

Dye Wastewater Treatment Using Self-made Nd doped Ti/SnO₂-Sb Electro-Catalytic Electrodes

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Neodymium was selected as a promoter for Ti/SnO₂-Sb electrode to enhance its electro-catalytic characteristics and Nd doped Ti/SnO₂-Sb electrodes were prepared by immersion method. The optimum conditions for Nd-doped Ti/SnO₂-Sb anode preparation were proved to be 1 mol % Nd/Sn and 550 °C as an annealing temperature. The prepared electrodes were characterized by scanning electron microscopy, electron dispersive spectrometry, X-ray diffraction and X-ray photon-electron spectroscopy. It was suggested that the introduction of Nd atoms into the surface coating of the electrode can increase the surface area, the number of active site and the proportion of lattice oxygen, thus increase the electro-catalytic ability of the Ti/SnO₂-Sb electrode. X-Ray photoelectron spectroscopy (XPS) analysis showed that the oxidation state of Sn, Sb and Nd were +4, +5 and +3, respectively and the probable forms are SnO₂, Sb₂O₅ and Nd₂O₃. The cyclic voltammetry and service life test showed that the Nd doped Ti/SnO₂-Sb electrode had higher oxygen evolution potential and performed a longer service life. The increase of the biodegradability of reactive brilliant red X-3B wastewater indicated that the prepared Nd-doped Ti/SnO₂-Sb electrode can be used in the pre-treatment of biological treatment.

Key Words: Electro-catalytic, Ti/SnO₂-Sb electrode, Neodymium, Dope, Biodegradability.

INTRODUCTION

With the development of industrial economy, enormous amount of refractory organics, such as aromatic nitro compounds, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, *etc.*, have been discharged into the natural water, causing severe environmental problems. The widely used conventional biological treatment is not able to degrade these pollutants completely, because it is known that huge organic molecules with many phenyl rings are difficult to biodegrade, mainly due to stereochemical interferences¹. Electrochemical processes have been proved to be a promising, versatile method for degrading refractory organics²⁻⁸.

The feasibility of electrochemical technology is dependent on the development of anodes that have high stability, high activity to targeted chemical and low cost. Since the discovery by Beer⁹, much work has been done on dimensionally stable anodes (DSA), which are typically prepared by the thermal deposition of a thin layer of a metal oxide (*e.g.*, SnO₂ or IrO₂) on a base metal. Different anodes have different performances on the degradation of the targeted pollutant and it has been found that electrodes based on SnO₂ or minor components added to SnO₂ in a dimensionally stable anodes, could achieve good degradation of refractory organics because of their high oxygen evolution over-potential¹⁰⁻¹². SnO₂ in its pure form is an *n*-type semiconductor with a wide band gap (3.87-4.3 eV)

and a high electrical conductivity that is due to a modest level of non-stoichiometric impurities (*i.e.*, an O:Sn ratio < 2). It has been shown that the electro-catalytic activity and the corrosion resistance of the electrode can be increased if some amounts of dopants, such as Sb, Cl, F and Br are used and the most promising electrodes are Sb-doped Ti-based SnO₂ anodes (Ti/SnO₂-Sb)¹³⁻¹⁵.

It has been reported that rare earth metals (RE metals) can enhance chemical catalytic processes by either acting as a catalyst or by assisting catalytic processes. Rare earth metals have been applied successfully in the petrochemical industry for oil refining and have shown a potential for use in fuel cell application¹⁶. Nevertheless, there are few studies on the use of rare earth metals for electro-catalytic degradation of pollutants. Some researchers have found that doping of rare earth metals can change some characteristic of the electro-catalytic electrodes, such as electric conductivity, pyrolysis temperature and oxygen evolution over-potential^{17,18}. In the present study, Nd was used as a promoter for Ti/SnO₂-Sb electrodes and their electro-catalytic abilities were examined using reactive brilliant red X-3B (C.I. reactive red 2) as a model compound. Characteristics of electrodes produced by the doping process were examined, including morphology, physical structure of the surface coating and the electrochemical behaviour of the electrode. Finally, it was analyzed that the enhancement of the

biodegradability of the reactive brilliant red X-3B wastewater during electrolysis with the Nd-doped Ti/SnO₂-Sb electrode.

