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# Heavy metal removal from produced water by chemicalmechanical treatment

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## Abstract

This paper proves the presentation features of chemical and mechanical aimed at action of heavy metal in produced water (PW). The Electro-catalytic (EC) is one of chemical- mechanical remained made and reflects the extent of its custom in purifying this wastewater. Throughout EC behavior, numerous operating limits were inspected, for instance titanium dioxide, rpm electrolysis time, and copper metal in produced water. The belongings of the working variables including the rpm (100-300), TiO2 concentration (10-30 mg/L), and the electrolysis time (5-15 min) by using Response surface methodology (RSM) and Minitab 17. The current and pH of the solution had remained occupied by way of 1 Amps, 3 respectively. Underneath the finest standards of the employed variables more than 98% removal of copper was found. The elective catalytic method is appropriate aimed at water contaminated by heavy metal, especially aimed at low concentrations of heavy metal in produced water.

Keywords: Produced water, water treatment, advanced oxidation processes, electro oxidation

# 1. Introduction

Water pollution was a unique and one of the world's most unwanted environmental difficulties that need a solution [1]. In oil and gas manufacture, Frequently, the wastewater produced remains more than the preserved volume of crude oil, within 0.4–1.6 creases by way of recognized as produced water [2]. The characteristically of PW includes high courtesies of dangerous aromatic pollutants and aliphatic mixtures which remain alike to crude oil [3]. The PW generates as of two imaginable fundamentals, which can remain originate below/above or privileged the hydrocarbon area or after added liquids, used in the crude oil extraction [4],[5]. The pollutants of organic and inorganic in produced water are of exact ecological concern [6],[7]. This water often is allowable to be discharged to the environment. Water's poisonousness and organic filling can usually describe the impact of discharging PW into the sea [8]. For the purpose that the wilds of oilfields reason ecological pollutions, treatment was energetic earlier removal [9]. The achievement of these wildernesses will be important in improved oil retrieval, separation of pollutants from water, protection of downstream facilities, and lastly, shadows health and ecological safety rules [10]. Heavy metals are not recyclable similar to organic contaminants in water and inclined to accrue in living organisms, and involved additional care owing to their poisonousness, tenacious chiefly [11, 12, 13]. The copper poisonousness in persons has remained lengthily reviewed through some academics. Severe copper killing afterward digestion might demonstrate universal belongings for instance hemolysis, liver and kidney injury, and less with flu syndrome [14]. The most classical approaches secondhand aimed at eliminating copper from wastewater comprise reduction, precipitation, filtration, biological method, and adsorption. The conservative separation approaches have numerous drawbacks, for example, the high capital and working cost, the manufacture of the quantity of heavy metal mud, and likely cohort of minor contamination subsequent in high removal costs [15], decomposable methods possess some exciting recompenses, for instance, high litheness, outstanding capability, extended agreement, and compatibility of environment. These topographies distinguish them from additional advanced oxidation processes (AOPs) [16]. This treatment alteration comprises the in-situ cohort of extremely free radicals is got in the system [17]. AOPs are basically physicochemical procedures in nature that make nearly oxidizing agent, mostly free radical (•OH) consume the maximum oxidation potential following the fluorine radicals [18, 19]. These methods have ability of wicked squalor of obstinate contaminants in the water environment. These processes can completely injury the contaminants into innocuous inorganic substances. In original year's maintenance have been intent on advanced oxidation developments remains nameless by way of electro-oxidation [20]. Though the first investigation on the request of electrochemical procedures aimed at the action of wastewater in the oil manufacturing was available in the late 1990s, there are still numerous chances to implement these skills at full scale [21]. The significant drawbacks of chemical action approaches are low elimination competence and extended separation time. This process requirements a big quantity of oxidant and conductivity alteration, creation the action not cost-effective [22]. Then in specific proves an incompetent manufacture of strong oxidants (e.g., free radicals (•OH)). Since •OH plays a significant role in the oxidation of headstrong organic and inorganic contaminants, this disadvantage of electro oxidation might lead toward a low elimination of pollutants, a high consumption of energy, in addition to a low current competence. TiO<sub>2</sub> has gathered important care, and has showed to be an outstanding electro catalyst aimed at free radical making because of its high oxygen evolution potential, single crystalline structure, in addition to its informal preparation and little cost [23]. This investigation focused on heavy metal removal and recycling in the South Iraqi Industrial oilfield. Therefore, this study purposes toward optimize the EC method to eliminate copper metal by means of the BBD at operational limits rpm solution, titanium dioxide concentration and electrolysis time.

