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Electrochemical oxidation of *amoxicillin, ciprofloxacin and erythromycin* in water: Effect of experimental factors on COD removal

Irum Firdaus[1], Asim Yaqub[1], Huma Ajab[2], Imran Khan[3],
Bilal Ahmed Zafar Amin[4], Ayesha Baig[5] and Mohamed Hasnain Isa[6]
[1]Department of Environmental Sciences, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, Pakistan
[2]Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad, Pakistan
[3]Department of Management Sciences, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, Pakistan
[4]Energy Research Centre, COMSATS University Islamabad, Lahore Campus, Lahore, Pakistan
[5]Department of Biotechnology, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, Pakistan
[6]Faculty of Engineering, Universiti Teknologi Brunei, Brunei Darussalam

Abstracts: An alternative method of electrochemical oxidation was employed to degrade persistent compounds in the form of antibiotics using strong oxidizing agents such as hydroxyl ions. A 2^4 factorial design was employed to check the effect of four factors namely pH, current density, electrolysis time and electrolyte concentration set at their high (+) and low (-) levels on the antibiotics (*amoxicillin, ciprofloxacin and erythromycin)* degradation in water. The response was obtained in the form of COD (chemical oxygen demand) removal. A prediction model was developed to predict the values of COD removal. Later the main effect, contribution and interactions were studied with Design Expert Software 7.0. About 89.5% COD removal was obtained when pH and time were set at their high level and the other two factors at their low level. It was determined that the pH when set at high level (pH 9) had the most effect (24.68) and contribution (43.6) in the degradation process and hence the removal of COD. This technology of electrochemical oxidation can be employed in industries to efficiently remove pharmaceuticals, paints, dyes and other organic compounds.

Keywords: Electrochemical, wastewater, antibiotics, factorial design.

INTRODUCTION

Synthetic organic compounds are considered as the most prominent surface and ground water contamination causing agents in the present century and are of great threat to the society who is dependent on these sources of water. Pharmaceutical compounds are considered as one of the very prominent class of synthetic organic compounds among dyes, plastic material and personal care products (Coledam *et al*., 2017). The pharmaceuticals have drawn the attention of the scientists regarding its presence in the environment due to its potential biologically active chemical nature (Sires and Brillas, 2012; Zezulka *et al*., 2019). Every year on a worldwide scale almost thousand tons of such chemical compounds are manufactured and sold to be used as medicine for the treatment of human and animal illnesses and as supplement in agricultural and consumer products. After its large scaled manufactures these pharmaceuticals are then largely consumed all over the world and the faction that remains unused coming from the sources like (household, industries, aquaculture, livestock, hospitals and services, and pets) eventually end up being thrown into the environment. Even though some of these drugs are exposed to incineration, but a substantial part of it be it an original drug or its metabolites has its fate at waste disposal sites or down the drain through a toilet into a wastewater (Esplugas *et al*., 2007; Khan *et al*., 2018). Once these pharmaceutical residues make it to the aquatic environment they are mostly detected in trace concentrations i-e in the ng/L or µg/L range. It is considered that probably the whole of or most of the urban wastewater is riddled with pharmaceutical/ medicinal compounds (Jones *et al*., 2005; Ahmadzadeh *et al*., 2017). Even at such low concentrations these pharmaceuticals are prone to affect the quality of the water and pollute the supplies of drinking water posing a serious long term threat to ecosystems, human and animal health (Ashfaq *et al*., 2016; Ashfaq *et al*., 2017).

Among the various classes the pharmaceuticals can be split into, antibiotics are receiving a lot of scrutiny throughout the world. In many countries antibiotics pollution in water becomes a serious problem and taken as an important environmental issue (Kümmerer, 2009; Sajid *et al*., 2016; Hua *et al*., 2019). Like other pharmaceuticals antibiotics are also poorly removed when subjected to wastewater treatment plants owing to its recalcitrant nature towards the physical methods of removal (Stackelberg *et al*., 2004; Homem and Santos, 2011). A couple of techniques under the umbrella of Electrochemical advanced oxidation processes have emerged as one of the efficient ways of removing and degrading *amoxicillin, ciprofloxacin and erythromycin* that are biologically toxic or non-degradable, recalcitrant in nature (Ahmadzadeh *et al*., 2017; da Silva *et al*., 2018; Shen *et al.,* 2018). These techniques work by producing strong oxidizing agent, the hydroxyl radical with the

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Corresponding author: e-mail: irum_firdaus@hotmail.com

provision of electricity which has the capability to non-selectively degrade organic compounds of the nature such as the antibiotics (Zhao *et al*., 2014).