EXPERIMENTAL

All chemical materials employed are analytically pure. Deionized water is used as solvent.

Electrode preparation: Titanium nets (3 cm × 5 cm) with a 3 mm × 8 mm rhomboidal mesh and a 1.5 mm × 1.0 mm thread cross section were used as the base metal for all oxide-coated electrodes. The base metal was polished using 120-grit and 600-grit sand papers, degreased in boiling 5 % Na₂CO₃ for 1 h and then in boiling 10 % oxalic acid for 2-3 h followed by thoroughly washing with deionized water. The electrode coating was prepared using immersion method. The pretreated Ti bases were dipped in a series of solutions, which consisted of 0.484 mol/L SnCl₄, 0.0726 mol/L SbCl₃ and a variable concentration of Nd(NO₃)₃ (molar ratios of Nd/Sn are 0:100, 0.5:100, 0.8:100, 1.0:100, 1.2:100 and 1.5:100, respectively). The solvent is an iso-volume mixture of *n*-butanol, isobutanol, isopropanol and ethanol. The electrode was then dried in an baking oven at 120 °C for 10 min. After five cycles of both dipping and drying, the Ti bases were heated in a muffle oven (450 °C, 15 min) for coating pyrolysis. The thickness of the doped SnO₂ film depends on the times of the dip-dry-pyrolysis sequences and this whole process was repeated 3 times to get optimum film thickness. Finally, further heat treatment for 1 h at different temperature was carried out in order to compare the effect of different pyrolysis temperatures.

Electrolysis: Taken reactive brilliant red X-3B as a model organic compound, the electrolysis cell was a 250 mL polymethylmethacrylate (PMMA) beaker. The Nd doped Ti/SnO₂-Sb anode prepared as above was used as anode and Ti plate having the same area was placed at a spacing of 30 mm and used as cathode. A direct current potentiostat (DC potentiostat) with a voltage range of 0-10 V was used as the power supply for organic degradation studies. Reactive brilliant red X-3B (100 mg/L, 200 mL) was placed in the cell with Na₂SO₄ (0.3 M) which was used as the supporting electrolyte. Electrolysis was performed under galvanostatic control at 0.12 A. The electrolysis lasted 1 h and the ultraviolet absorbency of the electrolyte was analyzed every 10 min to record the decolorizing rate of the electrolyte. The cell voltage was recorded at the same time.

Electrode characterization: Different techniques were applied to characterize the properties of the Nd doped Ti/SnO₂-Sb electrodes. The electrochemical behaviour of the doped SnO₂ electrodes was studied by cyclic voltammetry and service life test. The cyclic voltammetry experiment was carried out using a three electrode cell. Ti plate was used as a counter electrode and Hg/Hg₂SO₄(K₂SO₄) as a reference electrode. 0.5 mol/L Na₂SO₄ was used as electrolyte and a DC potentiostat was used as the power supply with scan rate of 20 mV/s and scan range of -2~ +3 V. The service life test was carried out under galvanostatic condition at 20000 A/m² using Ti plate, with a distance of 20 mm from anode, as cathode. 0.5 mol/L H₂SO₄ was used as electrolyte and 40 °C as the working temperature. The cell voltage was monitored during the service life

test and the time when the cell voltage exceeds 10 V was determined to be the accelerated electrode life.

Scanning electron microscopy (SEM) was employed to observe the surface morphology of the electrodes using a Jeol (JSM-7600 F). SEM also provided information on the different elements present on the surface using the energy dispersive spectrometer (Oxford INCA Energy x-sight, EDS). X-ray diffraction (XRD) patterns of the coating films on these electrodes were recorded on a D/MAX-RB XRD instrument (Rigaku, Japan), using CuK_α radiation and a graphite monochromator, with an operating voltage of 45 kV and current of 50 mA. The average particle size of the SnO₂ crystals was calculated from XRD data using the Scherrer equation¹⁹. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI5700 spectrometer with AlK_α radiation (ht = 1486.6 eV).

