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Mineralization of o-tolidine by electrooxidation with BDD, Ti/Pt and MMO anodes

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ABSTRACT

The present study deals with the electrooxidative mineralization of o-tolidine from aqueous solution using various Ti/Pt, mixed metal oxide (MMO) and boron doped diamond (BDD) anodes. The experiments were carried out in two phases. In the first phase, the effect of anode type on the total organic carbon (TOC) removal efficiency was investigated at various pH levels. Furthermore, the second phase was carried out with the most effective anode, to investigate the effects of various operating parameters on the TOC removal efficiency, such as current density, stirring speed, inter electrode distance, concentrations of o-tolidine and the electrolyte. Also, specific energy consumption (SEC) based on the amount of electricity consumed for TOC removal was estimated. The results showed that BDD anode was much more efficient than Ti/Pt and MMO anodes for the mineralization of o-tolidine. The current density and stirring speed were the most effective parameters. With BDD anode, TOC removal efficiency realized as 54.6% and 79.9% for the current density of 25 mA/cm^2 and 125 mA/cm^2 respectively, at 150 min of processing time. On the other hand, TOC removal efficiency realized as 51.5% and 79.1% at stirring speeds of 0 and 1000 rpm at 150 min.

Keywords: Mineralization; Electrooxidation; o-tolidine; BDD anode; MMO anode

1. Introduction

O-tolidine (4,4′-diamino-3,3′-dimethylbiphenyl, diaminoditolyl, 3,3′-dimethylbenzidine, 3,3′-dimethyl-4,4′-diphenyldiamine) is toxic and possibly carcinogenic. Animal studies have shown that animals exposed to o-tolidine developed tumors in the liver, kidney, and mammary glands [1]. O-tolidine is also a harmful chemical in the aquatic environment, causing oxygen depletion in the aqueous system.

O-tolidine and its salts are widely used in the dye industry and some analytical chemistry procedures. It is toxic when a discarded commercial chemical product or manufacturing chemical intermediate or an off-specification commercial chemical product or a manufacturing chemical intermediate. O-tolidine is chemically resistant to water and not expected to undergo hydrolysis due to a lack of hydrolyzable functional groups. O-tolidine, present at 100 mg/L, reached 3% of its theoretical BOD in 4 weeks using an activated sludge inoculum at 30 mg/L and the Japanese MITI (Ministry of International Trade and Industry) test, indicating that the compound is not readily biodegradable [2].

Surolia et al. investigated the photo catalytic degradation of o-tolidine with various nanocrystalline TiO$_2$ samples synthesized by sol-gel, solution combustion, and hydrothermal methods; at the end of 240 min of run time, TOC removal efficiencies reached 80%, 75% and 71% respectively [3].

Electrochemical treatment methods are widely used for wastewater treatment. They are efficient, effective, eco-friendly, and cost-effective processes. Furthermore, the electrooxidation process, with relatively simple operational requirements, the minimum requirement of chemicals and without needing any sludge removal process exhibits some advantages over others [4–13]. Electrooxidation

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is used to remove for may organic pollutant from equation media. Rabaaoui et al. study on the electrooxidation of nitrobenzene (NB) by using BDD anode. They found the best degradation in the presence of 0.05 M Na_2SO_4. After 8 h, 88% degradation of nitrobenzene was achieved using BDD electrodes at pH 3 and 60 mA cm^{-2} current density [14]. Carvalho et al. investigated the treatment of synthetic waste waters containing Methyl Green (MG) by anodic oxidation using Ti/PbO_2 anodes. They found the removal levels are as a function of applied current density, obtaining TOC removal efficiencies from 43 to 70% and 90% of color removal, depending on applied current density [15]. Bueno et al. study on the electrooxidation of leachate from a municipal land fill site, using oxide-coated titanium anode. They investigated the effect of current density on chemical oxygen demand, TOC, color, and ammonium removal. At a current density of 116 mA cm^2 and 180 min run time, the removal rates achieved were 73% for COD, 57% for TOC, 86% for color and 49% for ammonium [16]. Ukundimana et al. investigated the electrooxidation of the ultra filtration (UF) effluent from a landfill leachate treatment plant using BDD and different dimensionally stable electrodes anodes (DSA). They found the BDD anode performed better than the other DSA anodes under the tested conditions with removal efficiencies of 64.9–86.8% and 68.2–92.0% for TOC and chemical oxygen demand, respectively [17].

This study aimed to apply the electrooxidation process for removal o-tolidine from the aqueous medium, which was chosen as a model solute for its difficulty of removal by classic chemical/ biological methods. Initially, TOC removal efficiencies of BDD, Ti/Pt, and various MMO anodes were compared. Furthermore, the influences of the main operating parameters such as pH, current density, o-tolidine concentration, stirring speed, the distance between the electrodes and electrolyte concentration were investigated using the best electrode.

2. Materials and methods

2.1. Materials

All the chemicals used in the experiments were analytical quality Merck products. Ammonia was used to arrange pH, phosphoric acid as the supporting electrolyte. The characteristics of o-tolidine are shown in Table 1 and structure formula image in Fig. 1.