Electrochemical oxidation also known as anodic oxidation and has versatility, energy efficiency, environmental compatibility, cost effectiveness and amenable to automation, as its promising features and is now frequently employed for removing persistent organic pollutants (Martinez and Brillas, 2009; Cui *et al*., 2014).

Electrochemical oxidation can work by employing two mechanisms or processes: *(i)* By transferring an electron directly to the anode as electricity is provided and *(ii)* By aiding the production of heterogeneous ROS by splitting water into respective ions using electricity which results in physic-sorbed $^{\cdot}OH$ or chemisorbed active oxygen at the anode. This process is also known as indirect oxidation or mediated oxidation.

Once these species are formed in the electrolytic cell two phenomena can occur (Marselli *et al*., 2003; Panizza and Carisola, 2009): The complex, recalcitrant organics are converted into carboxylic acid which is very degradable in nature, by the action of chemisorbed active oxygen. This process is known as the electrochemical conversion. Electrochemical combustion can occur which is simply the mineralization of the organic compounds by the physicsorbed $^{\cdot}OH$ as shown by the reaction 1 below

$M+H_2O \rightarrow M(^{\cdot}OH)+H^{+}+e^{-}$ (1)

The objective of this study was to employ a factorial experimental design in order to determine the impact of pH, current density, and electrolysis time and electrolyte concentration on the electrochemical oxidation of the selected antibiotics *(Amoxicillin, Ciprofloxacin and Erythromycin)* in synthetic wastewater solution. And to develop a multiple linear regression model to predict the response in the form of COD removal and finally to check the main and interactive effects among the factors used.

MATERIALS AND METHODS

Materials

Commercially available capsules of 500 mg of *Amoxicillin Tri-hydrate, Ciprofloxacin and Erythromycin* were obtained from a local pharmaceutical store. From each of the three antibiotics 50 mg were dissolved in ultra pure water under constant magnetic stirring of five hours to obtain a stock solution of 150ppm. Sodium sulphate was employed as an electrolyte and was supplied by Sigma-Aldrich. Initial pH adjustments to make the solutions acidic or basic, were made using sulphuric acid and sodium hydroxide respectively.

Experiments for electrochemical oxidation

The electrochemical oxidation process was carried out in a batch system. The experiments for determining the degradation activity were performed in an acrylic cell closed from all four sides with dimensions of 5 × 8 × 8 cm and a capacity to with-hold 200 ml of sample and four electrodes shown in fig. 1.

The electrodes employed were two anodes and two cathodes. The electrodes were used in couples with one couple having Dimensionally Stable Anodes DSA (Ti/SnO_2-Sb_2O_5) and the other (Ti/RuO_2). The cathodes in the couples were made of Titanium. Each of the four electrodes had dimensions 8 × 1 cm. In the electrolytic cell the electrodes were arranged in a manner that an anode and a cathode were placed adjacent to one another with the same type of electrodes not being opposite to each other. Distance between the electrodes was maintained at 2 cm.

STATISTICAL ANALYSIS

A three-level factorial design was established with the help of the *Design-Expert version 6* software. Four factor 2^4 factorial design was used to determine the main effects of independent variables.

Experimental design and analysis

To check the electrochemical oxidation of the selected antibiotics four different independent parameters/ variables pH, current density (*milli Ampere per square centimetre*: mA/cm^2), time (*minute*: min) and electrolyte concentration (*milligram per litre*: mg/L) were selected and symbol as X_1, X_2, X_3 and X_4 respectively. In order to determine what sort of impact these variables have on the electrochemical oxidation of the antibiotics a factorial design was implemented. Factorial Design utilizes mathematical and statistical methods to design experiments, to evaluate any influence the variables might have and formulating models for the prediction of target responses. The four factors were set up at two levels, a high level (+) and low level (-) shown in table 1. The 2^4 factorial experimental design matrix shown in table 2.

