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Feasibility of electrochemical oxidation process for treatment of saline wastewater

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Abstract

Background: High concentration of salt makes biological treatment impossible due to bacterial plasmolysis. The present research studies the process of electrochemical oxidation efficiency and optimal levels as important factors affecting pH, salt concentration, reaction time and applied voltage.

Methods: The sample included graphite electrodes with specifications of 2.5 cm diameter and 15 cm height using a reactor with an optimum capacity of 1 L. Sixty samples were obtained with the aid of the experiments carried out in triplicates for each factor at 5 different levels. The entire experiments were performed based on standard methods for water and waste water treatments.

Results: Analysis of variance carried out on effect of pH, salt concentration, reaction time and flow intensity in elimination of chemical oxygen demand (COD) showed that they are significant factors affecting this process and reduce COD with a coefficient interval of 95% and test power of 80%. Scheffe test showed that at optimal level, a reaction time of 1 hour, 10 g/L concentration, pH = 9 and 15 V electrical potential difference were obtained.

Conclusion: Waste waters containing salt may contribute to the electro-oxidation process due to its cations and anions. Therefore, the process of electrochemical oxidation with graphite electrodes could be a proper strategy for the treatment of saline wastewater where biological treatment is not possible.

Keywords: Saline wastewater, Graphite electrode, Salinity removal, Electrochemical oxidation.

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Introduction

Saline wastewater contains high amounts of organic compounds and soluble inorganic salts which are produced from industries such as fish processing, sea food packing, tanning and petrochemicals (1). In biological treatment of wastewaters with high salt concentrations especially in the of aerobic activated sludge phase process, the efficiency of decontamination would be very low due to bacterial plasmolysis in high concentration of salt (over 1%) (2,3). Desalination is required before treatment process. Therefore, to treat the waste waters containing total dissolved solids (TDS), other advanced treatment methods such as ultra-filtration (4), nano-filtration (5), reverse osmosis (6), electro-Fenton processes (7), and photochemical electrodialysis (8) have been studied.

In the methods of membrane filtration of saline wastewaters where some solution is used for demineralization, the influent organic matter to the membrane should be zero level (9). Waste waters containing high salt appeared to have high electrical conductivity due to high concentration of cations and anions. Hence, this seems to be an appropriate method in combination with electrochemical methods in the treatment of such waste waters (10).

Many studies have been conducted on electro oxidation of organic compounds where various materials are used as anode. This method has been successfully employed in the treatment of wastewaters from industries such as textile, tanning, distillation and leachate industries as well as urban wastewater. Different anodes have been employed for the treatment of industrial wastewaters. Recently, electrode graphite has been widely used for the decomposition of organic matter because it is economical. Graphite has a large surface area; this feature enables it to increase the rate of organic matter removal through adsorption and electro-oxidation. These electrodes are more efficient compared with other electrodes. Hydroxyl radicals are dominant because of the physical adsorption of oxygen on to the graphite electrode where they cause com-

plete decomposition of organic materials. However, one of the considerable disadvantages of graphite electrode is its relative short life due to corrosion of the its surface especially when electric oxidation occurs in high potential difference (11).

Detoxification of tannery wastewater through electrolysis by the use of Ti/Pt anode and SS304 cathode was studied. The results showed a 52% decrease in chemical oxygen demand (COD) using electro oxidation process (11). In a study by Rao et al (12), using Ti/Pt electrode in the successful oxidation of tannery waste water, the study showed that the material of the electrode has an effect on COD removal. Kargi Dincer reported that biological treatment of saline wastewater by activated sludge resulted in low COD removal efficiencies as a result of plasmolysis of cells caused by high salt content (13). Szpyrkoicz et al suggested the electro oxidation process as a supplementary treatment after biological treatment as a more economical process of ammonium removal (14). In electrochemical oxidation, the organic pollutants are eliminated by chlorine and hypochlorite. During the oxidation process, the reaction of electrographite in the presence of sodium chloride produces chlorine (14).