## 2. Experimental

#### 2.1. Experimental resources and analytical test

Titanium Dioxide was used by way of chemical oxidant purchased from India. The pH of the produced water was attuned through the addition of HCL and NaOH purchased from Scharlau, Spain. Altogether solutions were prepared with ionic water. Aluminium and Iron electrodes were one of the greatest mutual resources rummage-sale in the electro catalytic scheme, which was rummage-sale in this work. The produced water was brought from the clearing of the wet oil unit, an oil station situated in Al-Ahdab Oilfield in Iraq. It was self-possessed in polypropylene ampule and conserved at 4 °C to remain preserved through an electro catalytic method utilizing the untried batch apparatus exposed in Fig. 1. The description of the PW is exposed in Table 1.

Table 1: The properties of produced water						
Limits	Copper metal	pН	Turbidity (TUR)	TSS (mg/L)	Organic content	
	(mg/L)		(NTU)		(ppm)	
Value	3.41	6.15	89.22	21.4	145.21	

At the finish of each test of Electro Fenton oxidation, Atomic Absorption Spectrometer (America, Perkin Elmer) was used to measure the copper metal in PW. Air-acetylene by 55 flow rates, slit heat 100 mm of 6 mm height to measure  $Cu^{2+}$  ion. Clarifications happen in the peak area mode finished 324.8 nm aimed at  $Cu^{2+}$  metal.

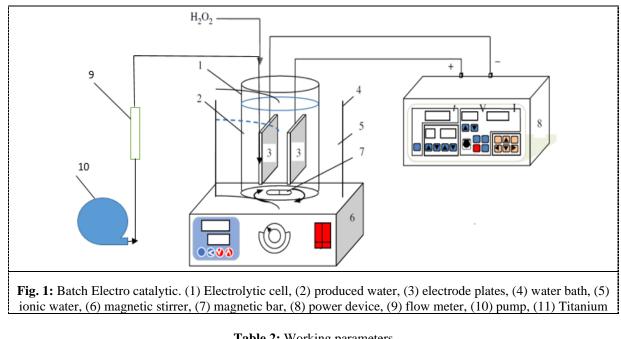
#### 2.2. E-Catalytic processes

The entire untried device comprised of three parts: Power device, magnetic stirring device, and reactor. A shape of the EC system is exposed in Figure 1. RXN-305D power supply remained rummage-sale in the electro catalytic device. In this work, the electro method used a constant current of 1 Amps for heavy metal removal in produced water. The dimensions of the cathode electron were  $(10 \times 6 \times 0.2)$  cm<sup>3</sup>. The anode electrode has dimensions of  $(10 \times 5 \times 0.15)$  cm<sup>3</sup>. In the EC procedure, the electrode's real area was upheld at 20 cm<sup>2</sup>, though the space of the internal electrode was preserved at 5 cm. The RXN-305D was worked for (6 min) toward sweep the iron ions in the glass reactor and at that time added different concentration of TiO<sub>2</sub> for all trials. Discount of heavy metal was expressed by way of the remaining copper after treatment C<sub>1</sub>) to initial copper before treatment (C<sub>0</sub>). The electrodes were stowed in distilled water once they are not been in use. Subsequently each usage, the 1M sodium hydroxide and 1N hydrochloric acid remain rummage sale toward eroding electrodes to remove any likely contamination. The copper removal (CR) might be intended by way of per Eq. (1):

$$\eta = \frac{C_{\bullet} - C_t}{C_{\bullet}} x 100 \tag{1}$$

#### 2.3. Experimental design

A statistical method, response surface methodology is same to statistical software (Minitab-17), was achieved to design the trials and predict the result of the working factors independently and in a communication manner between each other. The main variables of these issues: electrolysis time ( $X_1$ ), rpm ( $X_2$ ), and titanium Dioxide concentration ( $X_3$ ) were deliberate rendering to their ranges exposed in Table 2.