Biodegradability: BOD₅/COD ratio was used to evaluate the biodegradability of the reactive brilliant red X-3B wastewater. COD and BOD₅ were measured according to the standard methods for examination of water and wastewater²⁰.

RESULTS AND DISCUSSION

Optimization of Nd doped Ti/SnO₂-Sb anode preparation: Some researchers indicated that annealing temperature and doping amounts of foreign atoms are the two crucial factors in anode preparation^{21,22}. In present work, the two factors were evaluated to found the optimum conditions for anode preparation.

Electrochemical degradation of reactive brilliant red X-3B and the cell voltage fluctuation during degradation were used to evaluate the electrochemical ability of the Nd-doped Ti/SnO₂-Sb anodes. Fig. 1a shows the degradation curves of reactive brilliant red X-3B with electrodes prepared at different annealing temperature but the same Nd doping amount (molar ratio of Nd/Sn in the dipping solution was 1:100). Results show that electrode prepared at 550 °C gives the highest decoloring rate. And the most stable cell voltage also appears when using the electrode prepared at 550 °C (Fig. 1b).

Fig. 2a shows the degradation curves of reactive brilliant red X-3B with electrodes prepared at different Nd doping amount but the same annealing temperature (550 °C). A maximum removal rate of reactive brilliant red X-3B is achieved when the Nd/Sn molar ratio is 1 %. The 1 mol % Nd-doped Ti/SnO₂-Sb electrode also gives the most stable cell voltage (Fig. 2b).

Consequently, the optimum conditions for Nd-doped Ti/SnO₂-Sb anode preparation are 1 % as Nd/Sn mole ratio and 550 °C as annealing temperature.

Morphology and structure analysis of Nd-doped Ti/SnO₂-Sb oxides film: Freshly prepared Nd-doped Ti/SnO₂-Sb electrodes which had not been used for electrolysis were examined for morphology by SEM and the results are shown in Fig. 3. It can be ascertained from Fig. 3 that the surface coating of the Nd-doped Ti/SnO₂-Sb electrode (1 mol %, Nd/Sn) is much more compact and smooth than that of the control electrode (0 mol %, Nd/Sn), which means much higher surface roughness and larger surface area. The increase of surface roughness and surface area favours the electro-catalytic reaction.

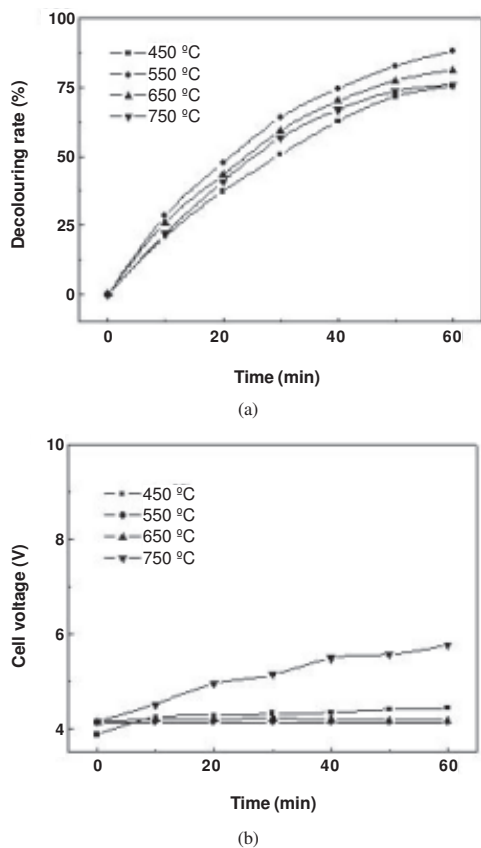


Fig. 1. Effect of annealing temperature on the performance of Nd-doped Ti/SnO₂-Sb electrode (a) reactive brilliant red X-3B degradation curves; (b) cell voltage fluctuation