COD was employed as the response variable of the factorial design and so COD of the sample at the completion of every experiment for determining the effect of electrochemical process on organic compound removal was done. COD was measured by the dichromate method. The experimental data was then fitted to a regression model with the following multiple linear regression equation (1)

$$Y= b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4\ b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{234}X_2X_3X_4 + b_{1234}X_1X_2X_3X_4 \quad (1)$$

Where b_0 represent the average value of the responses of the 16 assays; X_i is the coded variable (-1 and +1) and Y is the response which was in the form of COD (Karama *et al*., 2017).

RESULTS

Factorial design response and prediction

The results obtained as response variable (COD removal) by applying factorial design matrix composed of 16 experiments with different combinations of independent variables is shown in table 3. From the table it can be observed that the highest COD removal percentage was obtained when pH was set at 9 and electrolysis time was set at 240 min, current density and an electrolyte concentration being set at 17 mA/cm^2 and 1.5 mg/L, respectively. It is also evident that when variables were kept at their highest level did not show the desired removal. To predict the values of the response, a quadratic model was used which is given as in eq. (2). table 4 shows ANOVA for the multiple regression model.

$$Y = 52.01 + 12.35\, X_1 - 3.10\, X_2 + 4.52\, X_3 + 1.48\, X_4 + 0.76\, X_1X_2 - 2.45\, X_1X_3 - 4.70\, X_1X_4 - 1.13\, X_2X_3 + 4.97\, X_2X_4 + 2.67\, X_3X_4 - 2.72\, X_1X_2X_3 - 0.59\, X_1X_2X_4 - 4.37\, X_1X_3X_4 + 8.58X_2X_3X_4 - 0.97X_1X_2X_3X_4 \qquad (2)$$

The coefficients of the model were calculated using Design Expert Software 7.0. The results of the response obtained (actual value) and the predicted values are summarized in table 3.

The F_{obs} was calculated by employing the following equation (3):

$$F_{obs} = \frac{Regression\ Mean\ Square}{Residual\ Mean\ Square} \qquad (3)$$

Moreover the correlation coefficient R^2 and $R_{adj}{}^2$ of the regression model was calculated to be 0.99 and 0.98 respectively with the following equations (4) and (5).

$$R^2 = 1 - \frac{Residual\ SS}{Total\ SS} \qquad (4)$$

$$R_{adj}{}^2 = 1 - \left(1 - R^2\right)\frac{n-1}{n-(k+1)} \qquad (5)$$

Where *n* is number of observation and k is number of independent variables.

Residual Plot

A residual plot was also plotted to determine the significance of the model by employing the residues obtained as the difference between actual value and predicted values. The plot shown in fig. 2 depicts random distribution along with the absence of outliers which indicates that the simple linear regression model is appropriate for the data.

Main effect of independent variables

Table 5 shows the main effects of each independent variable and their interactions on the removal of COD or it can be said that the degradation of the antibiotics from the sample. Factor X_1 (i-e. pH) has shown the highest effect with a value of 24.69**.** The positive value here indicates that the initial pH set at the higher level showed the maximum effect i-e the removal of COD was highest when initial pH was 9. As evident from the table 5, no other individual variable could greatly affect the removal of COD as much as initial pH. While electrolysis time (X_3) also contributing well after initial pH with value of 9.04. As far as the interactions are concerned, the three-factor interaction between $X_2X_3X_4$ showed some significant effect with value of 17.16. Contribution of interactions X_2X_4 and X_3X_4 in COD removal were valued up to 9.93 and 3.33, respectively. These interactions also show that current density and time enhance the effect of electrolyte. Results from table 5 shows that no other interacting factors could yield enough COD removal. The negative values in the table 5 does not show that the factors have rendered a negative impact rather it indicate effect caused when factor was set at lower level.

Contribution of factors

Fig. 3 also throws light on the fact that current density and electrolyte concentration effect was very insignificant as compared to pH. Also the time has shown very little contribution in comparison with pH but has little more significant contribution as compared to current density and electrolyte concentration. A graph representing contribution of independent variables (pH, Current Density, Time and Electrolyte Concentration) in removing COD was plotted. This not only shows which variable(s) had the most contribution but also confirms the values of the effect. It is actually pH that has given maximum contribution in reduction of COD.

Interaction graphs

While the important effects and the contributing factors have been mentioned and it has been shown how individual factors have contributed in degradation process it is vital to mention what sort of interaction exists among the various factors. Following graphs highlights some of the interactions.

