

Solvent Extraction of Copper Ions from Wastewater Using Reverse Micelles: Experimental and Optimization

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ABSTRACT: *In this study, the optimum conditions for different process parameters were determined for solvent extraction of copper ions from wastewater using reverse micelles. The process parameters viz. copper ion concentration, sodium bis-2-ethyl hexyl sulphosuccinate (AOT) concentration, solution pH, organic to aqueous phase volume ratio, and NaCl concentration were taken into consideration in response surface methodology, ranging from 30-150 mg/L, 0.04-0.2 [M], 3-11, 0.2-1.0, 0-4 g/100 mL respectively and their effect on percentage removal of copper ions were studied. A regression model was developed by conducting response surface methodology for the analysis of the percentage removal of copper ions from wastewater. As many as fifty-four experiments were procured from the design of experiments for the percentage removal of copper ions. The developed model was employed to optimize the process parameters being considered to maximize the response. The optimum conditions were found to be 30 mg/L copper ion concentration, 0.20 [M] AOT concentration, 3.12 and pH, 0.57 organic to aqueous phase volume ratio, and 0.134 g/100 mL NaCl concentration. The obtained model was validated with experimental data and found to be best fitted within the tolerance limit. The effect of cross-interaction among the process parameters on the percentage removal of copper ions was also investigated. In this study, the copper ion concentration was analyzed by Atomic Absorption Spectroscopy (AAS).*

KEYWORDS: *Reverse micelle; Response surface methodology; Design of experiment; Regression; Interaction; AAS.*

INTRODUCTION

Heavy metals discharged through industrial effluents have received the utmost attention of researchers globally on account of being highly venomous at low concentrations (≥ 1 ppm) (Egorova & Ananikov, 2017; Fu & Wang, 2011), non-biodegradable, bio-accumulative, and intrinsically persistent (Barakat, 2011; Fu & Wang, 2011). Copper is

listed as a priority toxic element among heavy metals by the U.S. Environmental Protection Agency (Halim *et al.*, 2020). Cupric (Cu(II)) ions, in particular, which rest ubiquitously in the environment mainly through effluents from industries such as electroplating, mining, printed circuit board manufacturing, and metal finishing

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(Bilal *et al.*, 2013), have aggravated destructive degradations towards the aquatic life (Solomon, 2009), when effluents laden with Cu(II) ions are let off directly into the mainstreams. Subsequently, the treatment of polluted aqueous effluents has become the utmost environmental confrontation for the removal of precarious contaminants for researchers (Verma & Sarkar, 2017).

The conventional techniques for the removal of heavy metals and other pollutants from industrial effluents are chemical precipitation (Hu *et al.*, 2017), coagulation-flocculation (Martínez-Quiroz *et al.*, 2017), membrane filtration (Camarillo *et al.*, 2010), ion exchange (Siu *et al.*, 2016), and adsorption (Mousavi *et al.*, 2018; Goswami *et al.*, 2020). However, each of these techniques has its own drawback and none of them is found to be adequate for treating all kinds of industrial effluents (Halim *et al.*, 2020). Therefore, industries are looking for competing for alternative technologies which may overcome some of the inherent disadvantages of these methods. Membrane separation processes like vacuum membrane distillation (Upadhyaya *et al.*, 2016a, 2016b, 2018; Baghel *et al.*, 2017, 2020), air gap membrane distillation (Kalla *et al.*, 2019) with different types of membrane have shown great potential in commercial applications.

Since the 1940s (Tanda *et al.*, 2017), solvent extraction has been the dominating effluent treatment technique for metal ions on account of being highly efficient, highly selective, easily operational, and cost-effective (Noah *et al.*, 2018). It is based on the relative solubility of metal ions between an aqueous solution and an immiscible organic solvent. Usually, the organic solvent consists of an extractant and a diluent where the former binds metal ions while the latter controls the overall solvent conditions (Chang, 2014). It is also a conventional purification technology offering continuous operation with high throughputs (Sankaran *et al.*, 2019).

The application of micro-emulsified systems in heavy metal extraction has proved to be a good substitute, on account of being profitable when compared to conventional solvent extraction.

Many industrial effluents are let off to mainstreams without being treated properly and, as the environmental standards imposed upon them are rigorous, it is essential to develop modern methods to remove these defilers from industrial effluents before being discharged into mainstreams.

In recent years, solvent extraction using Reverse Micelles (RMs) has been studied extensively as a separation technique, mainly due to the fact that these systems can accommodate large-scale applications (Italiana *et al.*, 2004). The tendency of many water-soluble solutes to distribute into the aqueous core of RMs present in the organic phase has bred a great deal of interest in using such systems in the extraction of protein, amino acids, and enzymes (Pandit & Basu, 2002). Many people have explored RMs systems for the uptake of amino acids, proteins, and enzymes for their large solubilizing capacity (Cui *et al.*, 2011), and some theoretical models have been suggested. Whereas, very few works have been reported on the uptake of heavy metal ions by RMs (Italiana *et al.*, 2004). Due to the minimum step involved and being profitable when compared to conventional solvent extraction, heavy metal extraction using RMs may be exploited in many industrial applications in order to overcome environmental threats.

RMs are considered to be spontaneously and reversibly formed nanometer-sized aggregates of surfactant molecules surrounding microscopic water cores in non-polar solvents (Pandit & Basu, 2002, 2004; Senske *et al.*, 2018; Sankaran *et al.*, 2019). RMs are formed when an aqueous phase is contacted with an immiscible organic phase containing surfactants (Orellano *et al.*, 2017; Sankaran *et al.*, 2019). Different types of surfactants like anionic, cationic, zwitterionic, nonionic, and mixed surfactants can be used for the synthesis of RMs (Lépori *et al.*, 2016). sodium bis-2-ethyl hexyl sulphosuccinate (AOT) is an anionic surfactant, that has widespread use in the synthesis of RMs (Durantini *et al.*, 2013; Fuglestad *et al.*, 2016). The AOT-based RMs are readily synthesized without any co-surfactant and can entrap a huge amount of water serving as an aqueous core (Durantini *et al.*, 2013; Fuglestad *et al.*, 2016). Their formation takes place to downplay interactions between the polar heads of the surfactant molecules in the non-polar medium. In contrast to normal micelles in aqueous solution, the reverse micelles are inverted; the polar head groups of the surfactant molecules form the core of aggregates while their hydrophobic tails directed towards the apolar solvent. The polar heads remain submerged in water pools and thus they are isolated inside the aggregates (Sankaran *et al.*, 2019). The polar head groups of surfactant molecules are held together by hydrogen bonding in the presence of a minimal amount of

water and they are thermodynamically stable (Pandit & Basu, 2002, 2004). Moreover, the mean aggregation number of reverse micelles in dry solvents is significantly smaller than that of normal micelles; thus the traditional concept of the Critical Micellar Concentration (CMC) used for surfactants in aqueous solution is not generally admissible to reverse micelles. The water solubilization capacity of these aggregates varies widely with the molecular structure of the surfactants.

These reverse micelles, also known to be water-in-oil micro-emulsions (Peng et al., 2016), exhibit some special attributes like spontaneous formation (easy to prepare), isotropically clear appearance (easy to monitor spectroscopically), low viscosity (easy to transport and mix), relatively large interfacial area (accelerate the transfer process or surface reaction), ultra-low interfacial tension (flexible, high penetrating power), and large solubilization capacity as compared to many other colloidal systems.