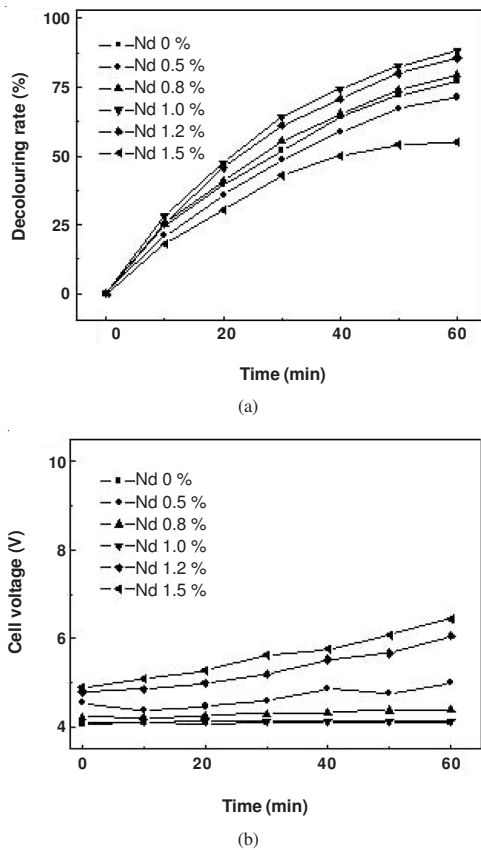
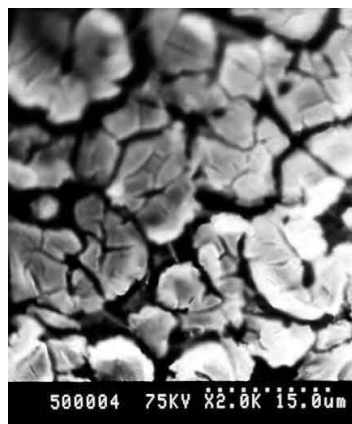
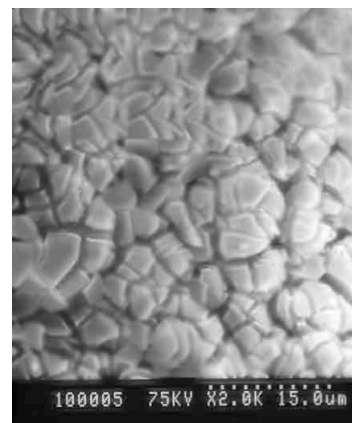


Fig. 2. Effect of doping amount on the performance of Nd-doped Ti/SnO₂-Sb electrode (a) reactive brilliant red X-3B degradation curves; (b) cell voltage fluctuation



(a)



(b)

Fig. 3. Micrographs ($\times 2000$) of surface coating of: (a) 0 mol % Nd-doped Ti/SnO₂-Sb electrode and (b) 1 mol % Nd-doped Ti/SnO₂-Sb electrode

The presence and distribution of Nd and Sb on the prepared electrodes were studied by EDS. Data shown in Table-1 were calculated using Sn as standard, which means the Sn atoms in the surface coating were supposed to be 100 %. Sb and Nd atoms were found to be enriched in the surface coating of the electrode when Nd atoms were introduced, which probably because Nd doped Ti/SnO₂-Sb electrode has larger surface area and smaller particle size of the SnO₂ crystals. Titanium was not detected in the EDS experiment which indicates that the thickness of the SnO₂ film is thicker than 2 μm ²³.

The XRD patterns of the surface coating of the 0 and 1 mol % Nd doped Ti/SnO₂-Sb electrodes are shown in Fig. 4. The XRD analysis demonstrated that the surface coating of both of the electrodes are mainly composed of tetragonal rutile structure SnO₂ crystal. Nd and Sb were not detected in the XRD pattern, probably because they are introduced into the SnO₂ lattices by replacing or filling. Ti was not detected in the XRD pattern, either, which consistent with the EDS result, indicating that the surface coating can cover the base metal completely. XRD data show that the rutile SnO₂ lattice in 1 mol % Nd-doped electrode is slightly expanded compared with the control electrode (0 mol %, Nd/Sn). A reasonable explanation for the lattice expansion is that Nd³⁺ ions entered the unit cell of the SnO₂ and the larger Nd³⁺ (0.0995 nm) ions replacing the smaller Sn⁴⁺ (0.071 nm) ones.