The fig. 4 (a) shows parallel lines of low and high current densities attributing no interaction between pH and current density fig. 4 (b) shows two parallel lines obtained between pH and time. fig. 4 (c) shows interaction between pH and electrolyte concentration. fig. 4 (d) depicts two parallel lines presenting negative trend towards COD reduction. Two intersecting lines were obtained in the graph showing interaction between current density and electrolyte concentration in fig. 4 (e). The interaction between time (min) and electrolyte concentration (g/L) in fig. 4 (f) has two lines of electrolyte concentration intersecting with each other.

Normality probability plot

In fig. 5 the pH of the sample (X_1) had the most notable effect on the degradation of antibiotics and thus played a vital role in removal of COD. All the other factors fall near the line which indicates very little contribution in causing effect on the degradation process. This normal probability plot offers another source of proof of pH being the noteworthy factor in degrading organics from the wastewater. Even though it may seem that the three factor interaction $X_2X_3X_4$ has a role in the removal of COD but when compared to the 44% contribution of pH, the contribution by test factors $X_2X_3X_4$ which is only 24% holds not much significant but is the only interacting test factor that has contributed up to some extent, which is not there in other interacting test factors.

DISCUSSION

According to literature there is apparently no effect on the mineralization or COD removal when the pH is adjusted between 2.0-6.0 or 4.0-10.0 (El-Ghenymy *et al*., 2013; El-Ghenymy *et al*., 2014). While according to (Wu *et al*., 2012; Garcia *et al*., 2015; Yaqub *et al* 2017a; Ajab *et al.,* 2020) the process shows its effect when the pH of the sample was kept at 3. In many studies, type of electrolyte veils the effects of pH e.g. NaCl which contributing in indirect oxidation by Cl^- and OCl^- oxidants (Yaqub *et al* 2017b; Yaqub *et al* 2017c). In this study, Na_2SO_4 released weak oxidants like $S_2O_8^{-2}$ ions.

What has caused this contradiction to occur can be explained in terms of the medium used to adjust the pH. To adjust the initial pH to 3, H_2SO_4 was employed. Once in water H_2SO_4 breaks down into H^+ ions and SO_4^- with the following reaction (2)

$$H_2SO_4 \rightarrow 2H^+ + SO_4^- \qquad (2)$$

While these ions may aid in the flow of electricity along with the added electrolyte, they may or may not contribute in the oxidation of the antibiotics. This can be explained by the phenomenon which occurs once sulphate ions from the electrolyte or pH adjusting H_2SO_4 gets into their ionic form. Once in the ionic form these sulphate ions being negatively charged migrate towards the anode where they get oxidized to produce per-sulphates which are oxidizing agents by reaction (3)

$$2SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^- \qquad (3)$$

Hence these sulphate ions are involved in the indirect oxidation of the organic compounds. But these same sulphate compounds can manifest its negative impact if they exceed a certain concentration. In such cases the increased sulphate ions causes increased production of per-sulphate ions which in turn causes an increase in the production of H_2O_2 instead of hydroxyl radicals and hence reduce the efficiency of the overall oxidation process. So even though electrolyte is added to assist in the flow of current, its effect may be supressed by these extra sulphate ions (Yang *et al*., 2016).

Similarly to adjust the pH to 9 NaOH was put into use. Once in the water it undergoes break-down as shown in reaction (4).

$$NaOH \rightarrow Na^+ + OH^- \qquad (4)$$

The OH^- then become physisorbed on the surface of the anode material as $^{\cdot}OH$ and is then involved in the indirect oxidation of the organic compounds. Hydroxyl radical are strong oxidizing agents with the standard reduction potential as (E^0= 2.80 V/SHE). Hence when NaOH is used as a medium to adjust the pH the number of hydroxyl radicals increase (hydroxyl radicals are also released by the break-down of water molecules by electricity) which then increases the oxidation of the organic compounds which are present in the form of antibiotics.

