to evaluate the effect of electrochemical treatment. The UV-vis (UV-7504, China) spectrum of the sample was recorded. The maximum visible absorbance wavelength was detected. The COD values of the sample were measured using a Dr. Lange LASA50 system. The color removal ratio was calculated as follows:

$$\% \text{decolorization} = \frac{\text{ABS}_0 - \text{ABS}}{\text{ABS}_0} \times 100\% \quad (1)$$

ABS₀ and ABS are the absorbance values before and after electrolysis, respectively.

Both the ICE of the electrolysis and the electrochemical oxidation index (EOI), which is an average value, were calculated from the values of the COD using the Eqs. (2) and (3), respectively [16–17]:

$$\text{ICE} = \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}]FV}{8I\Delta t} \quad (2)$$

$$\text{EOI} = \frac{\int \text{ICE} dt}{\tau} \quad (3)$$

where (COD)_t and (COD)_{t+Δt} are the COD values at *t* and *t* + Δ*t* (in gO₂ dm⁻³), respectively, *I* is the current intensity (A), *F* is the Faraday constant (96487 C mol⁻¹), *V* is the volume of the electrolyte solution (L), 8 is a dimensional factor for unit consistence and *τ* is the time at which ICE is almost zero. The cost of energy is also considered according to Eq. (4) as follows [18]:

$$E = \frac{UI \Delta t}{(\text{COD}_t - \text{COD}_{t-\Delta t})V} \quad (4)$$

where (COD)_t and (COD)_{t-Δt} are the COD values at *t* and *t* - Δ*t* (in gO₂ dm⁻³), respectively, *U* is the average cell potential (V), *I* is the current intensity (A), *V* is the volume of the electrolyte solution (L).

The cyclic voltametric behavior was examined through a conventional three electrode cell in conjunction with a computer controlled potentiostat/galvanostat (BAS100B). Ti/Co/SnO₂-Sb₂O₅ electrode was used as a working electrode, graphite as a counter electrode, and Hg/Hg₂Cl₂·KCl (sat) as a reference. Scanning electron micrographs (SEMs) were obtained with a

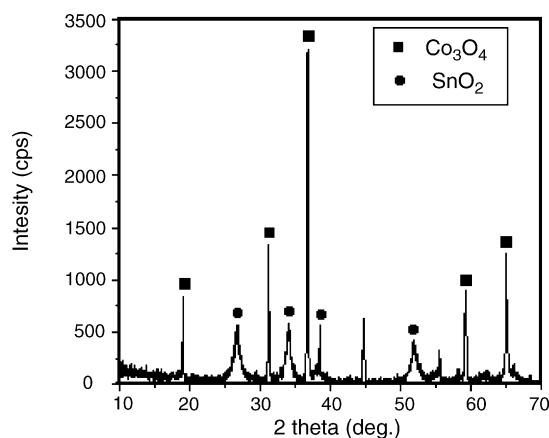


Fig. 1. XRD pattern of interlayer coating powders of Ti/Co/SnO₂-Sb₂O₅ electrode.

scanning electron microscope (Quanta 2000, Philips-FEI Corporation, Holland). Thermo gravimetric analysis (TGA): a TA instrument Q600SDT, USA) for the measurement of thermal decomposition properties of Co chlorides was used. The powder X-ray diffraction (XRD, D/Max-3c, Rigalcu, Japan) analysis was also carried out. The surface area of active carbon (AC) particles was measured via the N₂ sorption method using a quantachrome autosorb automated gas sorption system.

4. Results and discussion

4.1. The study of Ti/Co/SnO₂-Sb₂O₅ electrode

Fig. 1 shows the XRD pattern of interlayer coating powders of Ti/Co/SnO₂-Sb₂O₅ electrode. Diffraction peaks corresponding to Co₃O₄ and SnO₂ were detected, but the peaks representing CoO and Co₂O₃ were not found. It suggests that CoCl₂ had transformed into Co₃O₄ completely at the annealing temperature of 700 °C. Moreover, the fairly narrow shape of the peaks suggests a good crystallinity of the sample.