TABLE-1
COATING COMPOSITION OF ELECTRODES

Electrode	Sn	Sb (atomic %)		Nd (atomic %)	
		Theoretical	Observed	Theoretical	Observed
0 mol % Nd-doped electrode	100	13.04	9.17	0	0
1 mol % Nd-doped electrode	100	13.04	16.92	0.86	3.34

The theoretical composition is the calculated concentration of Sb or Nd in the dipping solution while the observed composition is the detected concentration of Sb and Nd in the surface coating using EDS.

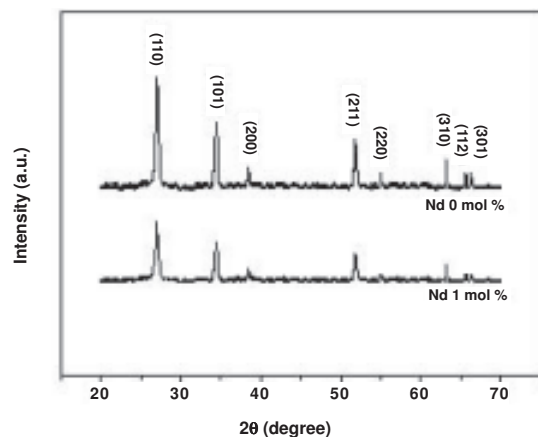
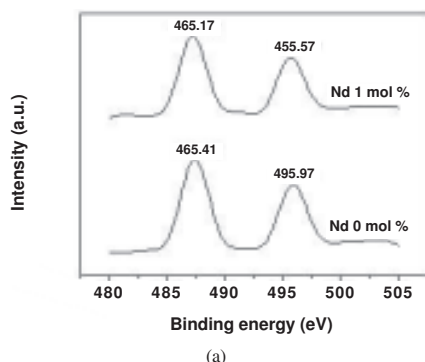


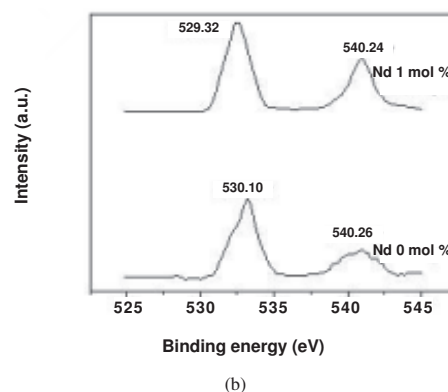
Fig. 4. Indexed XRD patterns of surface coating of the 0 and 1 mol % Nd-doped Ti/SnO₂-Sb electrodes

The average SnO₂ grain size, calculated with Scherrer equation, is found to increase from 14.43 nm (1 mol %, Nd/Sn) to 26.93 nm (0 mol %, Nd/Sn). As is well known for heterogeneous catalysis, a smaller size means a larger interface and more active sites²⁴. Thus, the introduction of Nd atoms enhanced the electro-catalytic ability of the Ti/SnO₂-Sb electrode.

