Original Research Paper

Optimization of a Combined Approach for the Treatment of Carbide Slurry and Capture of CO₂

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Abstract: The aim of this study is to evaluate the potential use of electrocoagulation in the treatment of carbide slurry, a wastewater generated during the production of acetylene, and in the capture of carbon dioxide. An electrochemical batch reactor was used to carry out several experiments at different current densities, ranging between 140-290 A/m^2. Pure air and a mixture of 10% of carbon dioxide in air were injected into the reactor system to ensure good mixing and solution homogeneity. Samples were collected from the treated effluent and analyzed for Total Hardness (TH), Total Dissolved Solids (TDS) and Chemical Oxygen Demand (COD). Response Surface Methodology (RSM) was conducted to design a matrix of experiments to optimize the conditions for the treatment process and determine the optimum response in terms of water treatment and CO$_2$ capture efficiency. For the pure air system, the overall optimum conditions were found to be 12, 27.5 and 284 A/m^2 as pH, temperature and current density, respectively. The percent reduction efficiencies were 47.5, 47.8 and 71.4% for COD, TH and TDS, respectively. For the air-CO$_2$ system, the overall optimum conditions were 12, 35 and 213.5 A/m^2 for pH, temperature and current density, respectively; the reduction efficiencies were 42, 75 and 74% for COD, TH and TDS, respectively.

Keywords: Wastewater Treatment, Carbide Slurry, Chemical Oxygen Demand (COD), Response Surface Methodology (RSM), Electrocoagulation

Introduction

Many countries, especially in the Middle East are facing water scarcity issues due to the rapid growth of population as well as the significant industrial developments in recent years. Therefore, treatment of industrial wastewater is becoming a necessity that is dictated by the ever-growing need for potable water. In the UAE, acetylene is produced by Emirates Industrial Gases Co. (EIGCO) using the carbide process in their Acetylene Plant in Dubai.

The company produces an average of 2370 kg/d of acetylene, while utilizing about 5960 kg/d of calcium carbide in a specially designed reaction chamber, according to Equation 1:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \qquad (1)$$
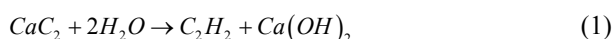
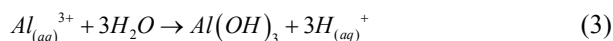As a result, the company generates 3500 to 4500 metric tons/yr of calcium hydroxide slurry (carbide slurry) as a by-product waste. Industrial wastewater permitted for discharge to the Dubai Municipality (DM) sewerage system should be within the DM effluent quality standards shown in Table 1.

Electrocoagulation (EC) refers to the destabilization of solids in an aqueous medium via applying an electric field to generate in-situ coagulants by electrolytic oxidation of sacrificial anode material. In EC, the coagulating ions are formed and it includes three phases: (1) Materialization of coagulants by the use of electrolytic oxidation of the 'sacrificial electrode', (2) deterioration of the pollutants and breaking of the mixtures and finally (3) combination of the destabilized phases to formulate flocs (Hasan *et al*., 2013; Kabdaþlý *et al*., 2012; Mollah *et al*., 2004). Therefore, the potential use of electrocoagulation (electrochemical) process for industrial wastewater treatment was worth investigating on the physical and chemical parameters such as Chemical Oxygen Demand (COD), Total Hardness (TH), Total Dissolved Solid (TDS) (Hasan *et al*., 2013).

Table 1. Maximum Allowable Limits for Discharge to DM System (GD, 2010)

Parameter	Max. Limit sewage	Max. limit harbor	Max. Limit Open Sea (Gulf)
Physico-chemical			
BOD, mg/L	1,000	30	30
COD, mg/L	3,000	100	100
pH	6-10	6-9	6-9
TDS, mg/L	3,000	1,500	1,500
Temperature, °C	45 or >5 of ambient	35	35