Anode reactions:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$
$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (2)$$
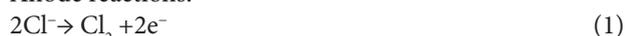
Cathode reactions

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

Reactions at the anode (Equations 1 and 2) and at the cathode (Equations 3) for man integrated cell at the anode. Hydroxide is produced at the cathode and reacts with chloride and hypochlorite. The compounds of hypochlorite and free chlorine are chemically reactive which decomposes organic pollutants into carbon dioxide and water, hence HOCl is produced:

HOCl decomposition reaction:

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \qquad (4)$$
$$HOCl \leftrightarrow H^+ + OCl^- \qquad (5)$$

Hypochlorite is a leading organic matter. The final reaction in the electro oxidation process is expressed according to Equation 6 below:

$$Organic\ matter + OCl^- \rightarrow interstitial\ material \rightarrow CO_2 + Cl^- + H_2O \qquad (6)$$

The present study was carried out to find out the factors such as salt concentration, reaction time, the intensity of voltage and pH affecting the treatment of saline waste water through electrooxidation process and determination of optimal conditions for each of the factors.

Methods

This research was a descriptive-analytical study conducted in a cubic-rectangular batch reactor made of Plexiglas with an optimum capacity of 1/L with dimensions of 14 cm × 7 cm ×15 cm. Graphite columns with diameter of 2.5 cm and length of 15 cm were interconnected by pieces of wire and embedded in the reactor as 2 series of parallel electrode. Each series of graphite electrode connected to direct current was supplied by AC/DC convertor (PAYANIK, RN-3003D). The experimental setup for the electro-oxidation studies is shown in Figure 1.

2.5 g bovine albumin serum and hydrochloric acid were used to prepare synthetic wastewater as well as required salt in the process and concentration of COD at the required level of saline wastewater. To balance the pH level, caustic 1 N and hydrochloric acid solutions made by Merck Company were used. All experiments were performed according to the standard methods for the analysis of water and wastewater (15). Experimental design was carried out based on the book for experimental design (16). The optimal level of each factor – pH, primary concentration of salt, current intensity and time – was determined separately. Since the present study aimed at comparing the mean percent of COD removal at different levels of the factors, graphs were used for choosing sample size. The frequency of each test was selected at a confidence interval of 95% and a power of test of 80%. A mean difference of 20% or higher for COD removal between the 2 levels of each factor in the experiment showed that it was statistically significant (17).

To determine the frequency of each test and the level of each factor, the standard deviation estimated to be 10% was evaluated based on the formula 7:

$$Q = \frac{1}{\sigma}\sqrt{\frac{\sum T_j^2}{r}} = \frac{1}{10} \times \sqrt{\frac{5 \times 15^2}{5}} = 1.5 \qquad (7)$$

Where:

r = Number of groups

σ = Equal to Q

T² = Mean difference between the two concentrations.

Using the following formula, Ω coefficient was calculated at 0.5 error levels and 80% power of test, and the ratio of the numbers of pH factor levels in the sample graphs. According to above mentioned book, 3 experiments were repeated for each level. As the results of the calculations, the total numbers of the experiments was estimated 60 samples (16).

After the experiments were conducted and laboratory data for the related parameters were collected, graphs were constructed using Excel and SPSS version 16. To identify optimal level of each variable, analysis of variance (ANOVA) and Scheffe test were used.

Results

Effects of pH

Tables 1 & 2 and Figure 2 show the results of wastewater COD changes (790 mg/L primary COD) at 10 g/L salt concentration, 1 hour reaction time, 15 V potential difference and different pH.

Also, ANOVA results for the effect of pH on COD removal at 10 g/L salt concentration, 1 hour reaction time, and 15 V potential difference showed that pH had a significant (F = 44.24, $P < 0.001$) effect on the process.
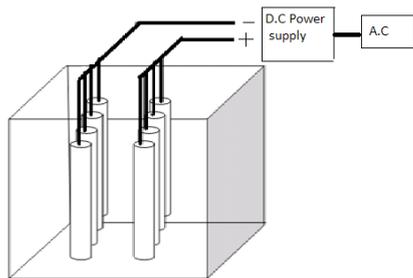
Figure 1. Schematic diagram of the reactor used in this study

Table 1. Data of reduction of COD at different pH levels with 10 g/L salt concentration, 1 hour reaction time, and 15 V difference

pH	No. of experiments	Mean	SD	SE	95% CI
3	3	42	3	1.7	34.54-49.45
5	3	52.3	6.6	3.8	35.79-68.87
7	3	63	6.5	3.7	46.71-79.28
9	3	80.33	4.5	2.6	69.13-91.53
11	3	87.33	2.3		77.29-97.37

Abbreviations: SD, standard deviation; SE, standard error.