In order to examine the electrochemical behaviors, cyclic voltammetry (CV) was performed in 0.5 M H₂SO₄, at 25 °C employing a scan rate of 50 mV s⁻¹ and the recorded voltammograms, for electrodes without and with Cobalt interlayer are

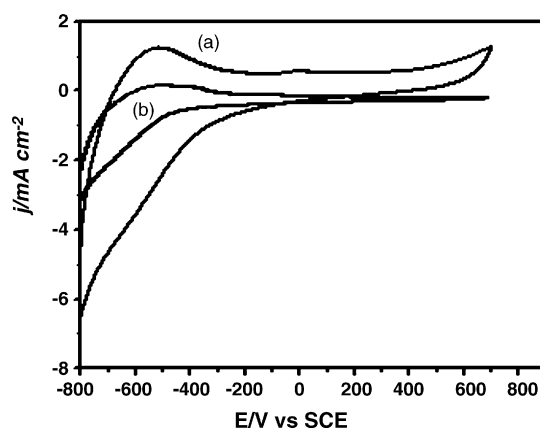


Fig. 2. Cyclic voltammograms obtained in 0.5 M H₂SO₄ at 25 °C, potential scan rate: 50 mV s⁻¹, (a) Ti/Co/SnO₂-Sb₂O₅ electrode, (b) Ti/SnO₂-Sb₂O₅ electrode.

shown in Fig. 2. The Ti/SnO₂-Sb₂O₅ electrodes are characterized by a small voltametric charge which may be attributed to the low porosity of the SnO₂-Sb₂O₅ coating [19]. The anodic peak between -0.6 and -0.8 V was observed for Ti/Co/SnO₂-Sb₂O₅ electrode, but not for the Ti/SnO₂-Sb₂O₅ electrode. This can be attributed to the redox couple Co²⁺/Co³⁺ on the surface of the electrode Ti/Co/SnO₂-Sb₂O₅. This indicates that cobalt oxidation is incorporated in the SnO₂-Sb₂O₅ coating by diffusion during the coating preparation.

The morphology of the interlayer and outer layer film of Ti/Co/SnO₂-Sb₂O₅ has been analyzed by SEM in Fig. 3. Fig. 3(a) shows that there are almost not cracks on the interlayer coating surface and the coating layer is compact. The significant compactness and low porosity observed indicates that incorporation of cobalt oxide and tin oxide components can improve the coating structure effectively which may contribute to the prolongation of the electrode lifetime. Fig. 3(b) shows that the outer layer film, consisting of SnO₂-Sb₂O₅ is relatively rough and little porous. This observation is consistent with the previous published studies performed by Cominellis and Chen [12,19].

The TGA and DTA spectra of CoCl₂·6H₂O are presented in Fig. 4. They show there are two important turning points in the sample's weight graph, namely 200 and near 700 °C. At the first the crystal line water molecule in the sample is volatilized

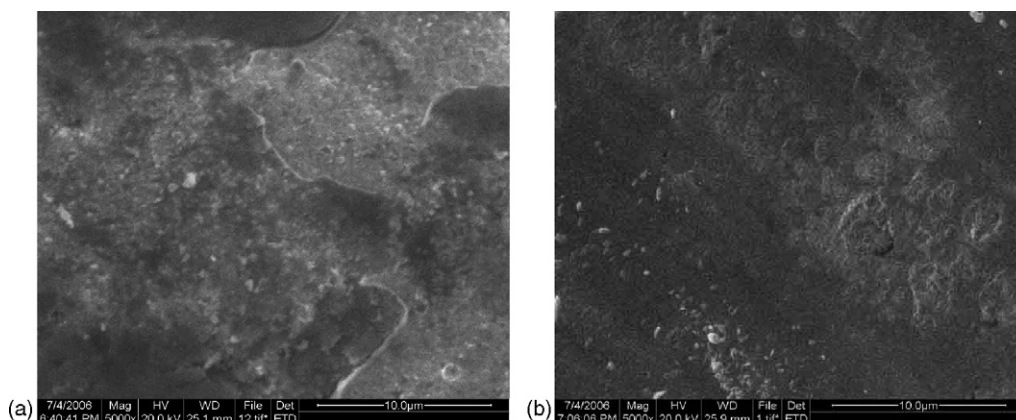


Fig. 3. Scanning electron micrographs of the interlayer (a) and outer layer (b) surfaces of Ti/Co/SnO₂-Sb₂O₅ electrode, magnification: (a) 5000×; (b) 5000×.