In electrocoagulation, cathodes and anodes are used to test the water. Applied current passes through the metal electrode and oxidizes the metal (M) to its cation (M^{n+}). Electro oxidation of the sacrificial metal anode generated in situ Al^{3+} metal ions, when a DC field was applied (Chen *et al*., 2000). Hydrogen (H^+) and oxygen are produced at the anode according to the oxidation of the water. Due to the water reduction, hydrogen and hydrogen oxide (OH^-) are generated at the cathode (Abuzaid *et al*., 1998). Cationic monomeric species (ex: Al^{3+} and $Al(OH)_3^+$) are created by the electro-oxidation of the aluminum anode. At exact pH values, they are changed to $Al(OH)_3$ at the beginning and then polymerized to $Al_n(OH)_3$ according to Equation 2 to 4 (El-Naas *et al*., 2009):

$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^-$$ (2)

$$Al_{(aq)}^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H_{(aq)}^+$$ (3)

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n}$$ (4)

The electrochemical reactions with a metal (M) as sacrificial electrode could be demonstrated as presented in Equation 5 and 6 (Feng *et al*., 2007; Yýldýz *et al*., 2008):

$$Anode: M \rightarrow M^{n+} + ne-$$ (5)

$$Cathode: 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$ (6)
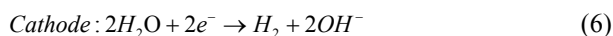
Materials and Methods

Wastewater Samples

Raw wastewater samples were brought from the Emirates Industrial Gases Co. (EIGCO), Dubai-UAE. In this case, the generated slurry (wastewater) is drained from the reaction chamber and pumped into a holding pond, where the calcium hydroxide settles out. The carbide lime is then removed from the pond and allowed to dry to a moisture content of about 25%, before it is sent for disposal. The generation of large amounts of carbide slurry represents a major environmental and economic challenge to the acetylene industry. The physical-chemical characterizations of the raw industrial wastewater are presented in Table 2.

For COD and TH analysis, wastewater samples were collected from the EC reactor using a pipette every 60 min and filtered using Schleicher and Schuell-MicroScience filter paper circles No.595 (185 mm). The samples were analyzed using HACH vials/HACH DR-3000 spectrophotometer to measure COD and solution titration using ammonium hydroxide and silver chloride to measure TH.

Experimental Apparatus

Preliminary experiments were conducted to screen out the operating conditions such as pH, temperature and current density varied in the range of (7-12), (20-35°C) and (143-284 A/m^2), respectively. The electrocoagulation experiments were conducted in 2 L cylindrical reactor made of Plexiglas having an effective volume of 1 L and an internal diameter of 14.5 cm. Two aluminum electrodes with dimensions of 6×5×3 mm that are spaced apart by 5.5 cm were immersed in the reactor and connected to a DC power supply. A magnetic stirrer was located at the bottom of the reactor to ensure good mixing while adjusting the mixing speed so as not to break the flocs. 100% Air and 10% CO_2 in air were injected from the top and the bottom of the reactor.

Response Surface Methodology

RSM was used to characterize and study the relationship between responses and quantitative factors. This is accomplished by building the model that describes the response over the applicable ranges of the factors. By definition, RSM is a graphical statistical approach to classify the setting of the factors that yield the best response and satisfy the process specifications.

Box-Behnken Design (BBD), which is a lesson of a second-order design based on three-level factorial design, was used to design the model (Ferreira *et al*., 2007; Tir and Moulai, 2008). The three most significant operating factors (initial wastewater pH (x1), temperature (x2) and current density (x3)) were optimized for the treatment of the wastewater. The range of pH, temperature and current density variations were between 7 to 12, 20 to 35°C and 143 to 284 A/m^2, respectively as shown in Table 3 (Ferreira *et al*., 2007; Tir and Moulai, 2008).
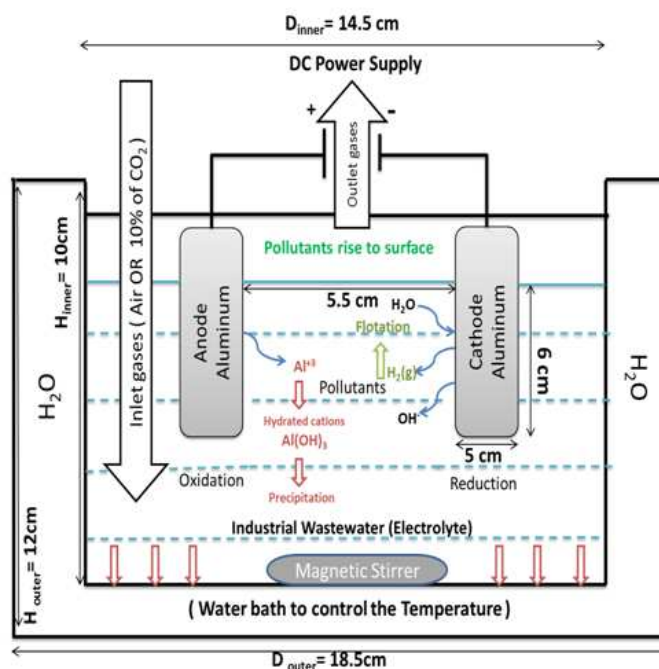
Fig. 1. A schematic representation of the Electrocoagulation process