A micro-emulsion is defined as a system created by the dispersion of micro-droplets of two immiscible liquids, stabilized by an interfacial membrane formed by the surfactant with or without the help of a co-surfactant. They are thermodynamically stable, homogeneous, and optically isotropic solutions (Neto et al., 2011; Ferreira et al., 2018). When the oil is in excess, the micro-emulsion is water-continuous (Winsor I) and in excess of water, it is said to be oil-continuous (Winsor II). In Winsor III, the middle micro-emulsion phase is in contact with an excess organic and aqueous phase, and in Winsor IV, only the micro-emulsion phase is present. Micro-emulsions are used in several processes involving the concentration of metal ions, such as chromium, iron, zinc, lead, nickel, copper, and manganese. The removal of metal ions in Winsor II system is found to be faster which is due to the tremendous rise of the micro-interfacial surface area in the micro-emulsion phase and the involvement of the micro-emulsion droplets to transfer metal ions from the aqueous phase to the organic phase.

In this study, the copper ions removal from the water was accomplished by using a reverse micellar extraction process. Subsequently, the organic phase is disunited from the aqueous phase leading to the significant removal of copper ions from water. This may be thought to be the enhanced solubility of copper ions due to its solubilization of it in the core of reverse micelles formed

by the surfactant in the organic phase. The effect of operating parameters on the percentage removal of copper ions using reverse micelles was investigated experimentally, which was not systematically studied by the researchers. The process parameters were optimized by means of a regression model developed by conducting response surface methodology. Moreover, the binary interaction effects among the process parameters on the percentage removal were also illustrated.

EXPERIMENTAL SECTION

Reagents

Sodium bis-2-ethyl hexyl sulphosuccinate (AOT, sigma) as surfactant and Isooctane (spectroscopic grade, Fluka) as solvent was used to prepare isooctane-AOT reverse micelles. All other chemicals were of analytical grade; freshly prepared distilled was used in all experiments.

Experimental setup

The schematic view of the experimental setup is shown in Fig. 1. A magnetic stirrer is used for the mixing of solvent and aqueous phase. The rpm of the mixer can be adjusted as per the requirement of mixing. A separating funnel, which is connected to the mixer, is used to separate the solvent and aqueous phases by gravity. Atomic Absorption Spectroscopy (AAS) is used to measure the copper ions removal from water.

Experimental procedure

The metal removal using reverse micellar extraction involved two steps. In the first step, a given volume of the aqueous solution with known copper ion concentration was added to a known volume of the isooctane (solvent) containing a known quantity of the AOT (surfactant) in a beaker. The range of AOT concentrations used was around the Critical Micelle Concentration (CMC). The content was agitated thoroughly on a magnetic stirrer at 400 rpm for 30 min and thereafter, the entire mixture was transferred into a separating funnel for 48 hours settling. It was noticed that equilibrium was attained during the stirring.

In the second step, the two-phase dispersion was transferred into a separating funnel to separate the solvent and aqueous phases by gravity. This resulted in the formation of two clear liquid phases; the solvent phase containing the copper ion encapsulated in the reverse

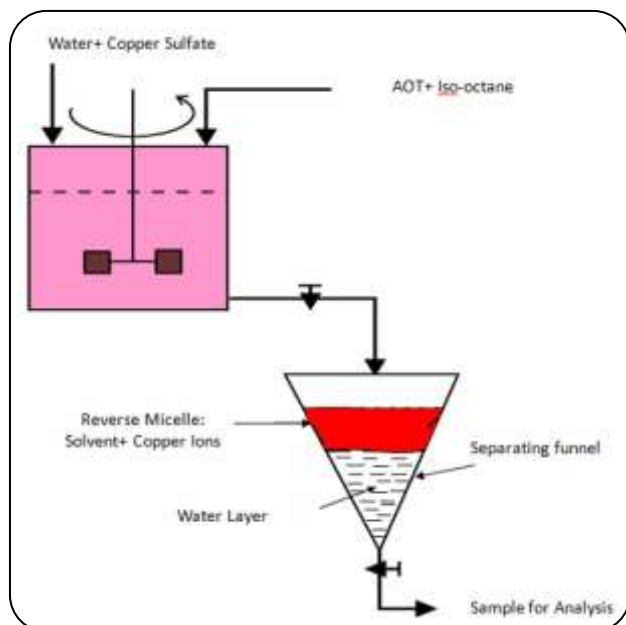


Fig. 1: Schematic diagram of reverse micellar extraction

micelles and the clear aqueous phase. To ensure the complete separation of pure phases, the two-phase dispersions were allowed to settle for 48 h. The samples were withdrawn from the bottom (aqueous phase) and analyzed for AAS in Material Research Centre, Jaipur to determine the amount of copper ions removed. The copper ions associated with the solvent were also analyzed to check the mass balance. These experiments followed by sample analysis were done several times in order to check the repeatability and accuracy of measurement. The variation in experimental data was in the range of 2-3%.

More experiments were done by changing parameters viz, copper ion concentration, AOT concentration, solution pH, organic to aqueous phase volume ratio, and NaCl concentration according to the requirement in the Design of the Experiment (DOE).

Experimental array

In this work, DOE array was developed which related the independent process variables to the response of the process and helped to determine the optimum condition among the variables. Numerous techniques such as Taguchi, Mixture (Simplex Centroid, Simplex Lattice, and Extreme Vertices), Factorial, Box-Behnken, and Central Composite Design (CCD) could be employed for optimization using DOE in order to determine optimum process variables in the minimum number of runs. Earlier,

a large number of experiments were used to be conducted to optimize the process variables by changing one variable at a time but that method was cumbersome as well as not effective for understanding the response of interacting variables where the relations were implicit. However, CCD was capable to deal with multivariable problems, interaction effects, and optimization in the least number of trials using the least square regression technique for the fitting nonlinear polynomial model. In this study, five process variables viz copper ion concentration (mg/L), AOT concentration [M], pH of the solution, organic phase to aqueous phase volume ratio, and sodium chloride concentration (g/100 mL) were considered to analyze their effect on percentage removal of copper ions using reverse micellar extraction. While designing the array, the variables were coded as ± 1 (-1 for lower and $+1$ for higher) for factorial points, 0 for center points, and $\pm\beta$ ($-\beta$ for lowest and $+\beta$ for highest) for axial points once the minimum value (a_{\min}) and maximum value (a_{\max}) were decided from an extensive literature survey. Using the above guidelines, the coded and actual values (uncoded) of each process parameter were estimated by the standard formula as represented in Table 1 with an array of all independent variables. The customized value $\alpha = 2$ was taken for analysis.

RESULTS AND DISCUSSION

Residual analysis

Response surface design comprising 5 factors, 5 levels, and 2 blocks were taken for 54 experimental runs. The experiments were conducted as per the developed design. The responses in terms of percentage removal of copper ions were measured for all 54 runs as shown in Table 2, which illustrated the actual values of operating variables along with respective experimental percentage removal. Residuals plots for the percentage removal of copper ions obtained from CCD design reflected that all experimental data represented the goodness of fit with the normality line as shown in Fig. 2. The residuals for percentage removal of copper ions fell in the range of -6 to 7 whereas permissible range was ± 10 . Moreover, residuals had also been illustrated in Fig. 2 for a better understanding of three different types of plots namely Histogram, Versus Orders, and Versus Fits. It was evident from residual plots that response data were well distributed normally.