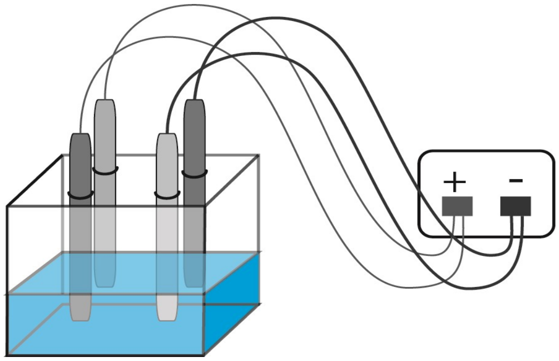

Fig. 1: Diagrammatic Representation of Electrolytic Cell Employed for Electrochemical Oxidation (the dark grey colour shows the anodes whereas the light grey electrodes signify cathodes)

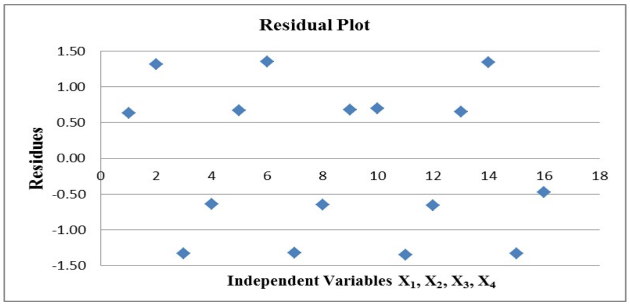

Fig. 2: Comparison of Actual and Predicted values

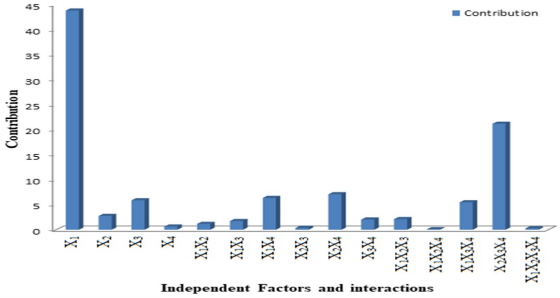

Fig. 3: Contribution of Experimental Factors in COD Removal

Two other factors, current density and supporting electrolyte play a vital role in electrochemical degradation process.