Table 2. Characteristics of wastewater collected from EIGCO

pH	COD (mg/l)	EC (ms/cm)	TDS (g/l)	TH (mg/l as $CaCO_3$)	Salinity (%)	TSS (g/l)
12-12.2	300-350	5-6	2.5-3.5	1000-1200	3-3.5	1-2

Table 3. Range and level of independent variables

		Level		
Independent variable	Symbol	-1	0	+1
pH	X1	7	9.5	12
Temperature, °C	X2	20	27.5	35
CD (A/m^2)	X3	143	213	284

After running the BBD experiments, a second-degree quadratic polynomial is set to represent the function in range of interest as shown in Equation 7:

$$Y = \beta_o + \sum_{i=1} \beta_i X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j \qquad (7)$$

Where:

Y = The predicted response, β_0 the offset term, β_i the coefficient of the linear effect, β_{ii} the coefficient of squared effect

X_i = The coded value of variable i

X_j = The coded value of variable j and β_{ij} the coefficient of interaction effect.

Results and Discussion

COD and TH Reduction

The optimum conditions for the best performance efficiency in terms of COD reduction in CA and EA systems were obtained under the same conditions of pH, temperature and current density: 12, 27.5°C and 143 A/m^2. However, for TH reduction in CA and EA systems, the values of pH, temperature, current density were 12, 27.5°C and 284 A/m^2 and 12, 35°C and 213.5 A/m^2 respectively.

The model adequacy was established by plotting the normal probability and residual plots for the responses. The residuals analysis showed that there was no evidence of outliers as all the residuals fell within the range of (-2 to +2) and (-3 to +3) for COD and TH % reduction, respectively. They were randomly distributed around zero, which shows a high degree of correlation between the observed and predicted values in CA and EA systems for COD and TH % reduction, respectively, as depicted in Fig. 2 and 3.