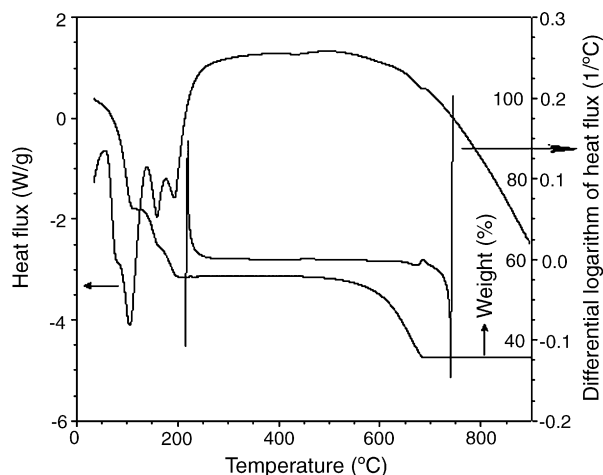


Fig. 4. TGA and DTA spectra of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

from 100 to 200 °C in the process of heating. Then, cobalt chloride is almost completely transformed to cobalt oxide at 680 °C approximately. It indicates that more than 680 °C is required for cobalt chloride to convert sufficiently to cobalt oxide. In view of this result, an appropriate temperature for the preparation of cobalt oxide interlayer is 700 °C.

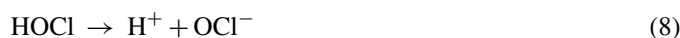
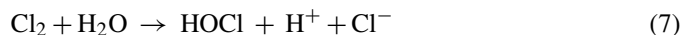
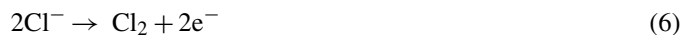
4.2. The electrochemical treatment effect

The plots of the dimensionless COD concentration of wastewater with time for experiments using the different treatment methods are shown in Fig. 5. As can be seen from this figure, for the case of 1357 mg L^{-1} initial COD concentration, the dimensionless COD concentration is 0.542 using $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$ electrode. Thus, the wastewater treatment effect is not satisfactory. This is probably due to the simultaneous production of oxygen and hydroxyl radicals on the $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$ anode, leading to the reduction of the later. In order to enhance the abatement effect, three-dimensional elec-

trodes of combining $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$ electrode with AC were employed through which the residual normalized COD reached 0.137 in the course of electrolysis at the end of 1 h. It indicates that COD concentration decreased much faster in the combining process than the process in absence of active carbon. From Fig. 5, it could be also anticipated that COD removal would be further improved with extended electrochemical oxidation. Thus, the most effective decrease of COD was achieved utilizing three-dimensional electrodes with $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$ anode. This can be explained by the electrogeneration of hydroxyl radicals from water on the $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$ electrode, which can degrade effectively organic compounds.



At the same time, because of their large surface area, AC particles adsorb organic pollutants. Besides, indirect oxidation could also take place in solutions.



Moreover, it can also be seen from Fig. 5 that the residual normalized COD was 0.781 employing the AC particles (only adsorption occurred) without electrolysis, which suggests that the role of the particle electrodes in electrochemical oxidation is not only adsorptive, but additionally electroactive.

The trend of color removal with reaction time during the electrolysis is shown in Fig. 6. It is found that the decolorization effect was the highest in the combining process and the same holds for the COD removal. The color removal attains 75% under electrolysis at the end of 1 h, while a slight decolorization was observed using AC particles without electrolysis (only adsorption), because the pollutants with color was not got rid of in the solutions.