Table 1
Typical properties of o-tolidine

Parameter	Value
Synonyms	3,3′-Dimethylbenzidine 4,4′-Bianisidine
CAS number	119-93-7
Molecular formula	$C_{14}H_{16}N_2$
Chemical formula	2-([-$C_6H_3(CH_3)$-4-$NH_2]_2$)
Molecular formula (g/mol)	212.29
Relative density at 20°C	1.2 g/cm^3
Water solubility at 20°C	1.3 g/L
Physical description	White to reddish crystals or powder
Categories of danger	Carcinogenic, toxic, irritant, dangerous for the environment
Acute oral toxicity (rat) LD_{50}(mg/kg)	404

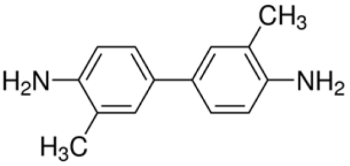

Fig. 1. Structure formula of o-tolidine.

2.2. Experimental apparatus and procedure

500 ml of o-tolidine solution was placed in the Pyrex glass reactor for each run. To provide conductivity, phosphoric acid was added to the solution as an electrolyte, and the pH of the solution was adjusted. Two electrodes in sizes of 60*200 mm, comprising of one anode and one cathode, placed at different inter electrode distances including 5, 10, 15, 20 and 30 mm, were used in the reactor. BDD (boron doped diamond), Ti/Pt and MMO (mixed metal oxide) electrodes (Ti/RuO_2-TiO_2, Ti/RuO_2-IrO_2, Ti/IrO_2-Ta_2O_5, Ti/Pt-IrO_2) were used as the anode, while a stainless-steel electrode was used as the cathode. BDD electrodes were supplied from DiaCCon GmbH Germany. Ti/Pt and MMO electrodes were supplied from Baoji Changli Special Metal Co., Ltd. China. Total active surface area of the anodes, depending on the immersion level in the solution was 40 cm^2. Before each run, the electrodes were wiped with acetone or phosphoric acid to remove impurities deposited on the surface and washed with distilled water. The effect of stirring speed was investigated by adjusting stirring speed to 0, 250, 500, 750 and 1000 rpm. For this purpose, Heidolph MR Hei-Tec model digital magnetic stirrers were used. Agilent and Rigol brand programmable (Agilent 6674A System; 0–60 V/0–35 A, Rigol DP832 0–30 V/0–3 A) digital (D.C.) direct current power resources were used in the system. The temperature increase caused by the inter electrode voltage in the reactor was prevented by blowing cold air to the reactor wall from the outside. Thus, the temperature of the solution was maintained at 25 ± 1°C during the run, which was monitored using a laser thermometer.

2.3. Analytical method

All the chemical analyses were carried out by the standard methods for the examination of water and wastewater [18]. TOC analyzer (Schimadzu, TOC-L) was used to estimate the TOC concentrations. All the experiments were repeated twice, for checking the reproducibility of the results using the magnitude of the experimental error.

The TOC removal efficiency, E, is calculated as

$$E = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i is initial TOC concentration (mg/L) and C_f is the final concentration (mg/L).

3. Results and discussion

In the first phase of the study, the effects of pH and anode type on the TOC removal efficiency were investigated. In the second phase, the effects of the parameters on the TOC removal efficiency, such as current density, stirring speed, inter electrode distance, the concentration of o-tolidine and concentration of electrolyte were investigated using the most effective anode. On the other hand, the applied potential, current, and dissolution of the electrodes directly affect the efficiency of the process and the operating cost as well [4]. Thus, specific energy consumption (SEC) based on TOC removal was calculated, which is the main component of the running costs of most electrochemical treatment processes. SEC is defined as the amount of energy consumed per unit mass of TOC removed (TOC_{rem}) and expressed in kWh/kg of TOC removed and is given as:

$$SEC = \frac{(V * I * t)}{TOC_{rem}} \tag{2}$$

where V is the voltage across the electrodes, I is the current in amperes, t is the time in h, and TOC_{rem} is the TOC removal.

The anode efficiencies (η) of the electrooxidation for the o-tolidine solution were calculated from the following equations in mg of TOC removed (TOC_{rem}) /h/A/m² where (TOC_{exp}) is the experimental TOC decay (or TOC_{rem}) (mg/L), V_s is the solution volume (L), I is the current in amperes, t is the time in h, S_{anode} is the effective anode area.

$$\eta\left(\frac{mg\,TOC}{Ahm^2}\right) = \frac{\Delta(TOC)_{exp} * V_s}{ItS_{anode}} \tag{3}$$

3.1. The effects of anode type and pH on the removal of TOC and the SEC (Specific Energy Consumption) for TOC removal performance

TOC removal was investigated for BDD, Pt and MMO anodes at pH 4, 6 and 8. The results for pH 4 are given in Fig. 2a. It is seen that during the run period, TOC removal increased substantially for the BDD anode; however, it increased fairly low in the case of Pt and MMO anodes. While TOC removal efficiency realized as 41.04% for the BDD anode, it realized for Pt and MMO anodes in decreasing order as follows; Pt-IrO_2: 12.22%, RuO_2-TiO_2: 6.5%, Pt: 3.5%, IrO_2-Ta_2O_5: 1.43%, RuO_2-IrO_2: 1.22%, at the end of the run period of 150 min.

In Fig. 2b, SEC values based on the TOC amount removed by each electrode for the current of 1 A (J = 25 mA/cm²) are depicted. As seen, lowest SEC value realized in the range between 4000–5200 kWh/kg TOC_{rem} for the BDD anode with the highest TOC removal efficiency; this value might be respectively 4, 10, 20 or 30 times greater the Pt and MMO electrodes.