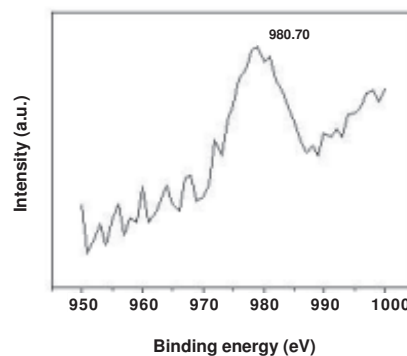
To confirm the above morphology and structure analysis results, further surface analysis was undertaken with XPS. The method provided additional information on the oxidation states of the surface coating of the electrodes. Fig. 5 shows the XPS spectra of 0 mol % and 1 mol % Nd doped Ti/SnO₂-Sb electrodes. The features corresponding to Sb(3d_{5/2}) and O(1s) are shown in Fig. 5(b). The binding energies corresponding to the features of Sb(3d_{5/2}), Sn(3d_{5/2}) and Nd(3d_{5/2}) were identified in the spectra. The comparison of the binding energy of Sb(3d_{5/2}), Sn(3d_{5/2}) and Nd(3d_{5/2}) with data from Handbook of X-ray photoelectron spectroscopy²⁵ indicate that the oxidation state of tin, antimony and neodymium are +4, +5 and +3, respectively, probably in forms of SnO₂, Sb₂O₅ and Nd₂O₃. It is noteworthy that titanium is not detected on the surface coating of both of the electrodes, which consistent with the results from EDS and XRD.



(a)



(b)



(c)

Fig. 5. XPS spectra of surface coating of the 0 and 1 mol % Nd-doped Ti/SnO₂-Sb electrodes (a) Sn, (b) Sb and O, and (c) Nd

A comparison of the O 1s spectra of freshly prepared 1 mol % Nd doped sample and the control (0 mol %, Nd/Sn) is shown in Fig. 5(b). It is clear that the O 1s binding energy of the 1 mol % Nd-doped sample is lower than that of the control, indicating that there is more lattice oxygen formed in the Nd-doped electrode than that of the control²⁶. The increase in the lattice oxygen results in the increase of hydroxyl radical activity, thus influence the catalytic performance of the SnO₂ electrode²⁷. Therefore, it appears that the enhanced performance of the Nd-doped electrode arose from an increased activity of adsorbed hydroxyl radicals due to the higher oxygen content of the crystal lattice in the presence of the Nd atoms.

Electro-catalytic characteristics of the Nd-doped Ti/SnO₂-Sb electrode: In Fig. 6, the voltammograms of 0 mol % Nd doped Ti/SnO₂-Sb electrode and that of 1 mol % were compared. The control electrode (0 mol %, Nd/Sn) has an initial potential of 1.53 V vs. SCE for O₂ evolution. In contrast, the initial potential for O₂ evolution on the 1 mol % Nd-doped Ti/SnO₂-Sb electrode is 2.24 V vs. SCE, 0.71 V higher than that obtained on the control electrode. It should be noted that high initial potential for O₂ evolution is desired because O₂ evolution is a side reaction in the process of anodic oxidation

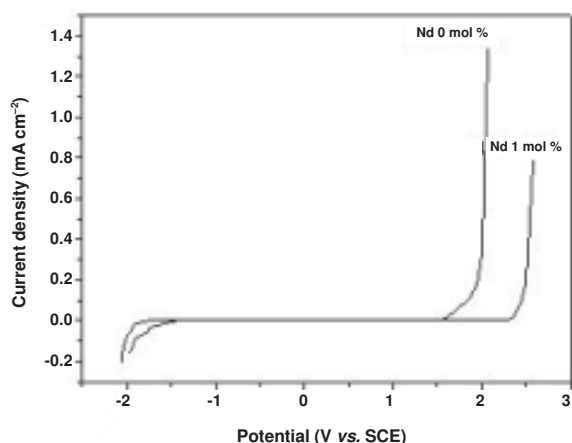


Fig. 6. Dynamic potential scanning curves of 0 and 1 mol % Nd-doped Ti/SnO₂-Sb electrodes

of pollutants. The much higher initial potential for O₂ evolution suggests that the Nd-doped SnO₂-Sb electrode may have much higher current efficiency for pollutant oxidation.