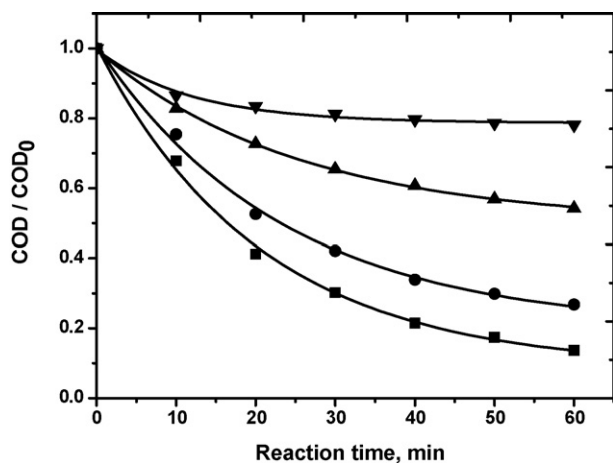


Fig. 5. Evolution of the dimensionless COD concentration of wastewater with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, (■) $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5 + \text{AC}$; (●) AC; (▲) $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$; (▼) AC (only adsorption reaction)).

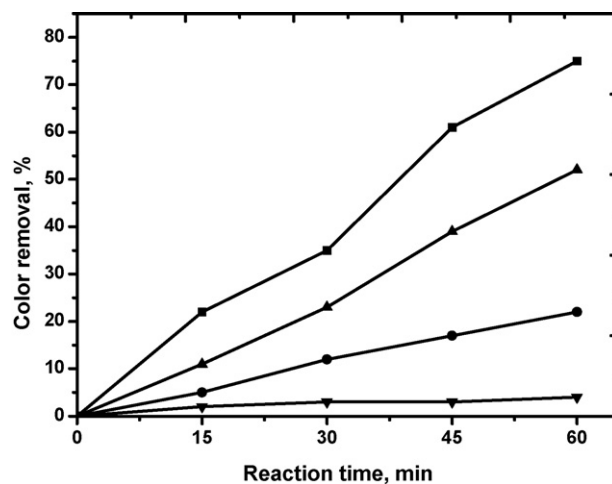


Fig. 6. Evolution of the color removal of wastewater with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, (■) $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5 + \text{AC}$; (▲) AC; (●) $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_5$; (▼) AC (only adsorption reaction)).

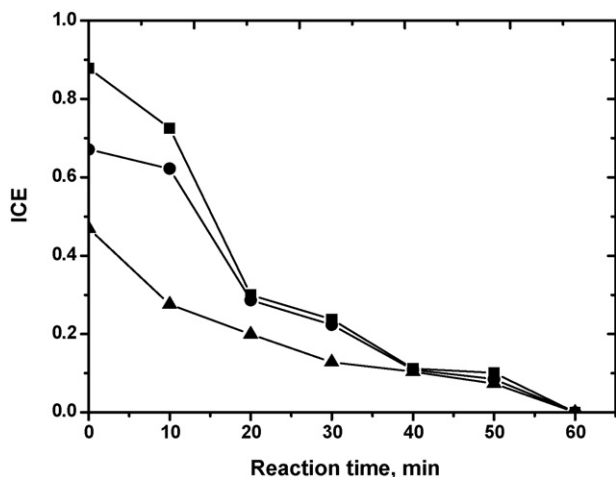


Fig. 7. Evolution of ICE with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, (■) Ti/Co/SnO₂-Sb₂O₅ + AC; (●) AC; (▲) Ti/Co/SnO₂-Sb₂O₅; (▼)).

In Fig. 7, the change of the ICE with reaction time during the electrochemical treatment is presented. As can be seen from this figure, the ICE value in the course of combinatorial disposal is the largest of all. The calculated ICE according to Eq. (2) is in accordance with the COD reduction. What's more, the ICE values in the first 40 min of treatment are higher than those in the last 20 min in all of the, which indicates that the degradation during the first 40 min of treatment mainly contributes to the whole process.

Fig. 8 shows the evolution of the energy consumption, in kWh kg⁻¹ COD, during the electrochemical treatment. The energy consumption calculated according to Eq. (4) in the combined process is less than in the other individual processes. This is due to the fact that the COD reduction in the combined process is the largest within the same time under application of equal electric power.