Table 2. Comparison test for different levels of pH factor in reducing COD at 10 g/L salt concentration, 1 hour reaction time, and 15 V potential difference at 95% CI

pH level compared	Other pH levels	Mean difference	SD	P
	3	38.33 (SE)	4.2	<0.001
9	5	28 (SE)	4.2	<0.001
	7	17.33 (SE)	4.2	<0.029
	11	-7	4.2	<0.615

Abbreviation: SD, standard deviation.

Effect of reaction time

Tables 3 & 4 and Figure 3 show the results of wastewater COD changes in this study with 10 g/L salt concentration, pH = 9 and 15 V potential difference at different reaction time.

ANOVA results for the effects of reaction time on COD removal at 10 g/L salt concentration, pH = 9, and 15 V potential difference showed that reaction time had a significant (F = 60.55, $P < 0.001$) effect on this process.

Effect of salt concentration

Tables 5 & 6 and Figure 4 show the results of wastewater COD changes at 1 hour reaction time, pH = 9 and 15 V potential difference time at different salt concentrations. ANOVA results for the effects of salt concentration on COD removal at 1 hour reaction time, pH = 9, and 15 V potential difference showed that salt concentration had a significant effect on this process (F = 0.4.72, $P < 0.05$).

Influence of applied voltage

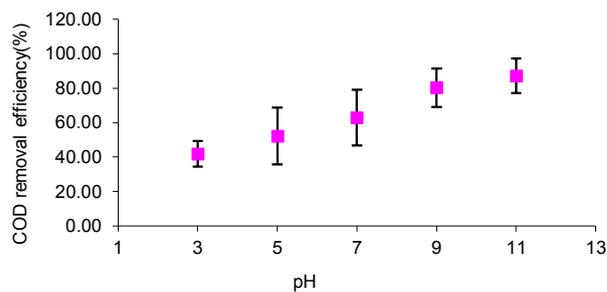Tables 7 & 8 and Figure 5 show the results of wastewater

Figure 2. The graph of COD removal changes at different levels of pH at 10 g/L salt concentration, 1 hour reaction time, and 15 V potential difference.
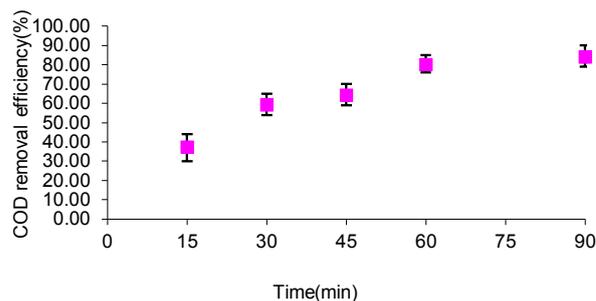

Figure 3. The graph of changes in COD removal at different levels of reaction time, 10 g/L salt concentration, pH = 9 and 15 V potential difference.

Table 3. Data description in reduction percent of COD at different reaction time with 10 g/L salt concentration, pH = 9 and 15 V difference

Time	No. of experiments	Mean	SD	SE	95% CI
15	3	37.23	2	1.2	30-44
30	3	59.33	5.5	3.17	54-65
45	3	64.33	5.5	3.17	59-70
60	3	80.33	4.5	2.6	76-85
90	3	84	1	0.57	79-90

Abbreviations: SD, standard deviation; SE, standard error.

Table 4. Comparisons of different levels of reaction time in reducing COD for the determination of optimal level at 95% CI

pH level compared	Other pH levels	Mean difference	SD	P
	15	43(SE)	3.39	<0.001
16	30	21 (SE)	3.39	<0.002
	45	16 (SE)	3.39	<0.013
	90	-3.66	3.39	<0.877

Abbreviation: SD, standard deviation.