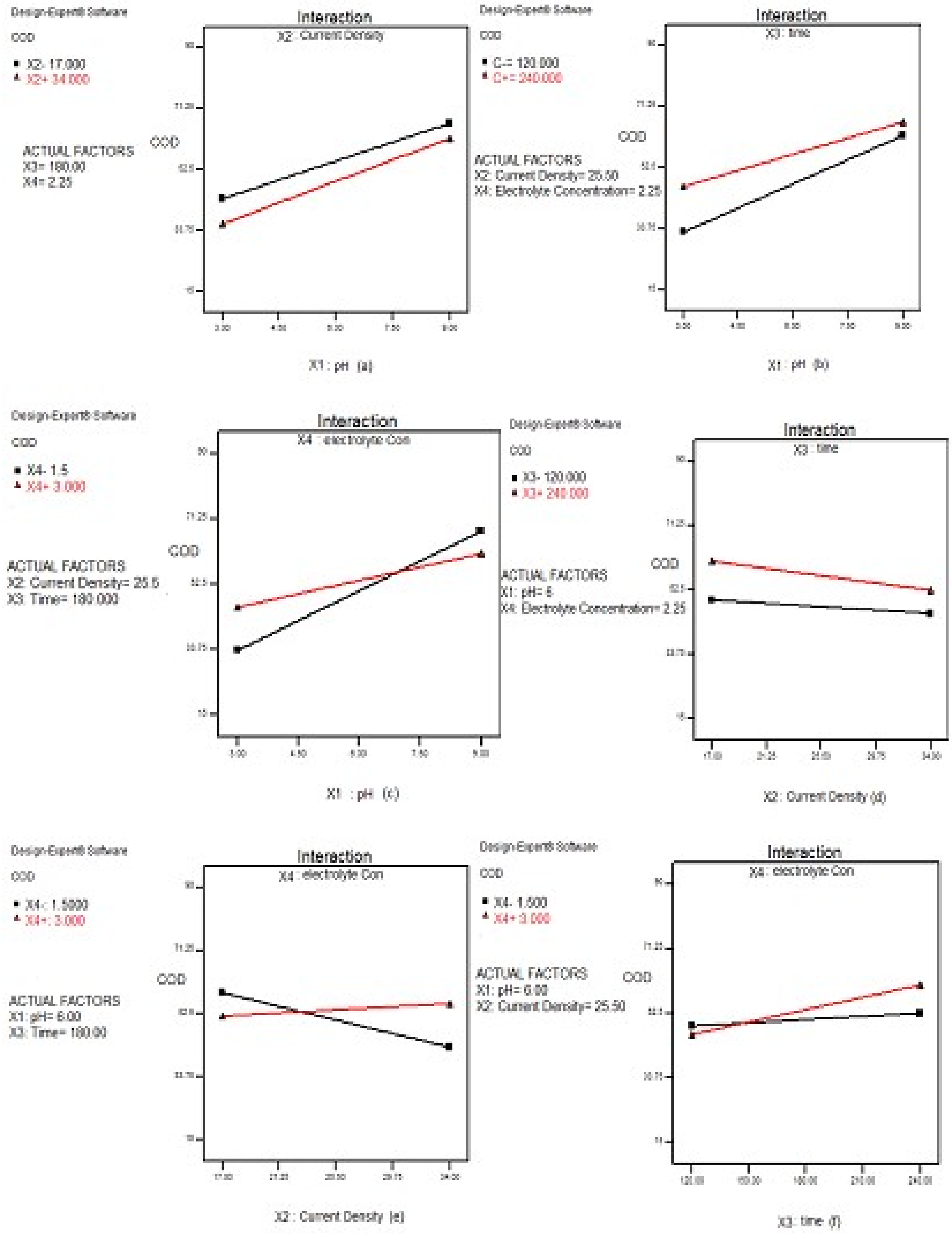

Fig. 4: Two Factor Interaction Between pH, Current Density, Time and Electrolyte Concentration.

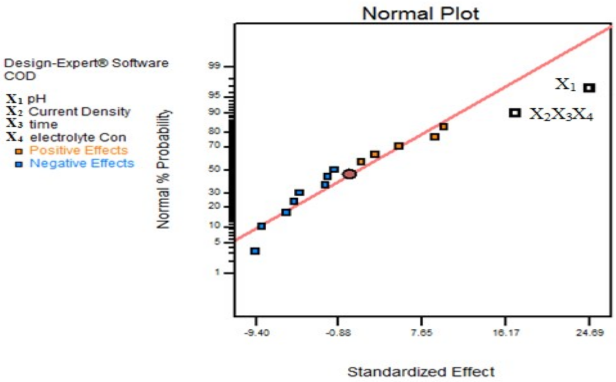

Fig. 5: Normal Probability Plot

Pertinent to important researches done, the electrolysis or the degradation efficiency of the process should increase by increasing the current density (to a certain limit) as it contributes towards producing more oxidants and the concentration of the electrolyte which aids the electrolysis process by providing ions which greatly enhances the flow of current (Orescanin *et al*., 2013; Fernandes *et al*., 2012). But contrary to it, the results show that the current density and electrolyte concentration has a small effect on COD removal as compared to the effect of pH. Also the time has shown very little contribution in comparison with pH but has little more significant contribution as compared to current density and electrolyte concentration.

While the contribution of the pH can be attributed to the medium used for adjusting the pH, the lesser contribution by current density and electrolyte concentration can be explained by the nature of the electrolyte and by the increase in the number of hydroxyl radicals. Electrical current influences the production of different oxidants that contribute directly or indirectly in the oxidation of organic compounds and how electrolyte can facilitate in the greater production of oxidizing agents by aiding the flow of electricity. In the experiments conducted Na_2SO_4 was utilized as an electrolyte. Although it contributes in the flow of electric current by the production of Na^{+2} ions and SO_4^- it may reverse the oxidation process. When NaCl is put into use as an electrolyte it not only facilitates the current flow but also contributes in the production of some oxidants (Körbahti *et al*., 2016). The indirect oxidation that occurs as a result of using active chlorine has its roots at the anodic oxidation with the chloride ions being oxidized as a result of NaCl break-down in water, which results in chlorine production (Cl_2).

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (5)$$

This chlorine immediately diffuses away only to be unevenly changed into hypochlorous acid (HClO) and chloride via reaction (6) (Panizza and Cerisola, 2009).

$$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+ \qquad (6)$$

This hypochlorous acid may add to the oxidation of the organic compounds by imparting its oxidation abilities. So what seems from the results obtained in table 5, Na_2SO_4 was only adding to aid the flow of current and not the oxidants, but even with this the contribution of current density remained un-noticed. This was probably due to the increase in the hydroxyl radicals at pH 9 which lasted a greater impact on the COD removal then the current density hence shadowing its effect and contribution.