The service life test was conducted to evaluate the working life time of the electrodes. It was compared that the accelerated electrode life and the real working life of the 0 and 1 mol % Nd doped Ti/SnO₂-Sb electrodes in Table-2. The real working life of the electrode is calculated as follows: $t_2 = t_1 \times (i_1/i_2)^2$, where t_1 , t_2 are the accelerated electrode life and real working life, respectively, i_1 and i_2 are the current density in accelerated life test and real work, respectively. Usually, i_2 is assumed to be 1000 A/m². Results in Table-2 show that the Nd-doped SnO₂-Sb electrode has a longer life time than that of the control electrode. This can be explained by the SEM results. The surface coating of the 1 mol % Nd-doped Ti/SnO₂-Sb electrode is much more compact and smooth than that of the control and can combine firmer with the titanium substrate. Thus, the titanium oxidation is the main reason for the invalidation of the Ti based oxide-coated electrode, is hard to occur.

TABLE-2
ELECTRODE SERVICE LIFE TEST

Electrode	Electrode service life	
	Accelerated electrode life (h)	Real working life (a)
0 mol % Nd-doped electrode	35.3	2.0
1 mol % Nd-doped electrode	57.5	3.2

Assuming the electrode worked continuously for 300 days every year.

Biodegradability test: The biodegradability of the reactive brilliant red X-3B wastewater through electrolysis using the 1 mol % Nd-doped Ti/SnO₂-Sb electrode as anode is shown in Fig. 7. The reactive brilliant red X-3B is toxically refractory and inert to microorganisms. The biodegradability of the reactive brilliant red X-3B wastewater increased by 490.9 %, from 0.11-0.65, after electrolyzed for 5 h. The increase of biodegradability is mainly due to the oxidation of refractory reactive brilliant red X-3B into low molecular weight, degradable intermediate organics. This result indicates that the prepared Nd-doped Ti/SnO₂-Sb electrode can be used in the pre-treatment of biological treatment.

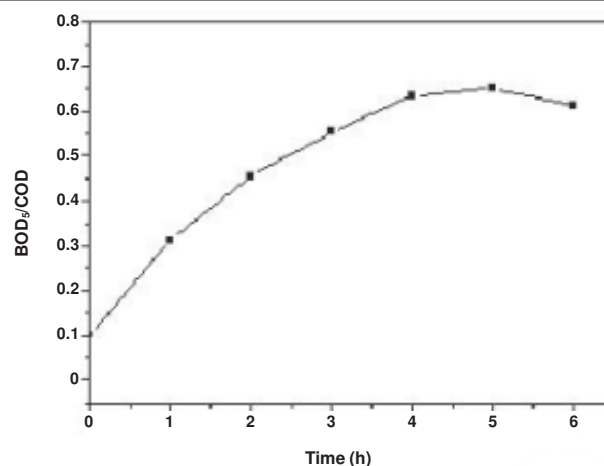


Fig. 7. Biodegradability fluctuation of reactive brilliant red X-3B wastewater through electrolysis

Conclusion

The Nd-doped Ti/SnO₂-Sb electrodes were prepared using immersion method and the optimum conditions for electrode preparation turned out to be that 1 % as Nd/Sn mole ratio and 550 °C as annealing temperature.

The addition of Nd improved the morphology and performance of Ti/SnO₂-Sb electrodes. The surface coating of the Nd-doped Ti/SnO₂-Sb electrodes were much more compact and smooth and have more active sites than that of the control (0 mol %, Nd/Sn). The XPS results showed that the oxidation state of the Sn, Sb and Nd in a SnO₂ electrode doped with the latter two metals, were +4, +5 and +3, probably as SnO₂, Sb₂O₅ and Nd₂O₃, respectively. The introduction of Nd atoms may increase the proportion of lattice oxygen also and thus enhance the performance of the Ti/SnO₂-Sb electrode.

Cyclic voltammetry and service life test were used to evaluate the electrochemical characterization of the prepared electrode. It was shown that the Nd-doped Ti/SnO₂-Sb electrode had higher oxygen evolution potential, which is favour for electrochemical oxidation for organic pollutants and longer service life compared with the control (0 mol %, Nd/Sn).

The BOD₅/COD of the reactive brilliant red X-3B wastewater was improved by 490.9 % after 5 h of electrolysis. This indicated that the prepared Nd-doped Ti/SnO₂-Sb electrode can be used in the pre-treatment of biological treatment.

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