The results carried out for pH 6 by different anodes are given in Fig. 3a. It is seen that TOC removal increased for all anodes during the run period. While TOC removal efficiency realized as 36.74% for the BDD anode, it realized respectively for Pt and various MMO anodes as; Pt-IrO_2: 25.87%, RuO_2-TiO_2: 15.37%, Pt: 11.54%, IrO_2-Ta_2O_5: 11.43%, RuO_2-IrO_2: 13.50% at the end of 150 min. When compared with the results for pH 4, a decrease by 5% was seen in the efficiency of BDD electrode for pH 6, while noticeable increases ranging between 2–10 times was realized in the efficiency of BDD anodes.

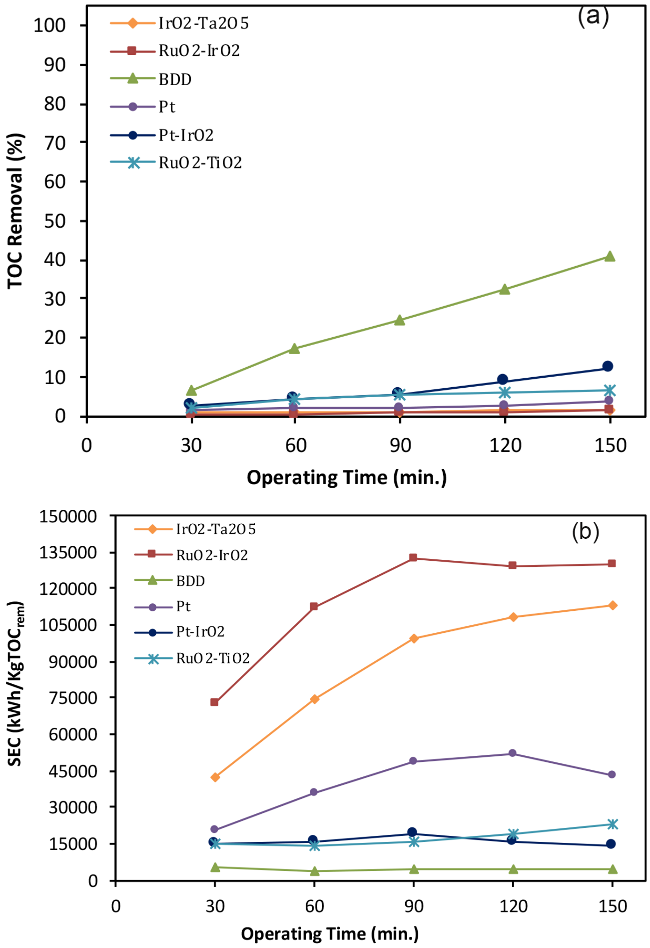

Fig. 2. (a) The TOC removal efficiency for Pt, MMO and BDD electrodes at pH 4 (b) Effect of electrode type on SEC at pH 4 (conditions: o-tolidine C0: 50 mg/L, current density: 25 mA/cm², stirring speed: 500 rpm, distance between the electrodes: 5 mm, electrolyte (phosphoric acid) concentration: 0.01 M, conductivity 823 µS/cm).

In Fig. 3b SEC values calculated based on the TOC removal by each anode for the current of 1 A (J 25 mA/cm²) are presented. As seen, while the lowest SEC value realized in the range between 5300–5600 kWh/kg TOC_{rem} for the BDD electrode with the best TOC removal efficiency; this value might be respectively 1.5 or 2.5 times greater for Pt and MMO electrodes.

Experimental results at pH 8 using different anodes are given in Fig. 4a. It is seen that TOC removal increased for BDD anodes. However, TOC removal efficiency didn't increase so much for the Pt and MMO anodes during the same run period. TOC removal efficiency realized as 56.32% for the

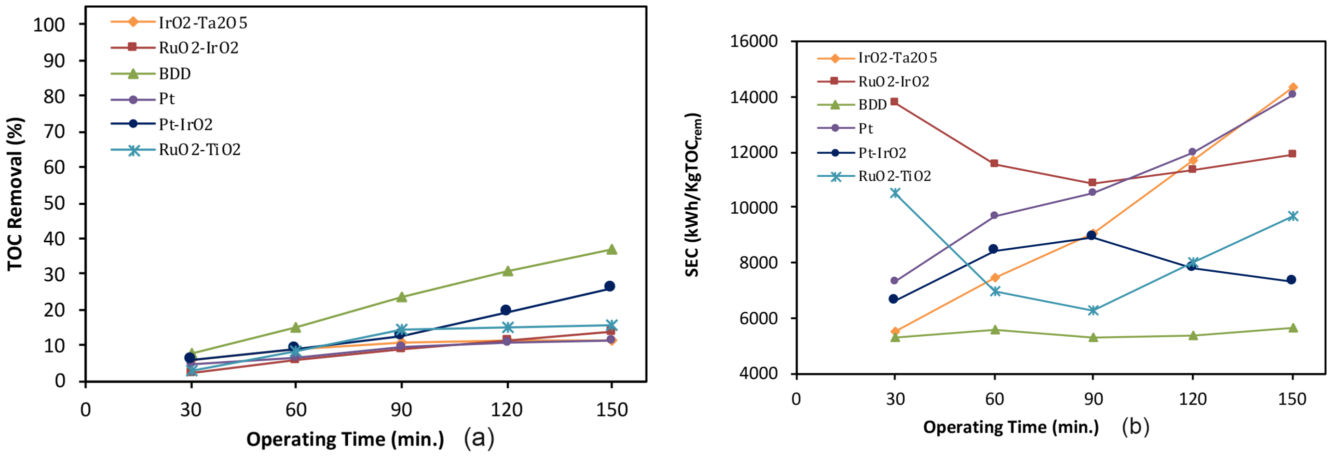

Fig. 3. (a) The TOC removal efficiency for Pt, MMO and BDD electrodes at pH 6 (b) Effect of electrode type on SEC at pH 6 (conditions: o-tolidine C_0: 50 mg/L, current density: 25 mA/cm^2, stirring speed: 500 rpm, distance between the electrodes: 5 mm, electrolyte (phosphoric acid) concentration: 0.01 M, conductivity 922 µS/cm).