A summary of the EOI values, obtained in the course of electrochemical degradation with different treatment methods, is

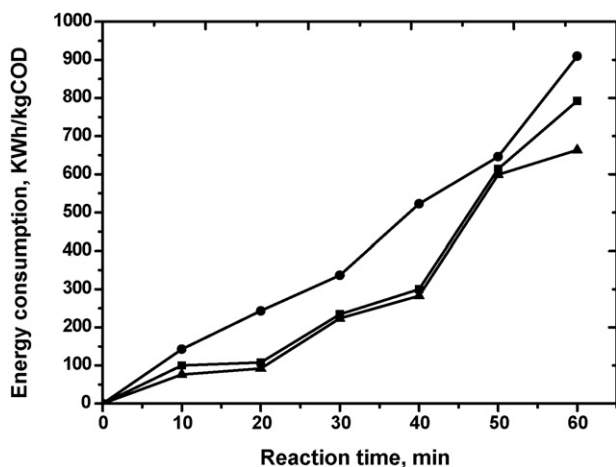


Fig. 8. Evolution of the energy consumption with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, (▲) Ti/Co/SnO₂-Sb₂O₅ + AC; (■) AC; (●) Ti/Co/SnO₂-Sb₂O₅; (▼)).

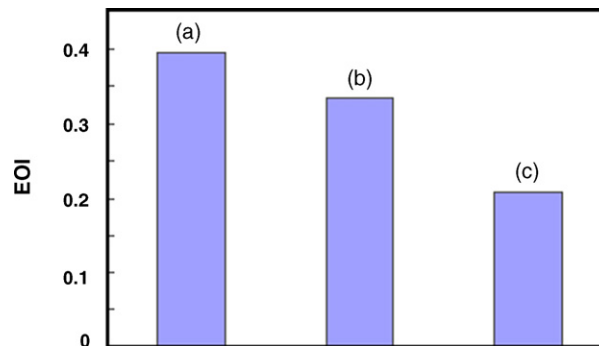


Fig. 9. EOI value in 60 min (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, (■) Ti/Co/SnO₂-Sb₂O₅ + AC; (●) AC; (▲) Ti/Co/SnO₂-Sb₂O₅; (▼)).

illustrated in Fig. 9. It is evident that EOI value calculated from Eq. (3) and based on the respective ICE values in the combining process is the highest of all. Thus, the use of a three-dimensional electrode system with Ti/Co/SnO₂-Sb₂O₅ as anode, proved to be effective for the disposal of paper mill wastewater.

4.3. Influence of operating variables on COD reduction

4.3.1. Influence of pH value

The influence of the initial pH on the reduction of the dimensionless COD concentration and the color removal as a function of time during the electrochemical oxidation, employing three-dimensional electrodes with Ti/Co/SnO₂-Sb₂O₅ anode, are presented in Figs. 10 and 11, respectively. As can be seen from these figures, there is a significant difference on the dimensionless COD concentration reduction and the decolorization depending on the pH of the solution. So, the initial pH is a crucial parameter that plays an important role in the treatment, because it influences the form of the electrogenerated active chlorine species (Eqs. (6)–(8)) and its oxidation potential [20–21]. These active chlorine substances are mainly composed of chlorine molecules and hypochlorite ions, which

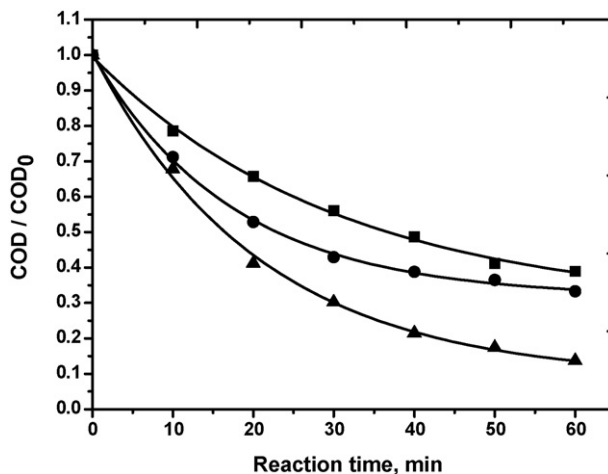


Fig. 10. Influence of initial pH on dimensionless COD concentration with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, initial pH: (▲) 11; (●) 7; (■) 3).