COD changes at 1 hour reaction time, pH = 9 and 10 g/L salt concentration, at different potential differences. ANOVA results for the effects of potential differences on COD removal with a 1 hour reaction time, pH = 9, and 10 gr/L salt concentration showed that potential difference had a significant effect on the process (F = 8.75, $P < 0.05$).

Table 5. Data description of percentage reduction of COD at different salt concentrations, 1 hour reaction time, pH = 9 and 15 V potential difference
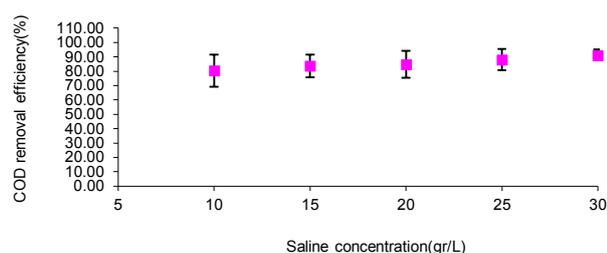
Saline concentration (g/L)	No. of experiments	Mean	SD	SE	CI %95
10	3	80.33	4.5	2.6	69.13-91.53
15	3	83.66	3.2	1.8	75.68-91.65
20	3	84.66	3.7	2.18	75.26-94.07
25	3	88	3	1.73	80.54-95.45
30	3	91	1.5	0.88	87.53-95.12

Abbreviations: SD, standard deviation; SE, standard error.

Table 7. Data description in COD reduction percentage at different potential differences, 1 hour reaction time, pH = 9 and 10 g/L salt concentration

Voltage	No. of experiments	Mean	SD	SE	CI 95%
2	3	64.66	4.5	2.6	53.46-75.8
5	3	70.66	3	1.7	63.7-78.25
8	3	73.66	3.21	1.8	65.68-81.65
10	3	77	1.7	1	72.69-81.3
15	3	80.33	4.5	2.6	69.13-91.53

Abbreviations: SD, standard deviation; SE, standard error.

Table 6. Comparison test for different levels of voltage percentage on COD reduction at different salt concentrations with 1 hour reaction time, pH = 9, and 15 V difference

Saline concentration level compared	Other time levels	Mean difference	SD	P
	15	-3.33	2.7	0.82
10	20	-4.33	2.7	0.65
	25	-7.66	2.7	0.17
	30	-11 (SE)	2.7	0.03

Abbreviation: SD, standard deviation.

Table 8. Comparison test for different levels of potential differences on COD reduction at 1 hour reaction time, pH = 9 and 10 g/L salt concentration

Voltage level compared	Other voltage levels	Mean difference	SD	P
	2	15.66 (SE)	2.9	0.005
15	5	6.66	2.9	0087
	8	3.33	2.9	0.329
	10	-11 (SE)	2.9	0.852

Abbreviation: SD, standard deviation.

Figure 4. COD removal changes at different levels of salt concentration, with a 1 hour reaction time, pH = 9 and 15 V potential difference.
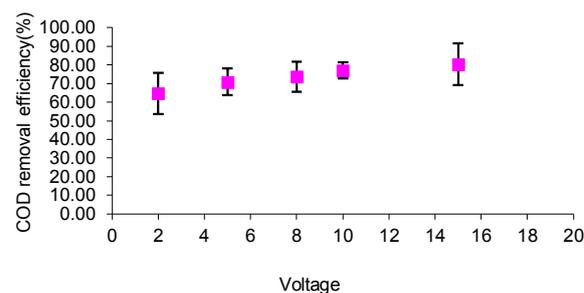
Figure 5. COD removal changes at different levels of potential difference, at 1 hour reaction time, pH = 9 and 15 potential difference.