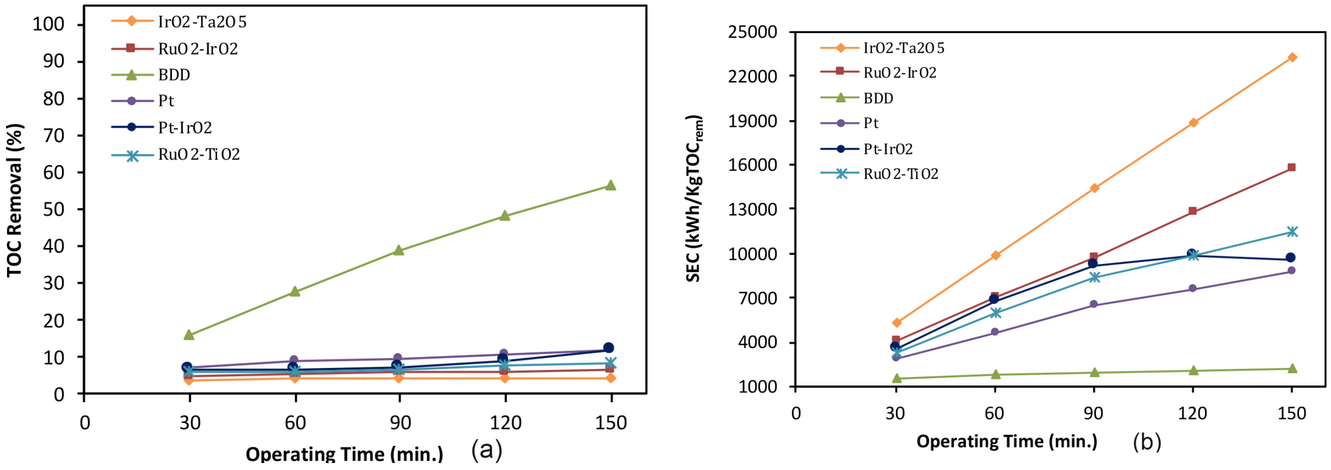

Fig. 4. (a) The TOC removal efficiency for Pt, MMO and BDD electrodes at pH 8 (b) Effect of electrode type on SEC at pH 8 (conditions: o-tolidine C_0: 50 mg/L, current density: 25 mA/ cm^2, stirring speed: 500 rpm, distance between the electrodes: 5 mm, electrolyte (phosphoric acid) concentration: 0.01 M, conductivity 1831 µS/cm).

BDD, while for Pt and MMO electrodes it realized respectively in decreasing order as; Pt-IrO_2: 11.81%, Pt: 11.77%, RuO_2-TiO_2: 8.21%, RuO_2-IrO_2: 6.40%, IrO_2-Ta_2O_5: 4.39% at the end of the trial period of 150 min. When compared with pH 4, an increase by 40% was seen in the efficiency of BDD electrode, increases ranging between 2-4 times were observed in the efficiency of Pt and MMO anodes.

In Fig. 4b SEC values calculated based on the TOC removal efficiency by each anode for the current of 1 A (J 25 mA/cm^2) are given. While the lowest SEC value realized in the range between 1500–2200 kWh/kg TOC$_{rem}$ for the BDD electrode with the best TOC removal efficiency; SEC values might be respectively 4 or 10 times greater for Pt and various MMO anodes when compared to BDD anode.

Table 2 shows the electrooxidation parameters end of the 150 min during the mineralization of o-tolidine by different anodes and at different pH.

In Table 2, it is seen how much the anode type and pH affect the process efficiency and economy. The anode efficiency was 1208.34 for BDD electrodes at the pH 8. This value is very big from the anode efficiency value of Pt and MMO electrodes.

In conclusion, according to experimental results presented above at pH 4, 6, and 8, BDD anode was more successful than Pt and MMO electrodes, with TOC removal efficiencies of 41.04%, 36.74%, and 56.32% respectively. With the lower success of mineralization of o-tolidine of Pt and MMO anodes, the best mineralization values were obtained at pH 6 ; in this case, the best TOC removal efficiency (25.85%) was obtained with Pt-IrO_2 anode, removal efficiency ranging between 11%–15% with other MMO anodes.

"Poisoning effect" is the leading cause of the failure of MMO electrodes. The main problem of electrooxidation at a fixed anodic potential before oxygen evolution is a decrease in the catalytic activity, commonly called the poisoning effect, due to the formation of a polymer layer on the anode surface. A light-brown thin polymer formed by (anodic) electropolymerization of o-tolidine

Table 2
Electrooxidation parameters during the mineralization of o-tolidine by different anodes and at different pH