Table 1: Experimental array of independent variables

Variables		Cu ⁺⁺ concentration (mg/L)	AOT concentration [M]	pH	Volume Ratio	NaCl concentration (g/100 mL)
Symbol		A	B	C	D	E
Coded Value	Lowest axial point	- β				
Actual Value		a_{\min}				
		30	0.04	3	0.2	0
Coded Value	Lower cube point	-1				
Actual Value		$[(a_{\max} + a_{\min}) / 2] - [(a_{\max} - a_{\min}) / 2\alpha]$				
		60	0.08	5	0.4	1
Coded Value	Center	0				
Actual Value		$(a_{\max} + a_{\min}) / 2$				
		90	0.12	7	0.6	2
Coded Value	Higher cube point	+1				
Actual Value		$[(a_{\max} + a_{\min}) / 2] + [(a_{\max} - a_{\min}) / 2\alpha]$				
		120	0.16	9	0.8	3
Coded Value	Highest axial point	+ β				
Coded Value		a_{\max}				
		150	0.2	11	1	4

Residual Plots for Copper Ion Percentage Removal

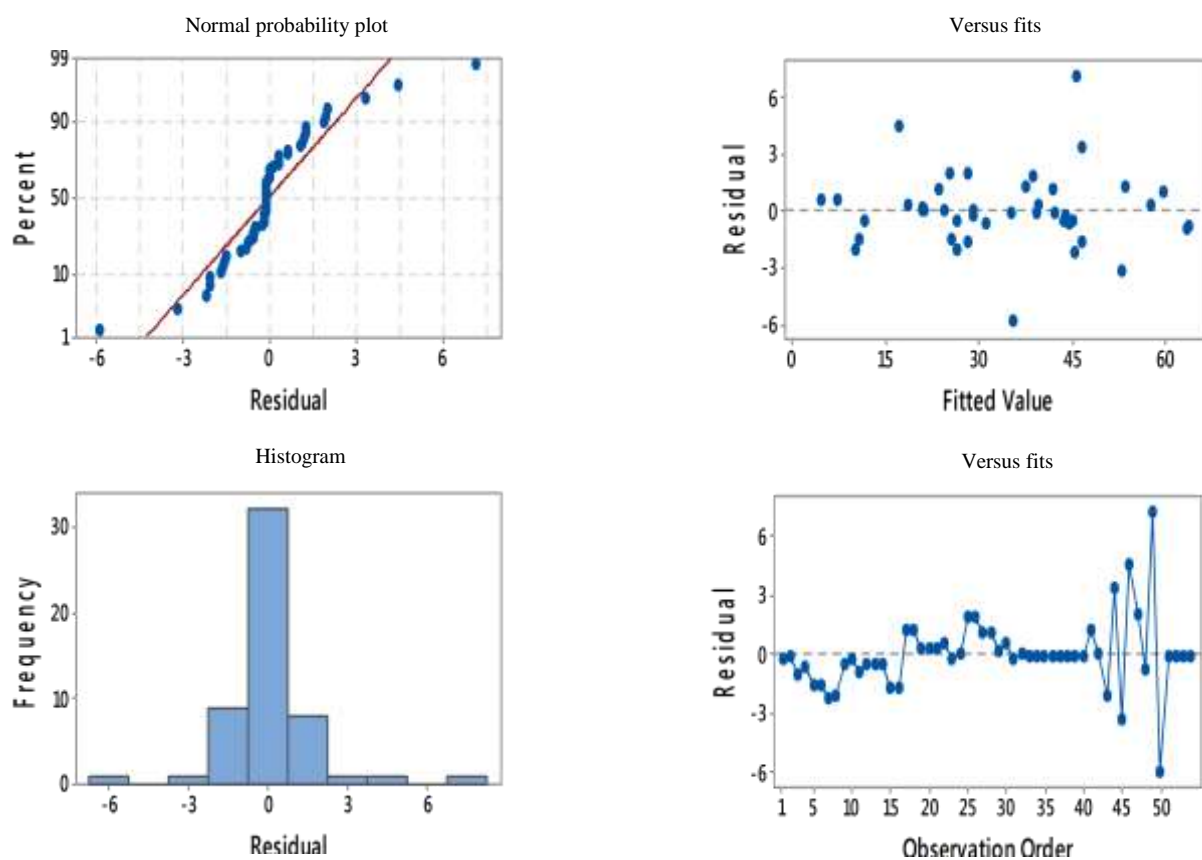


Fig. 2: Residuals plots for copper ion percentage removal.

Table 2: Five-factorial CCD and responses.

Run Order	Actual Values of Design Variables					Experimental Responses
	Copper Ion Conc. (A)	AOT Conc. (B)	pH (C)	Volume ratio (D)	NaCl Conc. (E)	Percentage Removal (% R)
1.	60	0.08	5	0.4	1	43.78
2.	120	0.08	5	0.4	1	29.12
3.	60	0.16	5	0.4	1	62.42
4.	120	0.16	5	0.4	1	43.94
5.	60	0.08	9	0.4	1	24.09
6.	120	0.08	9	0.4	1	9.21
7.	60	0.16	9	0.4	1	43.24
8.	120	0.16	9	0.4	1	24.43
9.	60	0.08	5	0.8	1	43.22
10.	120	0.08	5	0.8	1	29.01
11.	60	0.16	5	0.8	1	62.96
12.	120	0.16	5	0.8	1	44.78
13.	60	0.08	9	0.8	1	25.92
14.	120	0.08	9	0.8	1	11.23
15.	60	0.16	9	0.8	1	45.13
16.	120	0.16	9	0.8	1	26.41
17.	60	0.08	5	0.4	3	38.78
18.	120	0.08	5	0.4	3	24.76
19.	60	0.16	5	0.4	3	58.01
20.	120	0.16	5	0.4	3	40.12
21.	60	0.08	9	0.4	3	19.12
22.	120	0.08	9	0.4	3	5.32
23.	60	0.16	9	0.4	3	39.11
24.	120	0.16	9	0.4	3	21.23
25.	60	0.08	5	0.8	3	40.73
26.	120	0.08	5	0.8	3	27.20
27.	60	0.16	5	0.8	3	60.67
28.	120	0.16	5	0.8	3	43.13
29.	60	0.08	9	0.8	3	21.23
30.	120	0.08	9	0.8	3	7.97
31.	60	0.16	9	0.8	3	42.01
32.	120	0.16	9	0.8	3	24.44
33.	90	0.12	7	0.6	2	35.25
34.	90	0.12	7	0.6	2	35.27
35.	90	0.12	7	0.6	2	35.24
36.	90	0.12	7	0.6	2	35.25
37.	90	0.12	7	0.6	2	35.26
38.	90	0.12	7	0.6	2	35.27
39.	90	0.12	7	0.6	2	35.24
40.	90	0.12	7	0.6	2	35.25
41.	30	0.12	7	0.6	2	54.92
42.	150	0.12	7	0.6	2	21.10
43.	90	0.04	7	0.6	2	8.10
44.	90	0.20	7	0.6	2	50.10
45.	90	0.12	3	0.6	2	49.80
46.	90	0.12	11	0.6	2	21.60
47.	90	0.12	7	0.2	2	30.27
48.	90	0.12	7	1.0	2	30.50
49.	90	0.12	7	0.6	0	53.01
50.	90	0.12	7	0.6	4	29.70
51.	90	0.12	7	0.6	2	35.26
52.	90	0.12	7	0.6	2	35.25
53.	90	0.12	7	0.6	2	35.25
54.	90	0.12	7	0.6	2	35.26

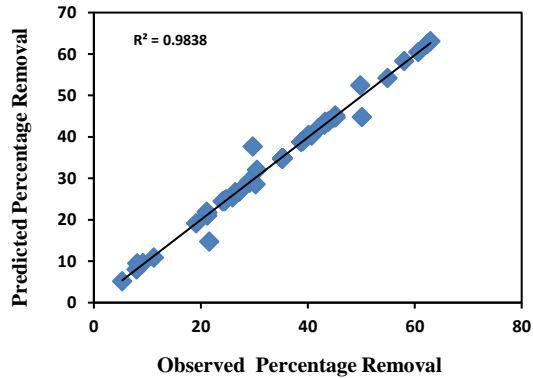


Fig. 3: Actual versus predicted data for the response.