In addition, the p-values of lack-of-fit at the 95% confidence level were 0.147, 0.096 and greater than 0.05 in EA and CA systems, respectively indicating that the lack of fit is not significant and the model fits the data well.
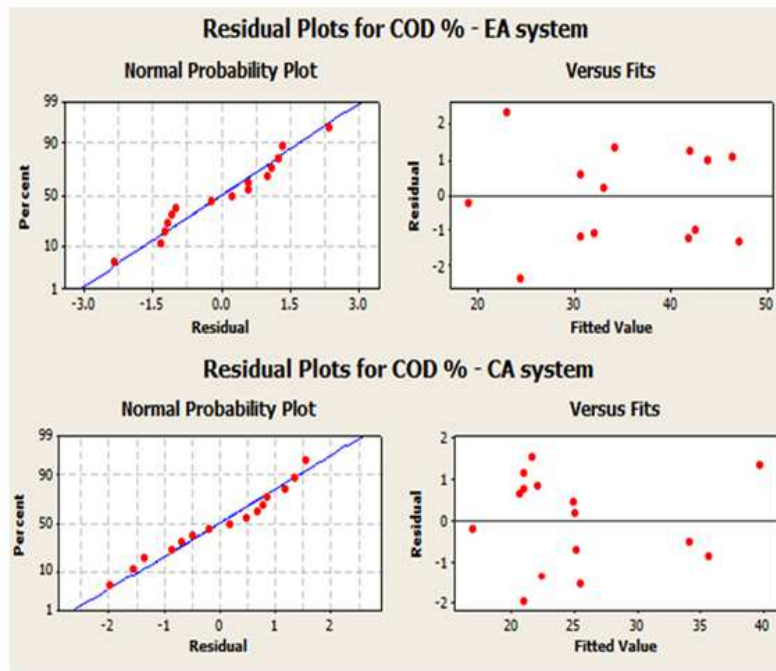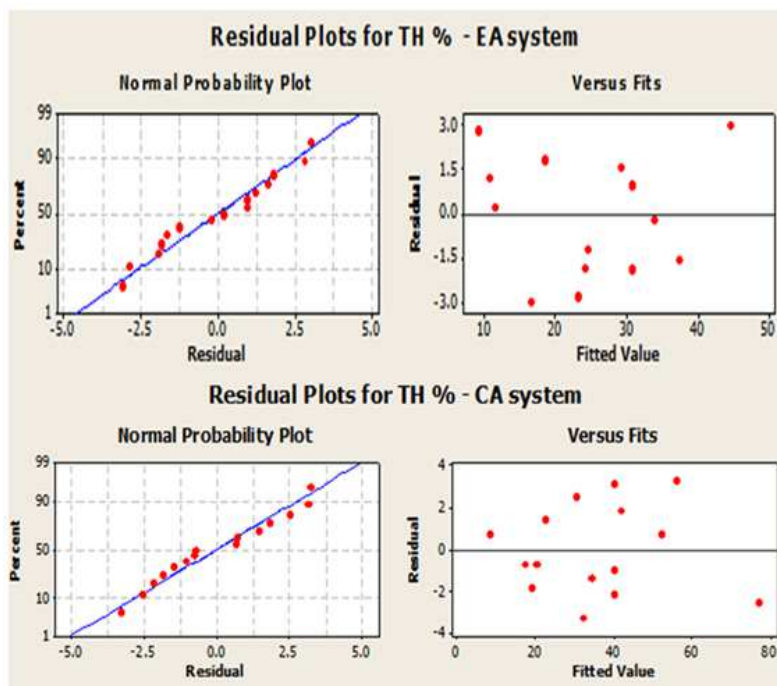
Fig. 2. Residual Plots for COD% reduction-EA and CA system

Fig. 3. Residual plots for TH% reduction - EA and CA systems

COD and TH Prediction

Minitab and RSM were used to create the model and calculate the predicted vales of the COD and TH % reduction in EA and CA systems by estimation of the regression coefficients. Figure 4 and 5 show the scattered plots for the experimental and the predicted values with R^2 of were 94, 98 and 98, 98, in EA and CA systems for COD and TH % reduction, respectively; it is worth noting that these values are very close to each other.
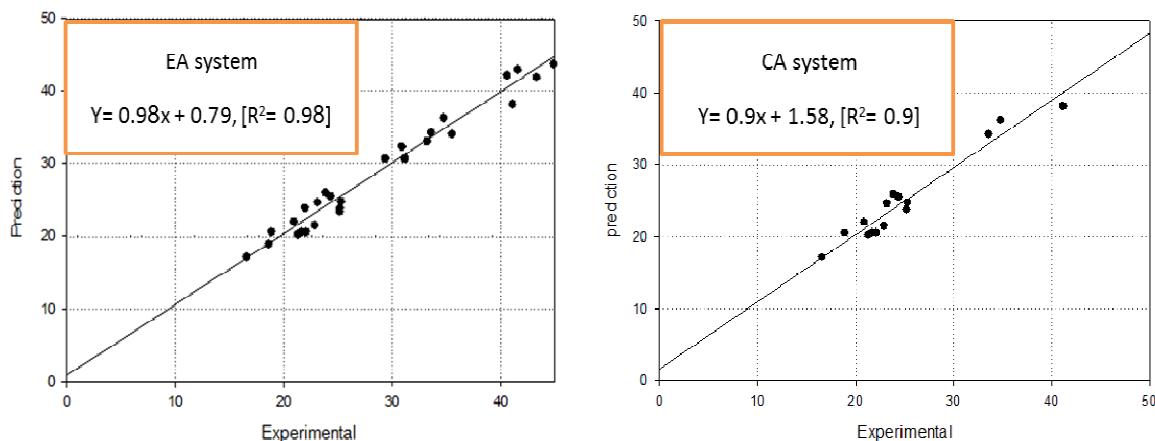
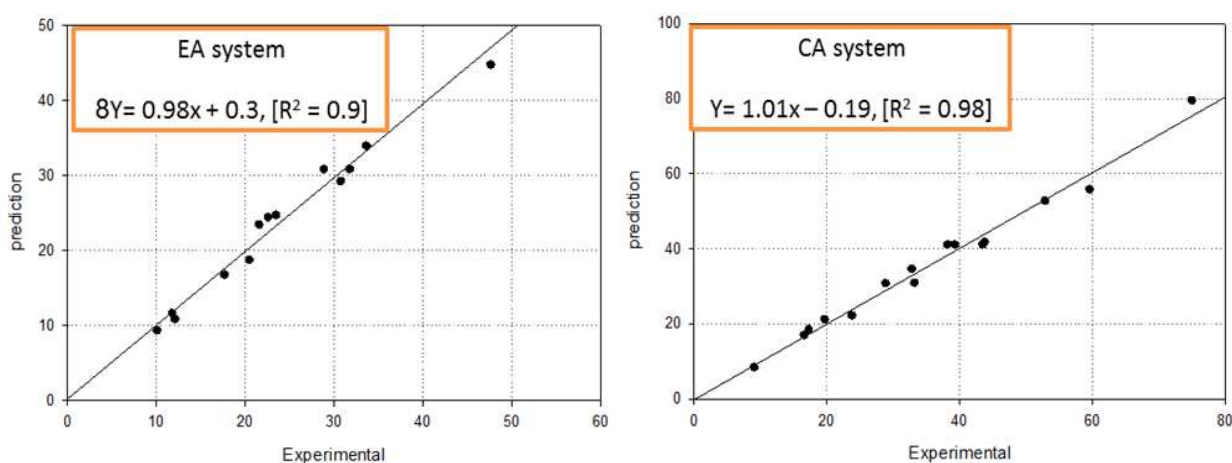Fig. 4. COD % reduction - Exp. Vs Prediction-EA and CA systems