Anot	pH	j	TOK_{rem}	U	SEC	η	MCE
		(mA/cm^2)	(%)	(V)	(kWh/kg TOK_{rem})	mg TOK/Ahm^2	(%)
BDD	4	25	41.04	15.01	4261.93	880.59	4.05
	6	25	36.74	17.71	5616.41	788.31	3.62
	8	25	56.32	10.51	2173.64	1208.34	5.55
Pt	4	25	3.57	13.26	43338.01	76.49	0.35
	6	25	11.54	13.91	14044.00	247.61	1.14
	8	25	11.77	8.86	8773.69	252.52	1.16
Pt-IrO_2	4	25	12.22	14.87	14178.40	262.12	1.20
	6	25	25.87	16.24	7314.89	555.03	2.55
	8	25	11.81	9.78	9644.62	253.41	1.16
RuO_2-TiO_2	4	25	6.50	12.69	22741.70	139.46	0.64
	6	25	15.37	12.74	9661.51	329.66	1.51
	8	25	8.21	8.07	11454.12	176.05	0.81
RuO_2-IrO_2	4	25	1.22	13.58	129962.21	26.12	0.12
	6	25	13.50	13.77	11886.05	289.63	1.33
	8	25	6.40	8.67	15770.99	137.37	0.63
IrO_2-Ta_2O_5	4	25	1.43	13.93	113113.42	30.78	0.14
	6	25	11.43	14.05	14328.34	245.14	1.13
	8	25	4.39	8.76	23225.69	94.25	0.43

U: average voltage between electrodes, : Anode efficiency, t for 150 min.

layer was observed on the anode surface. It is worth to note that almost no polymer layer was observed in the case of BDD anode. Anode surface deactivation due to the polymer layer depends on the adsorption properties of the anode surface and the concentration and the nature of the organic compound [19]. Ismail studied the preparation of poly(o-tolidine) films by the anodic oxidation of o-tolidine using Pt anode; during the electrochemical polymerization, accumulation of the polymer on the electrode surface was readily observable by naked eyes, the electropolymerization rate depends on the monomer (o-tolidine) concentration rather than the electrolyte [20].

A model proposed by Comninellis for the anodic oxidation of organics in acid media [21]. According to this model, the nature of the anode electrode material (M) is very important, and anode materials are divided for simplicity into two classes as active and non-active cases. Active anodes which present low oxygen evolution over potential are good electrocatalysts for Oxygen evolution reaction. Chemisorption of electrogenerated $OH^{\bullet}$ on M (high M- $OH^{\bullet}$ adsorption enthalpy) results in an increase of the electrochemical reactivity of $OH^{\bullet}$ (low oxidation power anodes, favoring side reaction) and consequently, partial oxidation of organics occurs. On the other hand, in the case of non-active anodes which present high oxygen evolution over potential are poor electrocatalysts for oxygen evolution reaction, physisorption of electrogenerated $OH^{\bullet}$ on M (low M- $OH^{\bullet}$ adsorption enthalpy) results in an increase of the chemical reactivity of $OH^{\bullet}$ (high oxidation power anodes, favoring main side reaction), thus the complete oxidation of organics occurs. Graphite and carbon, Pt, RuO_2 and IrO_2 are considered non-actives anodes with low oxidation potential. On the other hand, Sb-doped SnO_2, PbO_2 and BDD are considered non-actives anodes with high oxidation potential.

In our research on the mineralization of o-tolidine by electrooxidation, it is seen clearly that MMO anodes behave like the active case and BDD behaves like the non-active case. The characteristics of electrode material strongly affect both selectivity and effectiveness of the process. While particularly MMO anodes with an over potential of low oxygen production allow only partial organic oxidation, BDD electrode provides full oxidation of organics to CO_2, with over voltage caused by high production of oxygen. This study demonstrates the highest removal rate and stability of BDD electrodes, and accordingly, they look promising for the treatment of toxic and harmful waste waters.

3.2. TOC removal using BDD electrode

3.2.1. Effect of current density

The effect of the current density on the TOC removal efficiency was investigated for five different current densities (J 25, 50, 75, 100 and 125 mA/cm^2). The run duration was selected as 150 min. TOC values were measured taking a sample at every 30 min.

The effect of the current density on the TOC removal efficiency is presented in Fig. 5a, where a steady TOC removal rate is observed, and also a direct relationship between current density and TOC removal efficiency is detected. The TOC removal increases with increasing current density; which realized respectively as 54.6%, 60.9%, 67.7%, 73.2% and 79.9% for current density of 25, 50, 75, 100 and 125 mA/cm^2.

In Fig. 5b SEC values calculated for five different current density values are seen; SEC increases with increasing current density; it realized as 1716.3 kWh/kg TOC$_{rem}$ for current density of 25 mA/cm^2 and with 54.6% TOC removal efficiency, while it realized as 9451.8 kWh/kg TOC$_{rem}$ for current density of 125 mA/cm^2 and 79.9% removal efficiency. Although the difference between TOC removal efficiencies of two current densities is about 25%, SEC is about 5.5 times greater. This result indicates that the application of low current density is much more advantageous economically.

3.2.2. Effect of stirring speed

The effect of the stirring speed on the TOC removal efficiency was investigated at 5 different speeds, which is seen in Fig. 6a. Removal of TOC increases steadily during the run duration. Also, a direct relationship exists between the stirring speed and TOC removal efficiency. Amount of TOC being removed increases with increasing stirring speed. TOC removal efficiency realized respectively as 51.5%, 56.9%, 67.7%, 70.2% and 79.1% at stirring speeds of 0, 250, 500, 750, and 1000 rpm.

The increase in TOC removal efficiency by increasing stirring speed can be explained by the enhanced mass transfer of contaminating organic materials toward BDD anode surface to contact more effectively with physisorbed $OH^\bullet$.