Limits	Range
$X_1$ : electrolysis time (min)	5-15
$X_2$ : rpm	100-300
$X_3$ : Titanium Dioxide concentration (ppm)	10-30

## 3. Results and discussion

## 3.1. Statistical examination for EC processes

Fifteen statistically industrial trials remained designed to improve and test the combined consequence of self-governing variables aimed at a detailed group of procedure limits was improved by Minitab-17 software analysis independent variables aimed at PW in Table 3.

Run	X <sub>1</sub> :	X <sub>2</sub> :	X <sub>3</sub>	Copper removal
	Electrolysis time (min)	rpm	Titanium Dioxide(ppm)	(%)
1	5	100	20	88.54
2	15	100	20	91.34
3	5	300	20	92.34
4	15	300	20	94.12
5	5	200	10	85.14
6	15	200	10	88.10
7	5	200	30	95.60
8	15	200	30	98.18
9	10	100	10	85.30
10	10	300	10	89.20
11	10	100	30	91.40
12	10	300	30	93.70
13	10	200	20	88.60
14	10	200	20	88.91
15	10	200	20	89.04

Table 3: Results of experimental of BBD to remove copper metal

CR competencies following quadratic model was rummage-sale to attain development variables and express in terms of real units [13], regression Equation in Uncoded Units is:

 $85.72 - 1.443 x_1 + 0.0115 x_2 + 0.244 x_3 + 0.0918 x_1^2 + 0.000044 x_2^2 + 0.00610 x_3^2 - 0.00051 x_1 x_2 - 0.0019 x_1 x_3 - 0.0004 x_2 x_3$ (2)

Equation (2) for CR, exhibition the competence of copper remains pretentious through discrete variables (linear and quadratic). The positive constants values exposed that the elimination augmented with cumulative influences connected toward these constants within the confirmed variety though negative constant values exposed the opposite result clearly, the electrolysis time and rpm and titanium dioxide concentration have a positive result [24]. The competence of the perfect remained strong minded in ANOVA examination. Table 4 designed for copper exclusion founded on F test and P test. The equation of regression will show additional alteration in response if the Fisher value remains higher. BBD competence was

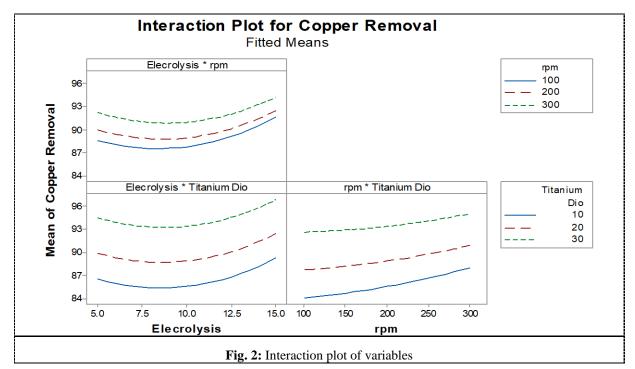
documented finished usage change parts finished done specific sources of change [2]. In general, the larger the magnitude of the F and the smaller the value of P (the probability of exceedance of F) the more significant is the corresponding coefficient term. The model is significant when the P-value is less than 0.05. Examination of the table shows that the model is highly significant as the Fisher F-test is 48.15 with a low probability (P) of exceedance value of 0.01 The high correlation coefficient ( $R^2$ ) of 0.97 demonstrates how well the model fits the experimental data [25].