Fig. 5. TH % reduction - Exp. Vs Prediction - EA and CA systems

Comparison between EA and CA Systems

According to the RSM, pH, temperature and current density were significant parameters for the COD reduction in the EA system with p-values less than 0.05. For TH reduction, pH and temperature were significant parameters with p-values less than 0.05 and current density had no significant with p-value greater than 0.05.

On the other hand, in CA system, pH, temperature and current density had no significant impact on the COD reduction as p-values greater than 0.05 that were obtained under full quadratic linear fit. It is worth to mention that pH is the only parameter had a significant impact on TH reduction with p-value less than 0.05. In addition, there is no interaction correlation between pH and temperature, pH and current density and temperature and current density in CA and EA systems.

The regression equation was graphically represented by 3D response surface roughness. Figure 6 displays the interaction between temperature and pH on the COD reduction (%) for EA and CA systems. In EA system, by increasing the temperature from 20 to 28°C, the COD reduction increased with high value of pH. In addition, the maximum COD reduction have achieved at pH level between (9-10) and a temperature range between (26-30). While with increase of the temperature over 30°C there was decline in the response and it means that there is no obvious effect on the COD reduction. Moreover, the negative effect of low temperature on COD reduction can be reverse by increasing the pH. On the other hand, in CA system, this interactive effect for temperature and pH on COD reduction was not very significant as p values are >0.05.