In Fig. 6b SEC values calculated basing on the amount of the removed TOC for five different stirring speed values are seen. As seen, SEC value decreases with increasing of stirring speed; it was 7360.9 kWh/kg TOC$_{rem}$ for no-stirring with 51.5% TOC removal efficiency, while it was 4103.5 kWh/kg TOC$_{rem}$ for 1000 rpm and 79.1% TOC

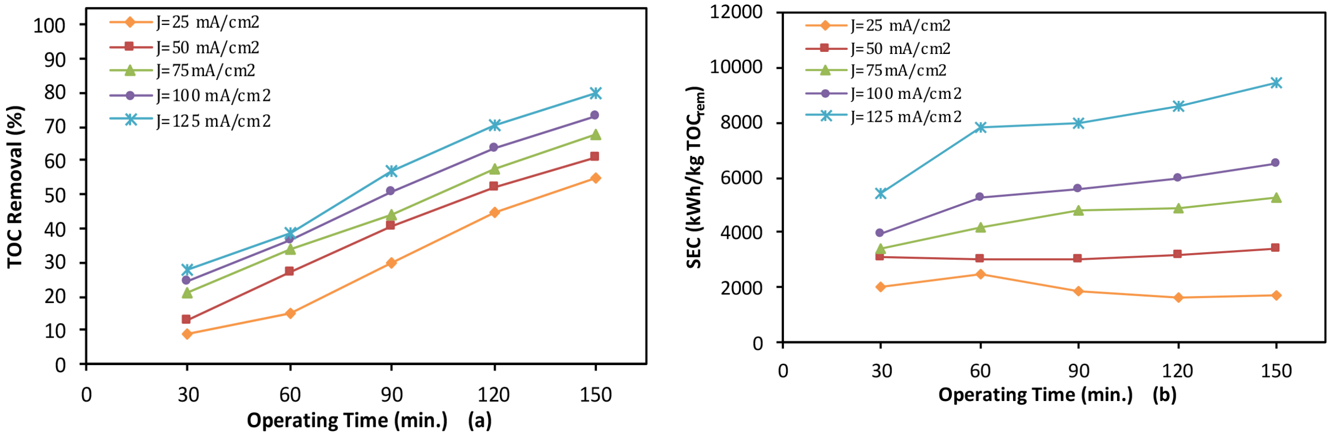

Fig. 5. (a) The effect of the current density on the TOC removal by BDD electrode (b) Effect of current density on SEC. (conditions: o-tolidine C_0: 50 mg/L, stirring speed: 500 rpm, distance between the electrodes: 15 mm, electrolyte (phosphoric acid) concentration: 0.25 M).

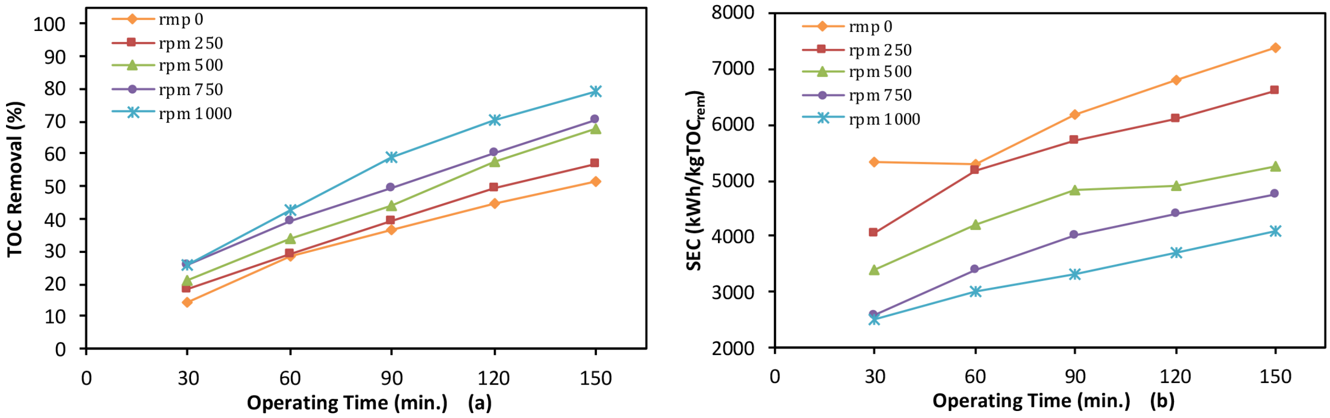

Fig. 6. (a) The effect of the stirring speed on the TOC removal by BDD electrode (b) Effect of stirring speed on SEC. (conditions: o-tolidine C_0: 50 mg/L, current density: 75 mA/cm^2, distance between the electrodes: 15 mm, electrolyte (phosphoric acid) concentration: 0.25 M).

removal efficiency. Although the difference of TOC removal efficiency between the highest stirring speed of 1000 rpm and no-stirring is about 28%, SEC increases proportionally about by 44%. This result indicates that the operation of the process at higher stirring speeds seems to be much more advantageous economically.

3.2.3. Effect of distance between the electrodes

The effect of the inter electrode distance on TOC removal efficiency was investigated at five different values (5, 10, 15, 20, and 30 mm). As seen in Fig. 7a, TOC removal efficiency realized as 59.2%, 67.8%, 67.7%, 68.2% and 66.1% at the inter electrode distances of 5, 10, 15, 20, and 30 mm respectively for an operation time of 150 min. According to experimental data, the lowest efficiency was obtained when inter electrode distance was 5 mm; similar efficiencies were obtained for inter electrode distances of 10, 15 and 20 mm. Furthermore, a slight decrease in the efficiency occurred when the distance increases to 30 mm. In Fig. 7b SEC values calculated for five different distances are seen; generally, SEC value increases with an increase of distance (except for 5 mm where TOC removal efficiency is also the lowest) due to increases of both resistance and potential difference. As an example, for 10 mm inter electrode distance, SEC value realized as 4546.4 kWh/kg TOC_{rem} with TOC removal efficiency of 67.8%, while for 30 mm it realized as 8000 kWh/kg TOC_{rem} for TOC removal efficiency of 66.1%. Thus, increasing of the inter electrode distance 3 times causes nearly 2 times increase of SEC value with similar removal efficiencies. In conclusion, a sufficient distance is required to ensure the inter electrode circulation of the solution but the distance should also be kept low enough about low SEC value.