Fig. 4 (a) suggests that when the pH shifts from 3 to 9 current density causes the increase in COD removal with the removal more notable at lower level of current density. This can be owed to the use of NaOH for adjusting pH to 9, which contribute strong oxidant in the form of hydroxyl radial in order to reduce the COD. As far as reduction at lower current density is concerned it might be due to the fact that when current density is increased too much the production of O_2 is favoured over $^{\cdot}OH$ radicals by the electric breakdown of water molecules and so a higher current density not only causes the over potential of the electrodes to rise but also increases energy consumption making the generation of oxidants difficult and costly (Yang *et al*., 2016).

Fig. 4 (b) as evident when either 120 min or 240 min of time is given for degradation, the COD removal is increased when pH shifts from 3 to 9, even though the removal is more significant at 120 min but still at 240 min the degradation of antibiotics can be seen to be at its maximum. At less pH the degradation is low probably because of the number of oxidants being less so the degradation can only be increased by increasing the time. As pH is increased the number of sulphate ions gets reduced and the number of hydroxyl radicals increase due to the use of NaOH to adjust the initial pH. Being the stronger oxidizing agent the degradation increases and when higher time is given the degradation processes increases and so does the COD removal as a result.

For the kind of interaction shown in fig. 4 (c) it can be seen that the trend is same as above i-e at higher pH there is more degradation. But it can also be seen that at lower level of pH the degradation caused by adding 3 g/L of electrolyte is more noticable as compared to when 1.5 g/L of electrolyte was added. Moreover it is clearly evident that the lower level of electrolyte has a far more significant effect on the removal of COD than the higher level when pH is changed from 3 to 9 and hence are intersecting each other. This suggests that at pH 3 the number of sulphate ions are large enough in quantity to impart a negative effect by causing persulphate ions to change into H_2O_2 disrupting the oxidation process by decreasing hydroxyl ions. On the other hand when the pH is set to 9 the number of sulphate ions being changed into persulphate ions are in the quantity suitable for increase in the oxidation since the sulphate ions are being balanced out by the addition of NaOH medium.

Table 1: Independent variables of the 2^4 factorial design of experiments

Coded Values	pH (X_1)	Current Density (mA/cm^2) (X_2)	Time (min) (X_3)	Electrolyte Conc. (mg/L) (X_4)
High (+)	9	35	240	3
Low (-)	3	17	120	1.5

Table 2: 2^4 Factorial matrix with 16 Assays

Standard Order	Factors				pH	Current Density (mA/cm^2)	Time (min)	Electrolyte Conc. (mg/L)
	X_1	X_2	X_3	X_4				
1	-	-	-	-	3	17	120	1.5
2	+	-	-	-	9	17	120	1.5
3	-	+	-	-	3	35	120	1.5
4	+	+	-	-	9	35	120	1.5
5	-	-	+	-	3	17	240	1.5
6	+	-	+	-	9	17	240	1.5
7	-	+	+	-	3	35	240	1.5
8	+	+	+	-	9	35	240	1.5
9	-	-	-	+	3	17	120	3
10	+	-	-	+	9	17	120	3
11	-	+	-	+	3	35	120	3
12	+	+	-	+	9	35	120	3
13	-	-	+	+	3	17	240	3
14	+	-	+	+	9	17	240	3
15	-	+	+	+	3	35	240	3
16	+	+	+	+	9	35	240	3

Table 3: Actual and Predicted values as Calculated by Quadratic Model

Standard Order	Run Order	Factors				COD Removal Y	Actual Removal %	Predicted Removal %
		X_1	X_2	X_3	X_4			
1	8	-	-	-	-	136.5	35.00	34.37
2	13	+	-	-	-	86	59.05	57.73
3	5	-	+	-	-	142.6	32.10	33.43
4	1	+	+	-	-	66	68.57	69.21
5	9	-	-	+	-	103.3	50.81	50.14
6	15	+	-	+	-	22	89.52	88.17
7	6	-	+	+	-	176.3	16.05	17.37
8	16	+	+	+	-	98.33	53.18	53.83
9	14	-	-	-	+	123.3	41.29	40.61
10	7	+	-	-	+	78.8	62.48	61.78
11	3	-	+	-	+	163	22.38	23.73
12	11	+	+	-	+	86	59.05	59.71
13	10	-	-	+	+	111.3	47.00	46.35
14	12	+	-	+	+	93	55.71	54.37
15	4	-	+	+	+	57.33	72.70	74.03
16	2	+	+	+	+	68.66	67.30	67.77

Table 4: ANOVA for multiple regression model

Source of Variation	Sum of Squares	DF	Mean Square	F-Value	F- Critical
Regression	5512.10	4	1378.025	943.55	3.3567
Residual	53.06	11	4.823636364		
Total	5565.16	15	371.0106667		

Table 5: Main and Interaction Effects of Independent Variables.