Non-linear regression and ANOVA

A non-linear regression model (Eq. (2)) comprising individual and interaction effects was fitted using developed DOE data from CCD design (Table 2) to develop the relationship between the input process variables and response.

$$y = a_0 + a_2A + a_2B + a_3C + a_4D + a_5E + a_{11}A^2 + a_{22}B^2 + a_{33}C^2 + a_{44}D^2 + a_{55}E^2 + a_{12}AB + a_{13}AC + a_{13}AC + a_{14}AD + a_{15}AE + a_{23}BC + a_{23}BC + a_{24}BD + a_{25}BE + a_{34}CD + a_{35}CE + a_{45}DE \quad (1)$$

Where A , B , C , D , E , a_i , a_{ii} , and a_{ij} are copper ions concentration, AOT concentration, solution pH, aqueous to organic phase volume ratio, NaCl concentration, coefficient of individual, coefficient of the square, and coefficient of interaction based parameters respectively. The subscripts i and j represent the order of parameters whose values were estimated by applying the least square method on DOE data. Thereafter, the uncoded model equation along with coefficients was obtained as below:

$$\begin{aligned} \text{Percentage removal} = & 48.75 - 0.3502A + 558.9B - 3.933C + 26.87D - 10.158E + 0.000896A^2 - 1209.4B^2 - \\ & 0.0786C^2 - 28.51D^2 + 1.5945E^2 - 0.8339AB - \\ & 0.00057AC + 0.0142AD + 0.00744AE + 0.969BC + \\ & 18.36BD + 4.59BE + 0.611CD - 0.0531CE + 1.953DE \end{aligned} \quad (2)$$

ANOVA was conducted in order to identify the significant process variables affecting the response that is the percentage removal of copper ions. Table 3 suggested that all the linear, as well as square interactions, had been

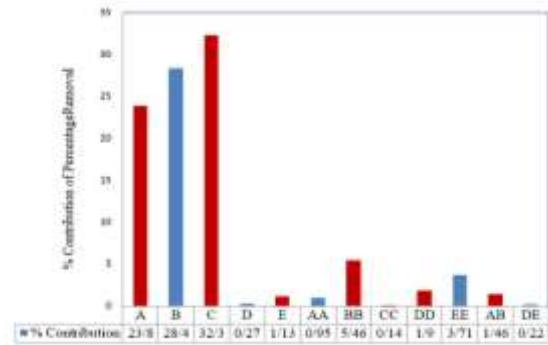


Fig. 4: Pareto graphic analysis of percentage contributions of each factor.

signed on the percentage removal of copper ions while four (A^*C , A^*D , B^*C , C^*E) cross interactions had insignificant contributions on the same. The significance of these variables was determined by their corresponding p-values as depicted in Table 3.

After having done all fifty-four experimental runs, the experimental values were compared with predicted values obtained from the regression equation and found to be aligned with experimental data with the R-square value being 0.9838, as elaborated in Fig. 3. Moreover, the R-square (adj) and R-square (predicted) were found to be 99.93% and 99.86% respectively with the help of Minitab software.

Fig. 4 indicated the synergetic and antagonistic effects of process variables and their interactions on the response that is percentage removal of copper ions. Synergetic effects were shown by blue bars and antagonistic effects by red bars while variables or interactions having negligible contribution were dropped out from the Pareto graph. From Fig. 4, it could be seen that the maximum synergetic effect on the percentage removal of copper ions was shown by AOT concentration, On the other hand, solution pH and copper ion concentration showed an antagonistic effect. Moreover, two interaction parameters had shown a synergetic effect out of which E^*E claimed to have a maximum contribution of 3.71% while four interaction parameters represented an antagonistic effect out of which B^*B contributed a maximum of 5.46%. The percentage contribution of process parameters and their interaction can be determined using the relation (Baghel et al., 2018).

$$\% \text{ Contribution} = \frac{e_i^2}{\sum_{i=1}^n e_i^2} \times 100 \quad (3)$$

Table 3: Analysis of variance for copper ion percentage removal.

Source	DF	Adj SS	Adj MS	F-value	P-value
Linear					
A	1	2616.27	2616.27	19163.31	0.000
B	1	3113.32	3113.32	22804.00	0.000
C	1	3546.44	3546.44	25976.48	0.000
D	1	29.79	29.79	218.21	0.049
E	1	123.83	123.83	907.04	0.000
Square					
A*A	1	22.00	22.00	161.11	0.000
B*B	1	126.66	126.66	927.77	0.000
C*C	1	3.34	3.34	24.47	0.000
D*D	1	44.00	44.00	32.31	0.000
E*E	1	86.00	86.00	629.96	0.000
2-Wa					
A*B	1	32.04	32.04	234.68	0.000
A*C	1	0.04	0.04	0.28	0.602
A*D	1	0.23	0.23	1.69	0.202
A*E	1	1.59	1.59	11.67	0.002
B*C	1	0.19	0.19	1.41	0.244
B*D	1	0.69	0.69	5.06	0.031
B*E	1	1.08	1.08	7.91	0.008
C*D	1	1.91	1.91	14.00	0.001
C*E	1	0.36	0.36	2.65	0.113
D*E	1	4.88	4.88	35.76	0.000
Error	33	4.51	0.14		
Lack-of-Fit	22	3.11	0.14	1.11	0.446
Pure Error	11	1.40	0.13		
Total	53	9746.27			

Where, e_i is the effect of individual, square, and cross-interaction parameters whose values are shown in Table 4.

Effect of process parameters

Effect of copper ion concentration

It was evident from the Fig. 5 that the percentage removal of copper ions decreased with an increase in copper ion concentration in an aqueous solution from 30 mg/L to 150 mg/L at a certain AOT concentration. Since reverse

micelles had a fixed capacity for metal (copper) ions encapsulation at a fixed surfactant (AOT) concentration, the number of reverse micelles formed was constant. Thus, the percentage removal of copper ions from the aqueous phase decreased with an increase in copper ion concentration (Pandit & Basu, 2004). It should be noted that the removal of metal ions was accomplished if oppositely charged metal and surfactant were used. Metal ions removal from the aqueous phase was not done if similarly charged metal and surfactant were chosen.

Table 4: Coded parameter effects for different responses.