3.2.4. Effect of o-tolidine concentration

The effect of the concentration of o-tolidine on TOC removal efficiency was investigated at five concentrations (12.5, 25, 50, 100 and 200 mg/L). The experimental data is depicted in Fig. 8a. In general, TOC removal efficiency is

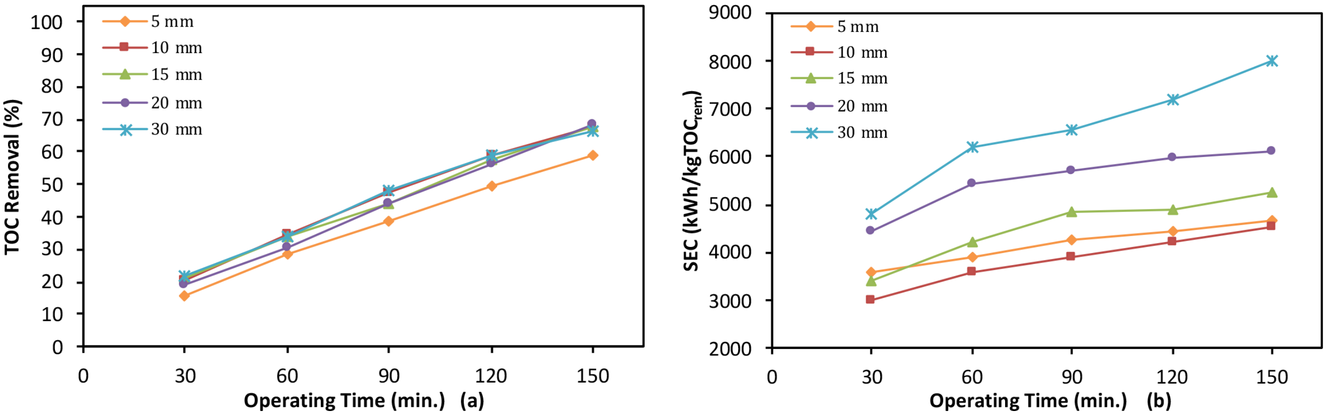

Fig. 7. (a) The effect of the distance between the electrodes on the TOC removal by BDD electrode (b) Effect of distance between the electrodes on SEC. (conditions: o-tolidine C_0: 50 mg/L, current density: 75 mA/cm^2, stirring speed: 500 rpm, electrolyte (phosphoric acid) concentration: 0.25 M).

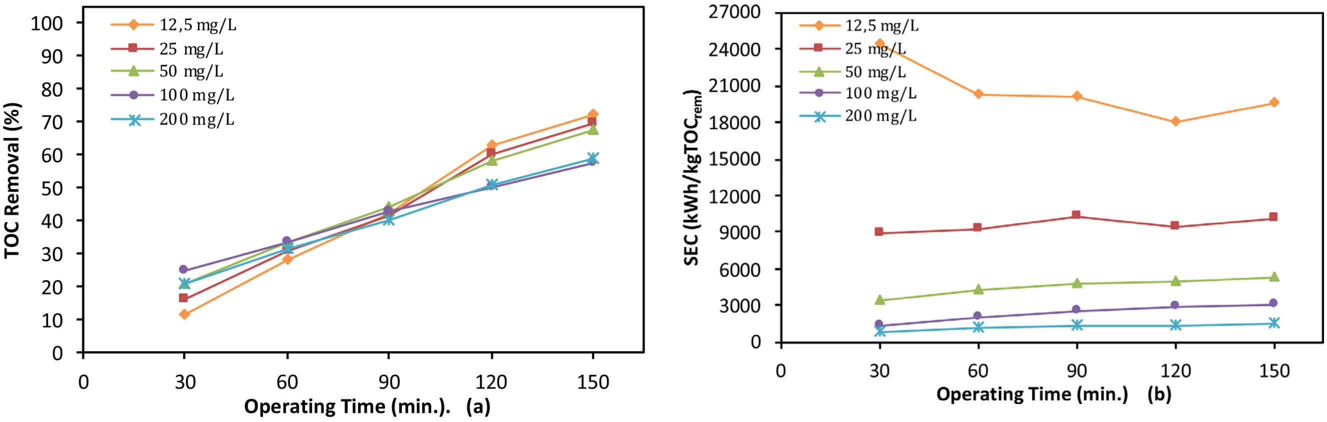

Fig. 8. (a) The effect of o-tolidine concentration on the TOC removal by BDD (b) Effect of o-tolidine concentration on SEC. (conditions: distance between the electrodes 15 mm, current density: 75 mA/cm^2, stirring speed: 500 rpm, electrolyte (phosphoric acid) concentration: 0.25 M).

inversely proportional to the o-tolidine concentration; TOC removal efficiency realized as 72%, 69.7%, 67.7%, 57.3% and 58.9% for 12.5, 25, 50, 100 and 200 mg/L respectively at the end of 150 min.