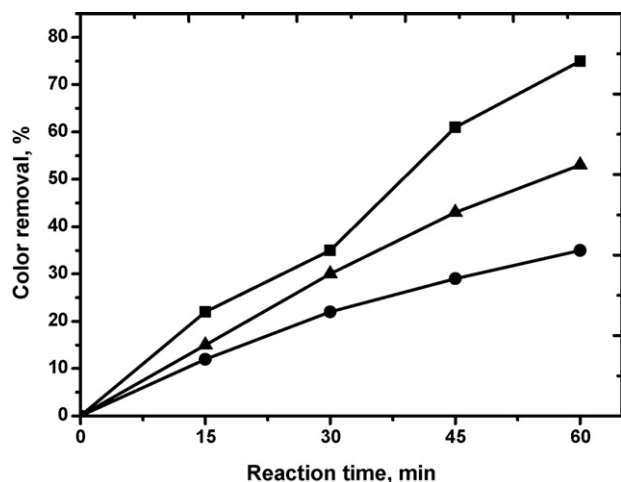


Fig. 11. Influence of initial pH on color removal with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, initial pH: (■) 11; (▲) 7; (●) 3).

could degrade the organic contaminants in the bulk of the solution.

4.3.2. Influence of current density

The influence of current density on the variation of the dimensionless COD concentration and the color removal during the electrolysis, when employing three-dimensional electrodes with Ti/Co/SnO₂-Sb₂O₅ anode is shown in Figs. 12 and 13. It seems like a common point exists in both figures, namely that there is higher COD removal and color removal for 111–167 mA cm⁻² than for 167–200 mA cm⁻² current density.

4.4. The study of biodegradable property of wastewater

Fig. 14 presents the BOD/COD variation during electrolysis, when the applied current density was 167 mA cm^{-2} and the initial pH value adjusted to 11. As can be seen from this figure, the ratio BOD/COD is optimal at around 40 min of electrolysis.

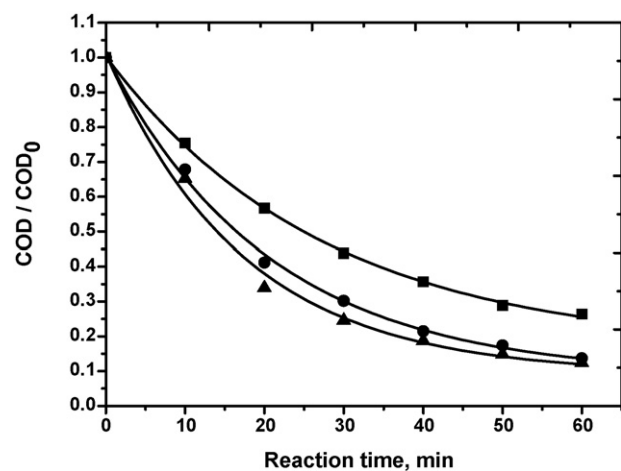


Fig. 12. Influence of current density on dimensionless COD concentration with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, electrolyte: 15 g L^{-1} NaCl, applied current density (mA cm⁻²): (▲) 200; (●) 167; (■) 111).

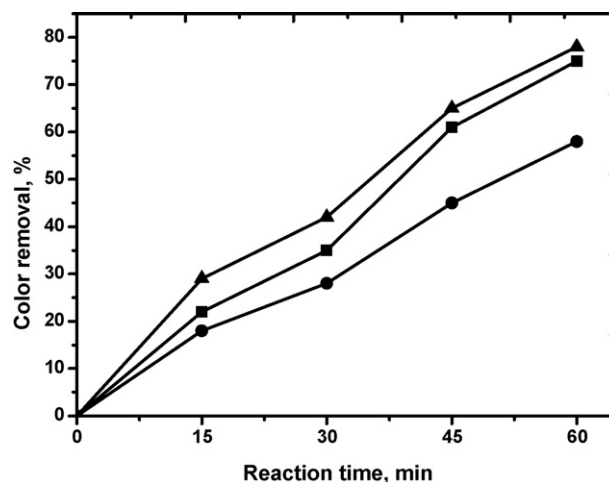


Fig. 13. Influence of current density on color removal with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, pH 11, electrolyte: 15 g L^{-1} NaCl, applied current density (mA cm⁻²): (▲) 200; (■) 167; (●) 111).