Effect	Effect Value
Main Effect	
X_1	24.6929
X_2	-6.1917
X_3	9.0464
X_4	2.9548
Two Factor Interaction	
X_1X_2	1.5262
X_1X_3	-4.9024
X_1X_4	-9.3988
X_2X_3	-2.2631
X_2X_4	9.9310
X_3X_4	5.3357
Three Factor Interaction	
$X_1X_2X_3$	-5.45
$X_1X_2X_4$	-1.1845
$X_1X_3X_4$	-8.7321
$X_2X_3X_4$	17.1690
Four Factor Interaction	
$X_1X_2X_3X_4$	-1.9464

Fig. 4 (d) shows that when current density is increased from 17 mA/cm^2 to 34 mA/cm^2 organic removal decreases for both levels of time but overall the COD removal remains maximum at 240 min of electrolysis time. So it can be said that when current density is maintained at its lower level and given a longer electrolysis time the COD reduction is significnt as compared to when the current density is shifted at its higher level. Since average value of the other two factors are taken and are kept constant, the best way to describe this kind of interation is by considering that the decreasing trend could be due to the fact that at higher current densities water molecules get oxidized to O_2 rather than $^{\cdot}OH$ radicals which gets bubbled away depriving the process of much needed oxidizing agent i-e O_2 production is favoured over $^{\cdot}OH$ production. This was proved by (Yang *et al*., 2016) when reduction in methyl orange became insignificant after increasing the current density to above 50 mA/cm^2.

When the current density is low, the COD removal is higher when 1.5 g/L of electrolyte was added which had contributed enough sulphate ions to impart a positive impact on degradation process. But when the current density is increased the same amount of electrolyte has shown a negative impact on COD reduction whereby there is no significant change for higher level of electrolyte. This decrease in COD removal can be attributed to two main reasons:

(i) The increase in the current density favoured the production of oxygen instead of hydroxy radicals hence suppressing the effect of electrolyte and reducing the over all degradation process (Yang *et al*., 2016).

(ii) The shift of current density to a higher level suddenly increased the number of sulphate ions causing persulphate to produce which halts the production of hydroxyl radicals and paves way for the formation of H_2O_2 (Yang *et al*., 2016).

From the fig. 4 (f) it can be said as time increases the higher level of electrolyte concentration causes more COD removal as compared to when lower level of electrolyte concentration is used which is very insignificant. Hence it can be said that at higher concentration of the electrolyte the negative sulphate ion effect is nil and hence degradation is significant. Whereas on the other hand lower level of electrolyte has caused less production of supporting ions for the current to flow contributing little in degradation process.

CONCLUSION

The experiments were conducted with four independent factors (pH, Current Density, Time and Electrolyte Concentration) to degrade antibiotics in synthetic wastewater showed the best response in the form of COD removal when pH and time were kept at their higher level while the current density and electrolyte concentration were set at their lower level. This combination of parameters managed to remove 89% of the organic compounds from the synthetically prepared sample. The amount of hydroxyl radicals, the main oxidants responsible for degradation were higher at longer electrolysis time and at initial pH 9.

To check the authenticity of the response obtained by applying 2^4 factorial design, a mathematical model with multiple linear equation was developed that enabled to calculate the predicted response. After obtaining predicted values ANOVA was applied to check the closeness of actual and predicted values. Using ANOVA R^2 and R_{adj}^2 were calculated to be 0.99 and 0.98 respectively. Being very close together, this shows that there was a strong relation between actual and predicted values. The fitness of the model was proved when F_{obs} came out to be greater than $F_{crit.}$

The interactions between the four factors pH, current density, time of electrolysis and electrolyte concentration was studied. It was shown that at higher pH degradation was more at lower current density, higher time of electrolysis and lower electrolyte concentration. Whereas, it was seen that at higher current density COD removal got lowered at both the levels of time except for electrolyte concentration which enhanced the degradation process at higher current density and higher value of electrolyte concentration. As far as interaction between time and electrolyte, concentration is concerned, the high

COD removal was found at higher electrolysis time was provided in the presence of 3 mg/L of electrolyte concentration.

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