Carbon Dioxide Capture

Experiments were carried out to determine the CO_2 capture efficiency and the results are shown in Table 4 for each experiment. The CO_2 capture has correlation with pH and CD with p values less than 0.05. Figure 7 shows that the optimum conditions for carbon dioxide capture were 9.5, 35 and 284 A/m^2 for pH, temperature and current density, respectively; the highest CO_2 capture efficiency was 84%.
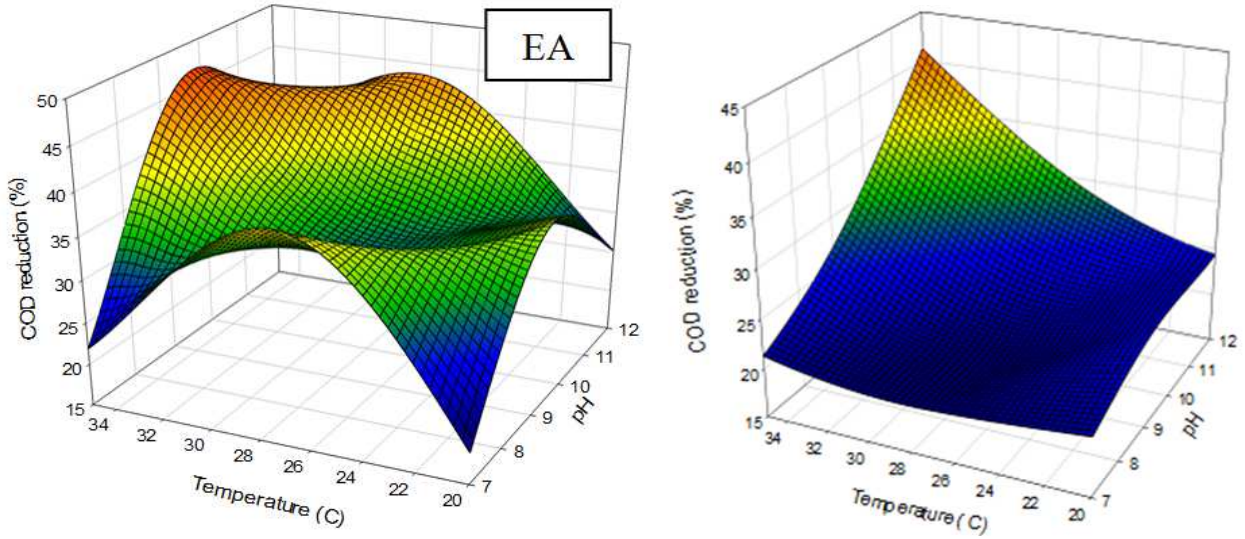
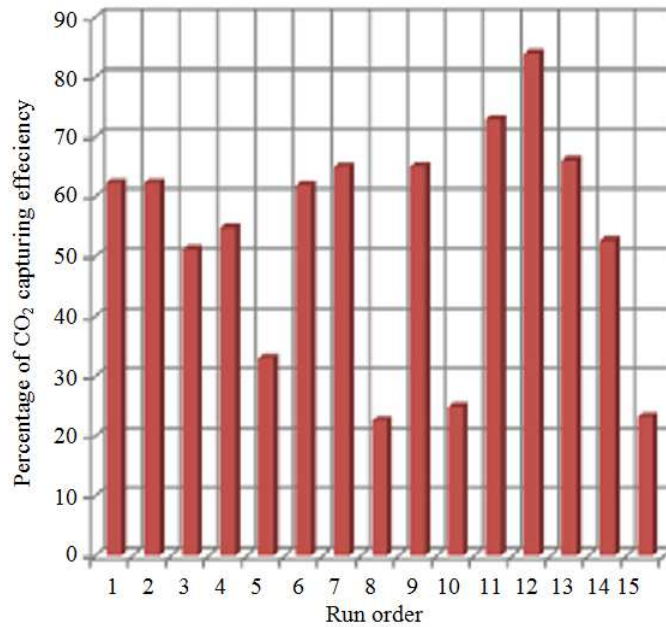Fig. 6. 3D plot relating pH, temperature and COD% reduction in EA and CA systems

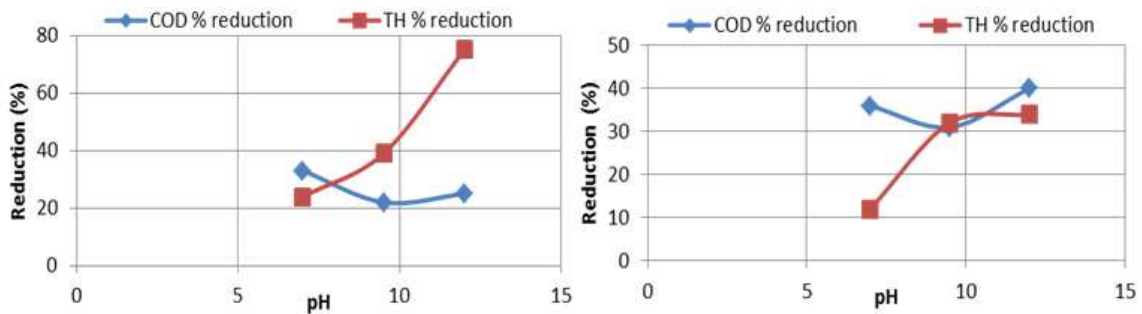Fig. 7. CO_2 capturing effeciency (%) Vs. Run order