Parameter	Percentage Removal				
	Effect	Coeff	SEC	t value	p value
Constant		34.820	0.105	330.95	0
A (β_1)	-32.35	-16.175	0.117	-138.43	0
B (β_2)	35.289	17.645	0.117	151.01	0
C (β_3)	-37.664	-18.832	0.117	-161.17	0
D (β_4)	3.452	1.726	0.117	14.77	0
E (β_5)	-7.038	-3.519	0.117	-30.12	0
A*A (β_{11})	6.451	3.225	0.254	12.69	0
B*B (β_{22})	-15.48	-7.740	0.254	-30.46	0
C*C (β_{33})	-2.514	-1.257	0.254	-4.95	0
D*D (β_{44})	-9.124	-4.562	0.254	-17.95	0
E*E (β_{55})	12.756	6.378	0.254	25.10	0
A*B (β_{12})	-8.005	-4.002	0.261	-15.32	0
A*C (β_{13})	-0.275	-0.138	0.261	-0.53	0.602
A*D (β_{14})	0.68	0.340	0.261	1.30	0.202
A*E (β_{15})	1.785	0.892	0.261	3.42	0.002
B*C (β_{23})	0.62	0.310	0.261	1.19	0.244
B*D (β_{24})	1.175	0.588	0.261	2.25	0.031
B*E (β_{25})	1.47	0.735	0.261	2.81	0.008
C*D (β_{34})	1.955	0.977	0.261	3.74	0.001
C*E (β_{35})	-0.85	-0.425	0.261	-1.63	0.113
D*E (β_{45})	3.125	1.563	0.261	5.98	0

Effect of AOT concentration

It was clearly indicated from Fig. 6 that on increasing the AOT concentration from 0.12 to 0.20 [M], the percentage removal of copper ions increased at all copper ion concentrations. At higher AOT concentrations the number of reverse micelles available for extraction increased which in turn yielded more solubilization of copper ions and thus more percentage removal. However, the rise in surfactant concentration may cause stable solvent-aqueous phase dispersion, resulting in poor separation of phases (Pandit and Basu, 2004). Thus, it was necessary to evaluate the requisite quantity of surfactant (AOT) to be added for a given amount of metal ions (copper) removal, and this selection certainly dealt with it. Thus, an optimum surfactant concentration should be used

for metal ions removal by reverse micelles so that phase separation time is not high and metal removal is not low.

Effect of pH

It was seen from Fig. 7 that the percentage removal of copper ions decreased steeply with an increase in pH of the solution at a fixed AOT concentration. For example, percentage removal decreased from 88.21 to 53.52 on increasing pH from 3 to 11 at 0.20 [M] AOT concentrations. This may be attributed that Cu^{+2} may be partially neutralized by OH^- at a high pH and thus the electrostatic attraction between copper ions and AOT surfactant decreased. This led to a decrease in the solubilization of copper ions in the reverse micelles formed by the anionic surfactant.

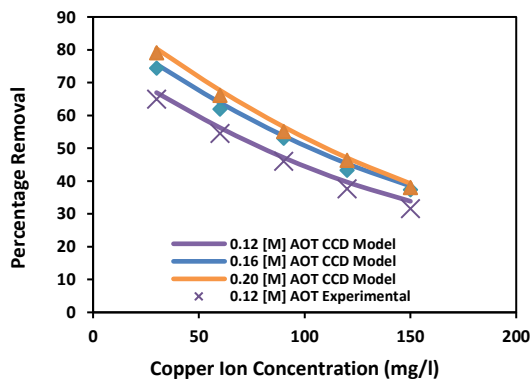


Fig. 5 : Effect of copper ion concentration on percentage removal. [$pH = 5$, Volume Ratio = 0.6 and NaCl Concentration = 1 g/100mL].

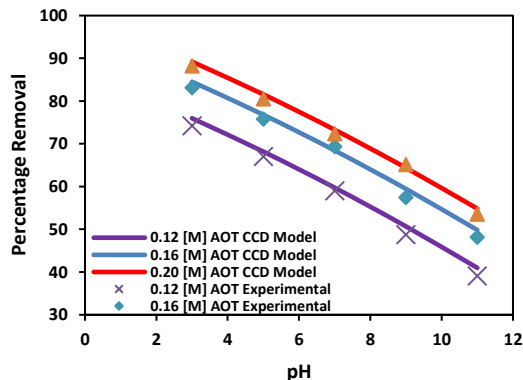


Fig. 7: Effect of pH on percentage removal. [copper ion concentration = 30 mg/L, Volume Ratio=0.6 and NaCl Concentration = 1 g/100mL].

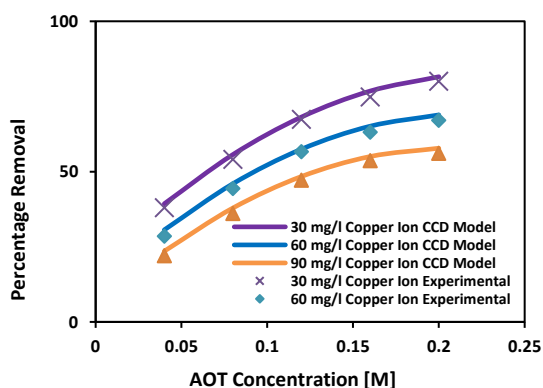


Fig. 6: Effect of AOT concentration on percentage removal. [$pH = 5$, Volume Ratio = 0.6 and NaCl Concentration = 1 g/100mL].

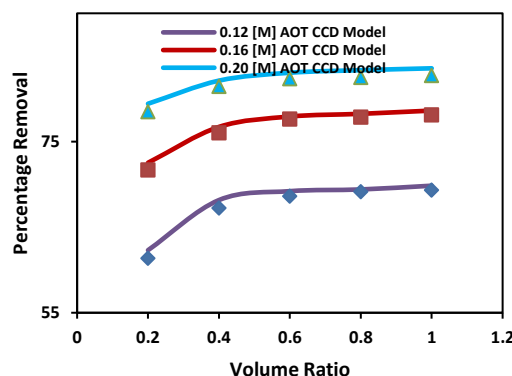


Fig. 8: Effect of volume ratio on percentage removal. [Copper ion concentration = 30 mg/L, $pH = 5$, and NaCl Concentration = 1 g/100mL].

Effect of volume ratio

Fig. 8 observed that the percentage removal increased significantly with the increase in solvent-to-aqueous phase volume ratio from 0.1 to 0.6. However, no significant rise was noticed beyond 0.5 volume ratio. Therefore, a low solvent quantity can be used in reverse micellar extraction (Pandit and Basu, 2004). This was because the increased water uptake by the solvent phase for the increased solvent-to-aqueous phase volume ratio resulted in increased water content of the reverse micelles. This led to an increase in the solubilization of copper ions which resulted in the increased percentage removal. This was an important result from the point of view of the economics of the extraction process.

Effect of NaCl concentration

It was seen from Fig. 9 that the percentage removal of copper ions from the aqueous phase decreased with

the increase in NaCl concentration from 0 to 4 g/100 mL at all AOT concentrations. In the presence of Na^+Cl^- the anionic charge of AOT surfactant may have screened due to the formation of the double layer. This led to a decrease in the repulsive force between the head groups of AOT molecules present side by side in the reverse micelles. Consequently, the size of the reverse micelles decreased leading to a decrease in the solubilization of copper ions in reverse micelles. Many researchers observed a similar effect of salt on protein and amino acid extraction by reverse micelles.