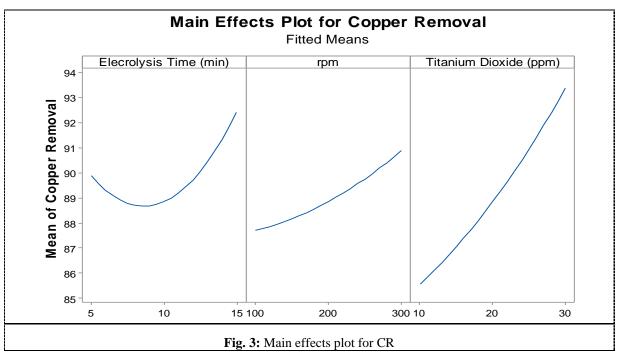
Foundation	DOF	Seq. SS	Adj. MS	F- Value	P-Value
1-Model	9	175.714	19.524	7.76	0.018
Linear	3	154.430	51.477	20.45	0.003
$\mathbf{X}_1$	1	12.802	12.802	5.09	0.074
$\mathbf{X}_2$	1	20.416	20.416	8.11	0.036
$\mathbf{X}_3$	1	121.212	121.212	48.15	0.001
Square	3	20.347	6.782	2.69	0.157
$X_{1}^{2}$	1	19.447	19.447	7.73	0.039
$X_2^2$	1	0.715	0.715	0.28	0.617
$X_{3}^{2}$	1	1.374	1.374	0.55	0.493
2-Way Interaction	3	0.936	0.312	0.12	0.942
$X_1 * X_2$	1	0.260	0.260	0.10	0.761
$X_1 * X_3$	1	0.036	0.036	0.01	0.909
$X_2 * X_3$	1	0.640	0.640	0.25	0.636
Error	5	12.586	2.517		
Lack-of-Fit	3	12.484	4.161	81.43	0.012
Pure Error	2	0.102	0.051		
Total	14	188.300			

Table 4: Al	NOVA	for	CR
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The penalties in Fig. 2 appearance that the high competence reply of removal along the time of oxidation aimed at all values of the heavy metal concentration excluding aimed at high concentrations which incline toward drop aimed at a certain period owing to the absence of adequate places on the surface of the oxidation substantial in the direction of attaining a comparatively high elimination ratio. The combined belongings of electrolysis time, rpm, and titanium dioxide had strong interaction aimed at CR for the reason that the lines in these cells are converging. In Fig.2, the copper oxidation in the EC increases with cumulative rpm,  $TiO_2$  and electrolysis time was upsurged from low to high level, the CR augmented slightly.

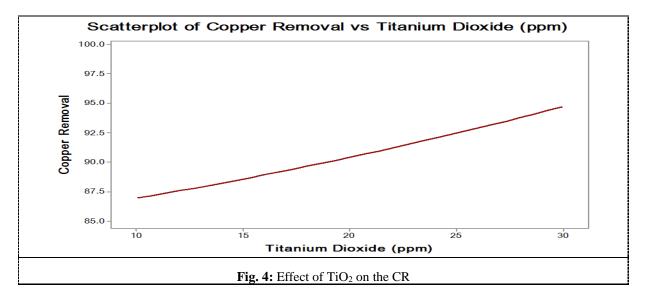
The consequences were examined through the "Minitab 17" software and the main effects amid issues were strongminded. The result of an issue remains defined by way of the change in reply produced through a alteration in the level of the issue. This is regularly named the chief effect since it mentions the primary issues of interest in the trial [27]. The main belongings of each limit on the CR are depicted in Fig. 3. Titanium dioxide concentration, rpm and electrolysis time was the most important variable affecting organic elimination in PW. This constant has a positive sign, the representative that cumulative temperature and electrolysis time within the investigated range would improve the CR [28].





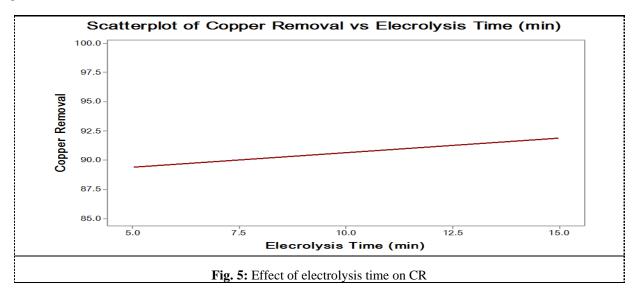
#### 3.1.1. Electro – Catalytic Presentation