Fig. 8. Impact of initial pH for COD and TH % reduction - CA and EA systems

Table 4. CO_2 capturing efficiency (%)

RO	Area	Total CO_2 in (mole)	CO_2 Captured (mole)	CO_2 Capturing efficiency (%)
1	11227.00	10.45	6.52	62.37
2	11227.00	10.45	6.52	62.37
3	9212.50	10.45	5.35	51.18
4	9864.50	10.45	5.72	54.80
5	5945.40	10.45	3.45	33.03
6	11142.50	10.45	6.47	61.90
7	11698.00	10.45	6.79	64.99
8	4063.50	10.45	2.36	22.58
9	11700.50	10.45	6.79	65.00
10	4476.00	10.45	2.59	24.87
11	13129.00	10.45	7.62	72.94
12	15111.00	10.45	8.76	83.95
13	11900.50	10.45	6.91	66.11
14	9474.25	10.45	5.49	52.63
15	4184.25	10.45	2.43	23.25

Impact of Initial pH

The initial pH of the solution is an essential parameter in determining the performance of the electrocoagulation process, (Do and Chen, 1994). It has been reported by several researchers (Yýldýz *et al*., 2008; Daneshvar *et al*., 2006) that the pH of the varied vary in the electrocoagulation process in order to affect the overall treatment performance in the effluent. Once the initial pH value is less than 4 (acidic), the effluent pH increases, while it tends to decrease when the initial pH value is more than 8 (basic); the pH of the effluent changes only slightly when the initial pH value is in the neutral range (around 6-8) (Kabdaþlý *et al*., 2012).

In addition, the chemical dissolution of aluminum gives rise to the pH increase which could be clarified by the excess of hydroxyl ions formed at the cathode and by the release of OH- due to the occurrence of a partial exchange of Cl⁻ with OH⁻ in Al (OH)₃ (Feng *et al*., 2007; Vik *et al*., 1984; Chen *et al*., 2000). Figure 8 shows that the effect of pH on COD and TH reduction efficiencies in CA and EA systems. The initial pH seems to have limited effect on COD but a more significant effect on the TH, especially for the CA system. The higher the pH the higher is the reduction in TH.

Impact of Current Density

The impact of current density on COD and Total Hardness reduction percentages for CA and EA systems is illustrated in Fig. 9. With the increase of current density from 143 to 284 A/m^2, the TH reduction efficiency also increases from 35 to 75% and from 22 to 33%, respectively in CA and EA systems. Conversely, the COD reduction percentage is not so significant within the same range of current density. Furthermore, increasing the electrical power reduces the lifetime of the electrodes; it means that the current is directly proportional to the voltage response. Hence, the optimum current densities for optimum COD and TH reduction are: 213.5 and 143 A/m^2 for the CA system and "284 and 213 A/m^2 for the EA system. Consequently, to achieve optimum performance in terms of COD and TH reduction, it is essential to ensure the attainment of the optimum current density in the electrocoagulation process.
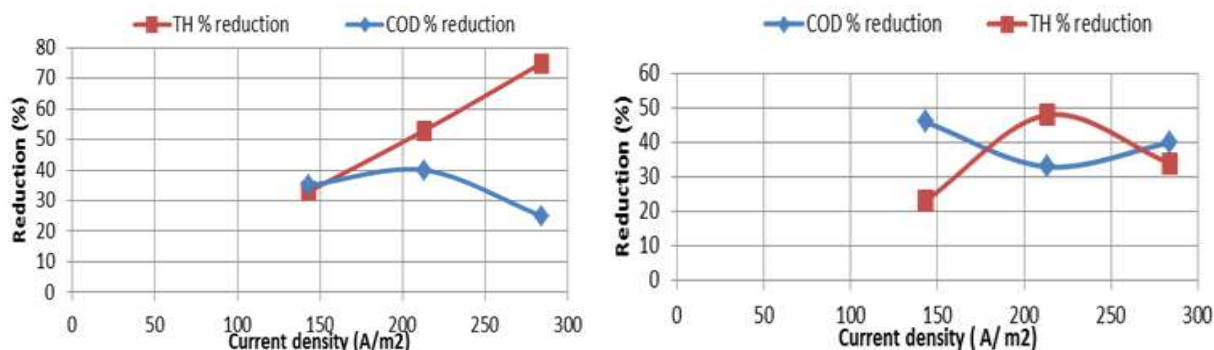