Optimization

The response optimizer toolbox available in CCD was utilized to find out the best suitable operating conditions at which the response that is the percentage removal of copper ions was maximum. The response was found

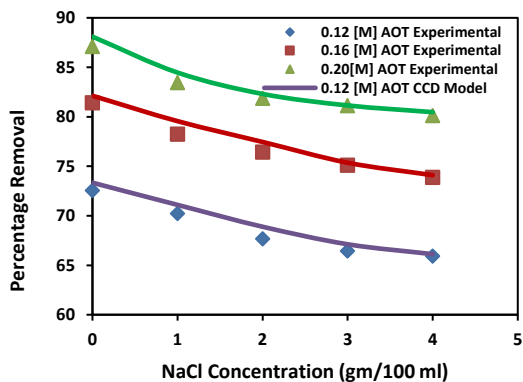


Fig. 9: Effect of NaCl concentration on percentage removal. [NaCl Concentration = 30 mg/L, pH = 5, and Volume Ratio = 0.6].

to be maximum at 30 mg/L copper ion concentration, 0.20 [M] AOT concentration, 3.12 pH, 0.57 organic to aqueous phase volume ratio, and 0.134 g/100 mL NaCl concentration as shown in Fig. 10. At optimum conditions, the desirability came out to be 1.0 which made the optimum conditions acceptable. Also, a comparison was done between observed and predicted values of response in order to check the acceptability of optimum conditions of the process parameters as shown in Table 4.

Simultaneous Interaction effect on Response

Binary interaction effects of two process parameters at a time on response were elaborated on 2D plots while the other three parameters were kept constant. These plots are known as contour plots which were obtained by CCD design.

The simultaneous interaction between copper ion concentration (A) and AOT concentration (B) on the percentage removal of copper ions was shown in Fig. 11a. It was evident that the AOT concentration played a significant role in the percentage removal of copper ions as compared to the copper ion concentration. Further, at higher copper ion concentrations (> 75.43 mg/L) the percentage removal of copper ions did not exceed 60% at any AOT concentration. In other words, at higher copper ion concentrations in the feed solution, the effect of AOT concentration on the percentage removal decreased. This could be anticipated to the antagonistic effect of interacting parameters as shown in Fig. 4. The maximum removal of 78.54% was obtained at 30.5 mg/L of copper ion concentration and 0.199 [M] of AOT concentration under specified hold values. The p-value of the interaction

effect was found to be zero (given in Table 3) clearly indicating significant interaction.

The cross interaction between AOT concentration (B) and NaCl concentration (E) on the percentage removal of copper ions was depicted in Fig. 11b. It was observed that AOT concentration influenced the percentage removal of copper ions to a larger extent as compared to NaCl concentration. It was also found that the removal was beyond 80% at AOT concentration close to 0.16 [M] under 30 mg/L copper ion concentration, 3.0 pH, and 0.6 volume ratio. Moreover, beyond this point, the percentage removal of copper ions was independent of the NaCl concentration. This could be attributed that, at AOT concentration > 0.16 [M], the number of micelles available was sufficiently large enough for the solubilization of copper ions, consequently the effect of NaCl concentration on the percentage removal turned negligible. The maximum removal was found to be 94% at AOT concentration of 0.199 [M], NaCl concentration of 0.1g/100mL under 30 mg/L copper ion concentration, 3 pH, and 0.6 volume ratio. The p-value of interaction was observed as 0.008 (given in Table 3) indicating a significant interaction effect.

The interaction between pH (C) and volume ratio (D) on the percentage removal of copper ions was represented in Fig. 11c. It indicated that pH had a vital role to play in comparison to the volume ratio on the percentage removal of copper ions. Further, the removal was beyond 85% at pH below 4.32 of the solution under the wide range of volume ratio from 0.2 to 1. The maximum removal was found to be 94.8% at 3.02 pH, 0.577 volume ratio under 30 mg/L copper ion concentration, 0.2 [M] AOT concentration, and nil NaCl concentration. It was also seen that the removal increased from 59% to 93% by decreasing the pH from 11 to 3.46 at a volume ratio of 0.6. The p-value of the interaction effect was seen as 0.001 which confirmed significant interaction.

From the cross interaction Fig. 11d between volume ratio (D) and NaCl concentration (E), it was observed that the removal decreased from 94.74% to 85% on increasing NaCl concentration from 0 to 2.66 g/100 mL at a volume ratio of 0.65 under the specified hold values. However, further increments in NaCl concentration beyond 2.66 g/100 mL showed a positive increment in removal from 85% to 88.58%. The reason for the decline of percentage removal on increasing NaCl concentration up to 2.66g/100 mL was due to the formation of a double-layer which might have

Table 5: Confirmation test

Operating Conditions		Percentage Removal	
Parameters	Optimum	Predicted	Observed
Copper Ion Concentration	30 mg/L	93.39	92.37
AOT Concentration	0.20 [M]		
pH	3.12		
Volume Ratio	0.57		
NaCl Salt Concentration	0.134 g/100mL		

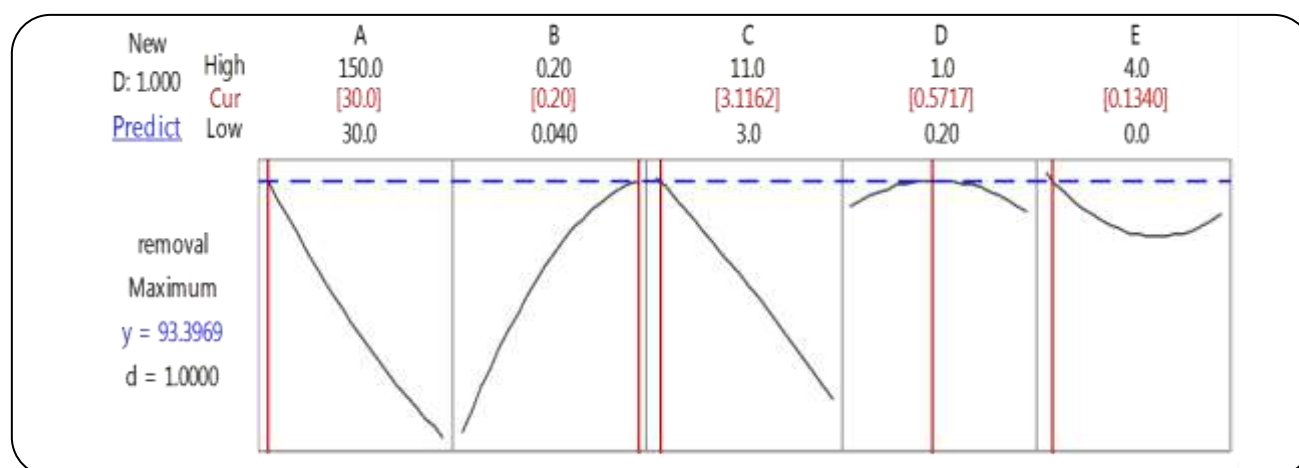


Fig. 10: Optimization of process parameters.

screened the anionic charge of AOT. This led to a decrease in the repulsive force between the head groups of AOT molecules present side by side in the reverse micelles. Consequently, the size of the reverse micelles decreased leading to a decrease in the solubilization of copper ions in reverse micelles. However, 2.66 g/100 mL might be the saturation point of NaCl concentration, thereby increasing the percentage removal beyond this point. Moreover, it could also be illustrated from the figure that the effect of NaCl concentration was more significant on the percentage removal of copper ions as compared to volume ratio. Furthermore, it was evident that under the wide range of volume ratio from 0.4 to 0.8, no significant variation in percentage removal was found at 0.2g/100 mL NaCl concentration. The p-value was observed as zero indicating the significant interaction (shown in Table 3).