One of the purposes of this effort remained toward evaluate the knowledge on electro catalysis, titanium dioxide by way of modulator agents. Titanium dioxide remains selected since it is able to endorse mechanical constancy [29]. Figure 4 exemplifies the copper elimination at different agent concentrations. From this figure, it can remain understood that the heavy metal elimination is augmented as the concentration of  $TiO_2$  increased from 87% at 10 ppm of  $TiO_2$  to the all-out elimination of 96.2 % at 30 ppm of titanium dioxide. The greatest amount of oxide agent has to be effect with the intention of evading the usage of the unnecessary catalyst in extra. The e increase in  $TiO_2$  concentration leads to upsurge in the catalyst surface area, so the removal of the heavy metal contaminants will upsurge [30].



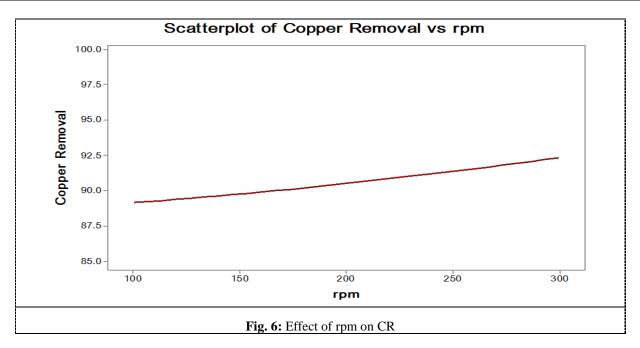
#### 3.1.2. Electrolysis time effect

Figure 5 demonstrates that the CR competence was better-quality with the electrolysis time. The all-out elimination was 92 % at 3 pH, 15 min electrolysis time at room temperature, the exclusion of heavy metal from PW was augmented by way of electrolysis time [31]. Higher electrolysis time occasioned higher elimination competencies of copper metal in the PW. This might remain credited toward the existence of a substantial activity of the adsorption through the EC procedure as the electrolysis time has been lengthy. Also, long oxidation times led toward step through step detoxification beforehand inorganic tin, water, and CO2 remained formed [20].



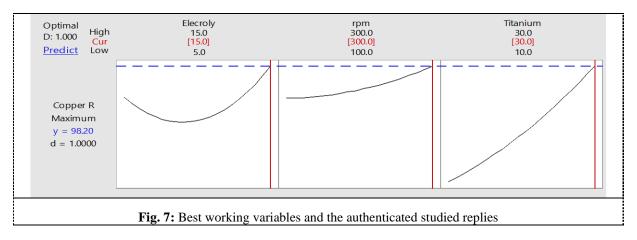
#### 3.1.2. Rpm effect

Electro-|catalytic oxidation of copper metal in produced water remained deliberate put-on variable grades of anxiety [32]. It was originated that the heavy removal augmented linearly though increase the stirrer speed, which touched an all-out of 92.1 % aimed at 300 rpm with 15 min and 30 ppm titanium dioxide concentration by way of exposed in (Figure 6). Lower copper eliminations were reached aimed at speed 100 rpm, which were 88.1 % in the same condition, it was experiential that the mass transfer remained gradually in higher agitation [33].



## 3.2. Enhancing the working variables

Best morals of active variables for instance electrolysis time, rpm, and titanium dioxide concentration remained found applying Minitab-17. Figure 7 defines the measurements consequences of the D-optimization. Best elimination competencies of copper metal were superior to 98 %.



# 4. Conclusions

This effort remains an effect to the applied study and technical growth of the EC procedure utilizing iron felt cathode and aluminum anode skillful the whole removal of copper metal in PW, working circumstances were enhanced and obtainable toward attaining the finest consequences with the highest discount in heavy metal. Aimed at all the deliberate replies, constants of high regression remained found in the proposed mathematical associations, the representative that the second-order polynomial perfect has remained altered sufficiently. The higher elimination 98.14 % CR below optimized working circumstances. The current work established the possibility of the EC development toward mineralize heavy metal and provided a basis aimed at the squalor of copper substances in PW through the EC procedure in applied requests.

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