Fig. 9. Impact of current density for COD and TH % reduction - CA and EA system
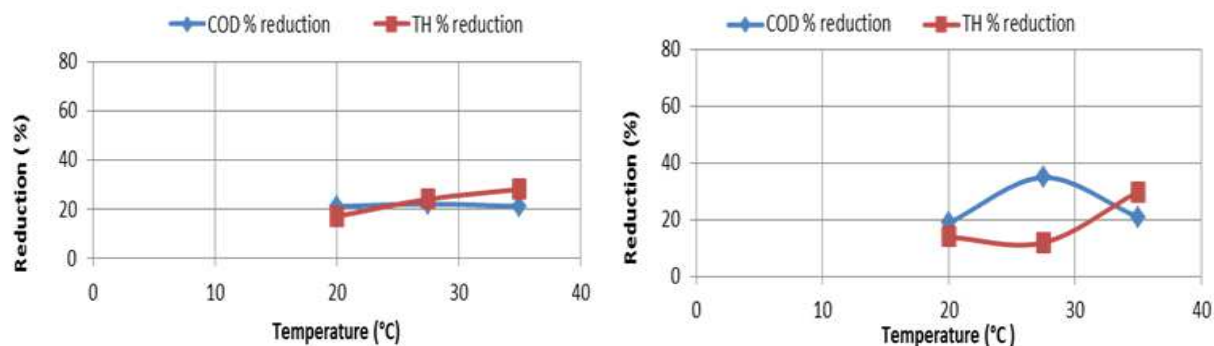
Fig. 10. Impact of temperature for COD and TH % reduction - CA and EA systems

Impact of Temperature

Solution temperature is one of the factors that were evaluated in the study. According to this study, there was no effective relation or certain trend between the COD reduction and the solution temperatures in both CA and EA systems. However, reduction in TH for EA system seemed to improve with increasing the solution temperature within the predetermined range between 20 to 35°C as shown in Fig. 10. Therefore, it is safe to say that the impact of temperature on reduction efficiency seemed to be negligible for both systems and depends on the reduction mechanism of the contaminants.

Conclusion

Wastewater treatment by electrocoagulation is an environmentally friendly process that requires no addition of chemicals, yields high quality effluent and requires short treatment times and simple operation. The highest reduction percentages achieved by the EA and CA systems were: 48%, 75% for TH; 47%, 41% for COD; 71%, 74% for TDS, respectively.

The overall optimum conditions in the EA system were 12, 27.5 and 284 A/m^2 for pH, temperature and current density, respectively. In contrary, the highest % reduction in CA system was at 12, 35 and 213.5 A/m^2 as pH, temperature and current density, respectively.

Statistical analysis showed that COD, TH and TDS reductions were significantly affected by pH and CD. However, temperature seemed to only have a minor effect on the reduction of TH in the EA system and no effect on the CA system.

Acknowledgment

Author's Contributions

Shereen Hasan: She made considerable contributions to carrying out the experimental work, analyzing and modeling the experimental data. She also prepared the initial draft of the manuscript.

Muftah El-Naas: He made considerable contributions to designing the research plan and experimental procedure. In addition, he supervised the experimental work and revised the draft of the manuscript.

Ethics

This paper is original and includes unpublished materials. The corresponding author confirms that all other authors have read and approved the manuscript.

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Symbols

CA	10% Carbon Dioxide system
CCD	Central Composite Design
CI	Confidence Interval
COD	Chemical Oxygen Demand
EA	100% Pure Air System
EC	Electrocoagulation
Exp.	Experimental result value
R^2	Determination coefficient
RSM	Response Surface Methodology
TH	Total Hardness