The simultaneous interaction between pH (C) of the solution and NaCl (E) concentration was shown in Fig. 11e. It could be demonstrated that the effect of pH on the percentage removal of copper ions was more than that of NaCl concentration. Further, on lowering the pH to 4.17,

the removal was beyond 80% at a wide range of NaCl concentration under 30 mg/L copper ion concentration, 0.2 [M] AOT concentration, and 0.6 volume ratio, and subsequently, it became independent of NaCl concentration. At pH below 4.17, the concentration of the cation may have increased leading to the increased electrostatic attraction between cations and AOT surfactant. This led to an increase in the solubilization of copper ions in reverse micelles formed by anionic surfactant. The maximum removal was found to be 94% at 3.08 pH and 0.07g/100 mL NaCl concentration. The p-value was noted as 0.113 in Table 3 shows insignificant interaction.

The cross-interaction plot copper ion concentration (A) versus volume ratio (D) was illustrated in Fig. 11f. It indicated that copper ion concentration had more roles to play as compared to the volume ratio on the percentage removal of copper ions. Further, at copper ion concentrations lesser than 41 mg/L, removal was obtained beyond 85% under the wide range of volume ratio from 0.2 to 1. Furthermore, the maximum removal was found to be 94% at 31 mg/L copper ion concentration and 0.57 volume ratio

under 0.2 [M] AOT concentration, 3 pH, and nil NaCl concentration. It was observed that the removal increased from 53% to 94% when copper ion concentration decreased from 150 mg/L to 31 mg/L at 0.6 volume ratio. The p-value was read as 0.202 from Table 3 confirming insignificant interaction.

The binary interaction plot copper ion concentration (A) versus pH (C) was represented in Fig. 11g. It could be understood that the copper ion concentration affected the percentage removal of copper ions to a larger extent as compared to the pH of the solution. Further, at higher pH (> 9), the removal was not greater than 68% at any copper ion concentration which means that at higher pH, the effect of copper ion concentration lowered down. The reason is given to the fact that Cu^{+2} may be partially neutralized by OH^- at a higher pH causing decreased electrostatic attraction between copper ions and AOT surfactant. This led to a decrease in the solubilization of copper ions in the reverse micelles formed by anionic surfactant. The maximum removal of 94% was found at 31 mg/L copper ion concentration and 3.06 pH under 0.2 [M] AOT concentration, 0.6 volume ratio, and nil NaCl concentration. The p-value was found to be 0.602 indicating insignificant interaction.

From the cross interaction Fig. 11h between copper ion concentration (A) and NaCl concentration (E), it could be seen that the former affected more the percentage removal of copper ions than the latter. Moreover, at copper ion concentration close to 41 mg/L, the removal was more than 80% under the wide range of NaCl concentration from 0 to 4 mg/100 mL. Furthermore, below this point, the removal was no more dependent on NaCl concentration. This might be given to the fact that, under the specified hold values, the size of the reverse micelles was more than enough to solubilize copper ion concentration lesser than 41 mg/L, hence double layer formation due to the presence of NaCl was no more effective. The maximum removal of 94% was achieved at 31 mg/L copper ion concentration and 0.05 g/100 mL NaCl concentration under 0.2 [M] AOT concentration, 3 pH, and 0.6 volume ratio. The p-value was recorded as 0.002 which confirmed significant interaction.

The binary interaction between AOT concentration (B) and volume ratio (D) was illustrated in Fig. 11i. It indicated that AOT influenced to a larger extent as compared to volume ratio on the percentage removal of copper ions. At AOT concentration close to 0.165 [M],

the percentage removal was beyond 80% under 30 mg/L copper ion concentration, 3 pH, and 1 g/100 mL NaCl concentration. Moreover, beyond this point, the percentage removal of copper ions was found to be almost independent of the volume ratio. The reason could be given to the fact that, at AOT concentration larger than 0.165 [M], the number of reverse micelles available for solubilization must have been large enough to accommodate copper ions under prevailing conditions. Therefore, the increased water content of reverse micelles by increasing solvent to aqueous phase volume ratio leading to an increase in solubilization, could be no more effective. Furthermore, the maximum removal was found to be 88.44% at 0.199 [M] AOT concentration and 0.612 volume ratio under the specified hold values. The p-value was noted in Table 3 as 0.031 which showed significant interaction.

The cross interaction between AOT concentration (B) and pH (C) of the solution was depicted in Fig. 11j. It was clear that AOT concentration affected the percentage removal of copper ions more significantly than pH of the solution. Further at higher pH (> 9.43), the percentage removal could not exceed 60% at any AOT concentration which means that at higher pH in the feed solution, the effect of AOT concentration on the percentage removal of copper ions decreased. This was submitted to the fact that copper ions might have got partially neutralized by hydroxyl ions at a higher pH causing decreased electrostatic attraction between copper ions and AOT surfactant. This led to a decrease in the solubilization of copper ions in the reverse micelles formed by anionic surfactant. Moreover, the percentage removal was found to be 88% at 0.199 [M] AOT concentration and 3.1 pH under 30 mg/L copper ion concentration, 0.6 volume ratio and 1 g/100 mL NaCl concentration.

CONCLUSIONS

The effect of various operating parameters *viz* copper ion concentration, AOT concentration, solution pH, organic to aqueous phase volume ratio, and NaCl concentration on percentage removal was studied experimentally. Moreover, in order to understand the process systematically, the design of the experiment using response surface methodology through central composite design was implemented for the optimization of process parameters. Copper ion concentration, AOT concentration, solution pH, organic to aqueous phase volume ratio, and