After 40 min of treatment, the ratio reduces mainly due to the minor decrease of COD.

4.5. Mechanism and kinetic of degradation

The mechanism of electrochemical abatement process of organic compounds, using three-dimensional electrodes with Ti/Co/SnO₂-Sb₂O₅ anode, includes direct and indirect oxidation. In the direct electrochemical degradation, direct oxidation takes place at the electrode surface. Simultaneously, hydroxyl radicals electrogenerated by the water discharge in the region very close to electrode could also remove the pollutants. Moreover, organics could be adsorbed and oxidized on the AC particles. In the indirect electrochemical treatment, active chlorine could also degrade the organic contaminants in the bulk of the solution.

The kinetic behavior of the electrochemical process can be described by the COD reduction rate as follows (Eq. (9)).

$$-d[\text{COD}]/dt = k[\text{COD}][\text{OH}^\bullet][\text{Cl}_2] \quad (9)$$

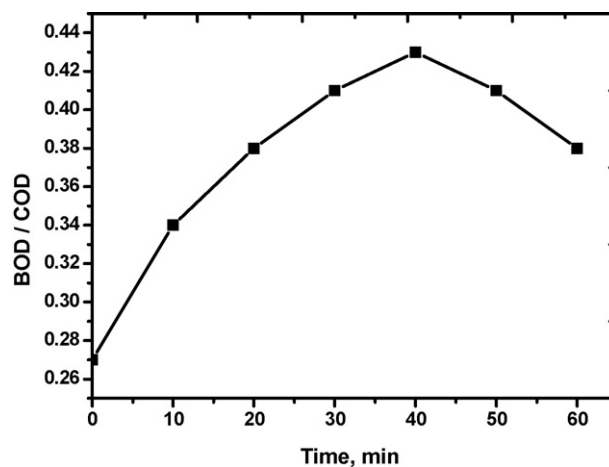


Fig. 14. Evolution of BOD/COD with time (condition: agitation speed = 300 rpm, $T = 20^\circ\text{C}$, applied current density = 167 mA cm^{-2} , electrolyte: 15 g L^{-1} NaCl, initial pH 11).

Table 1
Calculation of kinetic constant in the electrochemical processes

Process	Kinetic constant, k (min^{-1})	Coefficient
Ti/Co/SnO ₂ -Sb ₂ O ₅	0.039	0.9996
AC	0.043	0.9986
Combining process	0.049	0.9989

Chloride was converted to chlorine and hypochlorite by oxidation at the anode. The chlorine and hypochlorite will oxidize the organic compounds and then get reduced to a chloride ion. The process is then repeated in a catalytic fashion. Therefore, the concentration of chlorine/hypochlorite during the electrolysis is assumed to be a constant. Similarly, the value of $[\text{OH}^\bullet]$ in Eq. (9) will remain to be constant under a given set of experimental condition. So, the Eq. (9) can be written as an apparent pseudo-first order kinetic expression (Eqs. (10) and (11)).

$$-d[\text{COD}]/dt = k[\text{COD}] \quad (10)$$

$$[\text{COD}] = [\text{COD}]_0 e^{-kt} \quad (11)$$

where k is the apparent pseudo-first order kinetic constant. The values of k in the combined process using three-dimensional electrodes with Ti/Co/SnO₂-Sb₂O₅ as anode, the same electrode system without AC particles and AC alone, are calculated in Table 1.

5. Conclusion

The interlayer of Ti/Co/SnO₂-Sb₂O₅ electrode is compact and not porous. It should be prepared at 700 °C, because CoCl₂ is completely transformed into cobalt oxide Co₃O₄. The effect of treating paper mill wastewater is unsatisfactory using Ti/Co/SnO₂-Sb₂O₅ anode without addition of AC. In order to improve the degradation efficiency, the three-dimensional electrode system of combining active carbon particles with Ti/Co/SnO₂-Sb₂O₅ anode is employed. In this way, the electrochemical treatment can be successfully carried out for the disposal of paper mill wastewater using NaCl as electrolyte. The influence of pH and current density on the residual COD concentration and color removal is significant.

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