On the other hand, as seen in Fig. 8b, the SEC value decreases with increase of o-tolidine concentration at the end of 150 min; in the case of 12.5 mg/L, SEC realized as 19633.2 kWh/kg TOC_{rem} with TOC removal efficiency of 72%, and in the case of 200 mg/L it realized as 1517.8 kWh/kg TOC_{rem} for TOC removal efficiency of 58.9%. This is because SEC is based on the total amount of TOC removed (which is equal to the product of TOC concentration and removal efficiency) which may increase with increasing TOC concentration despite lower removal efficiency.

3.2.5. Effect of electrolyte concentration

To evaluate the anodic oxidation performance of the anode electrodes, phosphoric acid is used as an electrolyte instead of salts such as NaCl or acids such as HCl, since it is necessary to prevent the formation of oxidizers (, etc.) to be formed anodically.

The effect of the electrolyte concentration on the TOC removal efficiency was investigated at five concentrations (0.05, 0.10, 0.25, 0.50, and 0.75 M).

The effect of the concentration of electrolyte on the TOC removal efficiency is seen in Fig. 9a. The TOC removal efficiency realized respectively as 59.4%, 63.6%, 67.7%, 65.4% and 64.1% for electrolyte concentrations of 0.05, 0.10, 0.25, 0.50, and 0.75 M at the end of 150 min. According to experimental results, the lowest removal efficiency was obtained when the concentration of electrolyte was 0.05 M; the highest efficiency was obtained in the case of 0.25 M. Meanwhile; a slight decrease in the effect occurs when the electrolyte concentration is over 0.25 M.

In Fig. 9 (b), the SEC values that calculated for five different concentrations of electrolyte are seen; despite similar removal efficiencies, there are great differences between SEC values. The increase of SEC value with the decrease of electrolyte concentration stems from the decrease of the conductivity and increase of the applied cell voltage. For example, at the end of 150 min, SEC value realized as 7041.4 kWh/$kgTOC_{rem}$ for with TOC efficiency of 63.6%, while it realized as 3718.1 kWh/$kgTOC_{rem}$ for 0.75 M electrolyte concentration with TOC removal efficiency of 64.1%. Thus, by increasing 7.5 times the concentration of electrolyte with similar TOC removal efficiencies causes SEC value to decrease nearly 2 times. It is seen that electrolyte concentration similarly; solution conductivity has the stronger effect on SEC than TOC removal efficiency.

In the mineralization study conducted under best-operating conditions as; o-tolidine C_0: 50 mg/L, current density: 125 mA/cm^2, stirring speed: 1000 rpm, inter-electrode distance: 20 mm, electrolyte concentration: 0.25 M, o-tolidine concentration: 50 mg/L , time: 190 min, TOC removal efficiency of 99.1 % was realized with SEC value of 10331.7 kWh/kg TOC_{rem}.

4. Conclusion

Electrooxidation process was successfully applied to mineralization of o-tolidine by using BDD anode. The TOC removal efficiency was found to be dependent on the anode material, the solution pH, the current density, the stirring speed, the inter electrode distance, the concentrations of o-tolidine and electrolyte. The characteristics of anode material strongly affect both the selectivity and the effectiveness of the process. Poisoning effect was observed in the case of MMO anodes. This effect decreased the mineralization of o-tolidine sharply. With high mineralization rate and stability, electrooxidation with BDD anode is an effective method for the treatment of toxic and harmful waste waters.

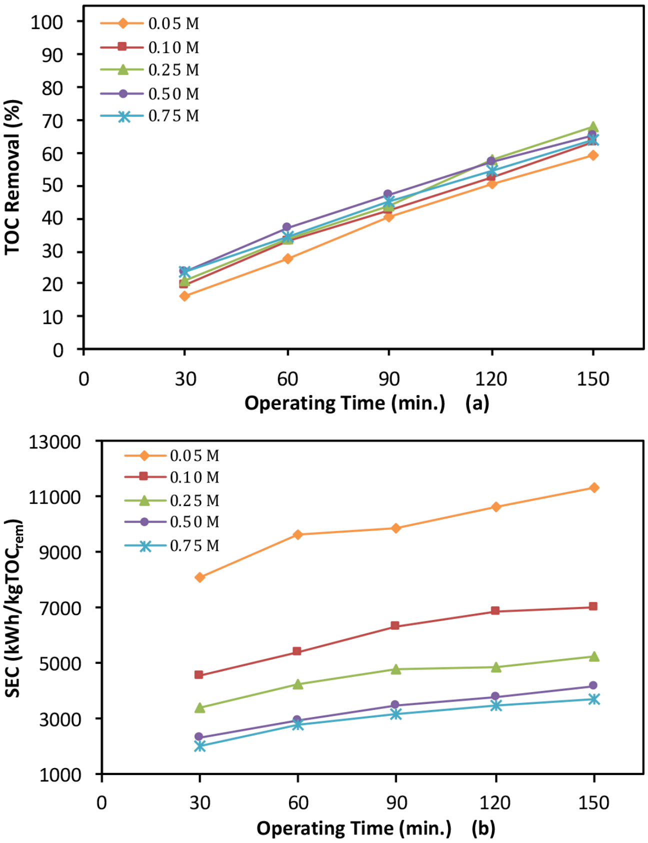

Fig. 9. (a) The effect of the electrolyte (phosphoric acid) concentration on the TOC removal by BDD electrode (b) Effect of electrolyte (phosphoric acid) concentration on SEC. (conditions: o-tolidine C_0: 50 mg/L, current density: 75 mA/cm^2, stirring speed: 500 rpm, distance between the electrodes 15 mm).

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