Discussion

ANOVA results for the effects of pH on COD removal at 10 g/L salt concentration, 1 hour reaction time, and 15 V potential difference showed that pH had a significant effect on this process (F = 44.24, $P < 0.001$). The results showed that an increase in pH from 3 to 11, resulted in a COD decrease from 87% to 42%. Scheffe test for the comparison of different levels of pH factor was significant and showed that as pH increases, removal of COD increases as well which could be due to hydroxyl radical production in the electro-oxidation process. The findings of this study are in accordance with those of Sundarapandiyan et al (2) which showed that an increase in pH from 5 to 11, causes a COD decreases from 89% to 57%. According to Equations 1-5, the reason for this is that in acidosis state, hypochlorite ions, CLO⁻, remain unstable and in combination with hydrogen ion tends to form HCLO. The hypochlorite which is formed in an alkaline state accounts for the most important factor inorganic matter oxidation. However,

Yan et al (18) reported a higher removal of COD in acidic conditions using the Fenton process a sit is more efficient in acidic conditions.

ANOVA results for the effects of reaction time on COD removal at 10 g/L salt concentration, pH = 9, and 15 V difference showed that reaction time had a significant effect on this process (F = 60.55, $P < 0.001$). The mean COD removal of was 37.33% at a 95% CI and 80% power of test at 15 minutes reaction time (Table 3). Scheffe test for the comparison of different levels of reaction time factor was significant and showed that with increase in reaction time, COD removal also increases. In comparing different levels of time, it is observed that 60 minutes interval is significantly different from 15, 30, and 45 minutes intervals. There was, however, no significant difference at 90 minutes time interval where COD reduction rate increased by 3% which does not seem reasonable with the amount of energy consumed. Therefore, a reaction time of 60 minutes is suggested to be an optimal level. The finding of this

study is in accordance with those of Zhang et al (19)and Yazdanbakhsh et al (20). However, Yan et al and Javid et al showed a higher time for COD decrease which could be due to the difference in potential difference used in the process (18,21).

ANOVA results for the effects of salt concentration on COD removal at 1 hour reaction time, pH=9, and 15 V potential difference showed that salt concentration had a significant effect on the process ($F = 4.72$, $P < 0.05$). The mean COD removal was 80.33% at 95% CI and 80% power of test at 10 g/L salt concentration (Table 5). The reason is likely due to an increase in the production of hypochlorite ions which occurs through the addition of NaCl. This is consistent with Sundarapandiyan et al study (2). Scheffe test for the comparison of different levels of salt concentration factor was only significant at 10 and 30 g/L, however it was insignificant at other levels. This shows that although salt acts as a facilitator, its increase in the environment has no effect on the efficiency of the process. ANOVA results for the effects of potential differences on COD removal at 1 hour reaction time, pH=9, and 10 g/L salt concentration showed that it had a significant effect on the electrochemical oxidation process ($F = 8.75$, $P < 0.05$).The mean COD removal was 64.66% at 95% CI and 80% power of test at 15 minutes reaction time (Table 7). Seems that rendering increase of voltage results in hypochlorite ion increase; this is consistent with Sundarapandiyan study (2). Also, Al-Qaim et al (22) reported that with the increase of voltage the removal efficiency of caffeine by electrochemical oxidation increased to 95% at 10 V from 75% at 6 V and 10% at 3 V. Also, the study by Duan et al (23) showed that phenol removal efficiency is almost 100% at 3 V after 300 minutes of polarization, with only 40% and 83% of phenol removed at 1.5 and 2 V, respectively (23). Scheffe test was used for the comparison of different levels of reaction time which was significant; although potential difference is effective in the electrochemical oxidation process considering the useful capacity of the reactor, an 8-15 Voltage difference seems to be sufficient. An increase in potential differences with this capacity causes foam formation and discoloration due to destruction of graphite electrode. The study of Yan et al showed an increase in COD removal with an increase in voltage. It indicates that some organic compounds are decomposed following voltage increase (18,20).

Conclusion

ANOVA analysis showed that pH, salt concentration, reaction time, and flow intensity are significant in COD removal at a CI 95% and test power of 80%. Scheffe test showed the optimal levels for the factors thus; reaction time 1 hour,10 g/L concentration, pH = 9 and 15 V electrical potential difference. The electrochemical oxidation process with graphite electrodes could be a proper strategy for the treatment of saline wastewater where biological treatment is not possible.

Ethical issues

It is hereby certified by the authors that all data collected during the study are original and have not be published elsewhere.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

All the authors contributed equally to this study and therefore reviewed and approved the final draft of the manuscript.

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