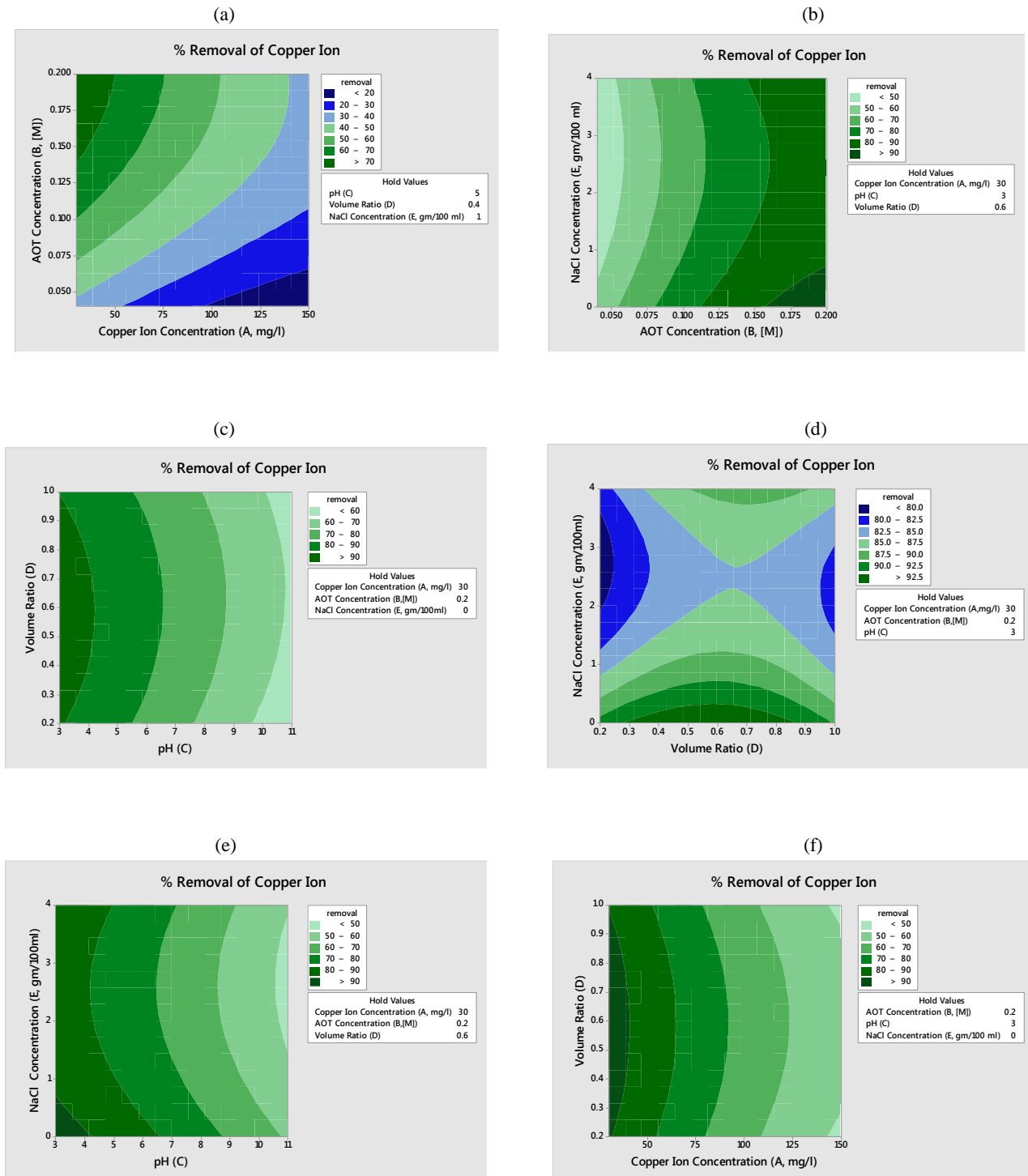


Fig. 11: Interaction plots for percentage removal of copper ions. [(a): AOT Concentration and Copper Ion Concentration, (b): NaCl Concentration and AOT Concentration, (c): Volume Ration and pH, (d): NaCl Concentration and Volume Ratio, (e): NaCl Concentration and pH, (f): Volume Ratio and Copper Ion Concentration, (g): pH and Copper Ion Concentration, (h): NaCl Concentration and Copper Ion Concentration, (i): Volume Ratio and AOT Concentration, and (j): pH and AOT Concentration.

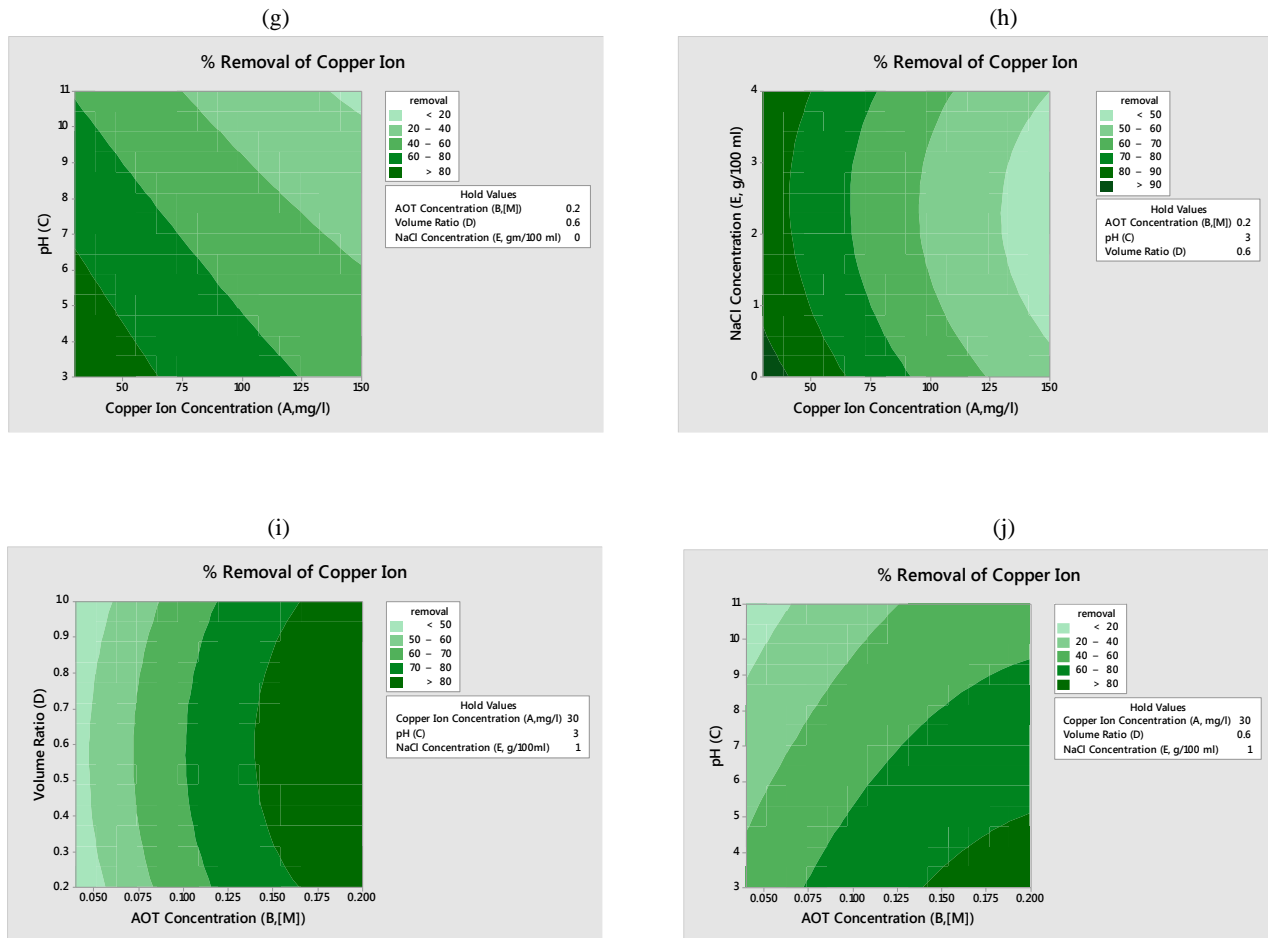


Fig. 11: Interaction plots for percentage removal of copper ions. [(a): AOT Concentration and Copper Ion Concentration, (b): NaCl Concentration and AOT Concentration, (c): Volume Ratio and pH, (d): NaCl Concentration and Volume Ratio, (e): NaCl Concentration and pH, (f): Volume Ratio and Copper Ion Concentration, (g): pH and Copper Ion Concentration, (h): NaCl Concentration and Copper Ion Concentration, (i): Volume Ratio and AOT Concentration, and (j): pH and AOT Concentration. (Continued)]

NaCl concentrations were considered in the range of 30-150 mg/L, 0.04-0.2 [M], 3-11, 0.2-1.0, and 0-4 g/100 mL respectively. The optimum conditions for the percentage removal of copper ions were found to be 30 mg/L copper ion concentration, 0.20 [M] AOT concentration, 3.12 pH, 0.57 organic to aqueous phase volume ratio, and 0.134 g/100 mL NaCl concentration. A non-linear regression model was developed for the analysis of the percentage removal of copper ions from wastewater. The obtained model was validated with experimental data and found to be best fitted with an R-square value being 0.9838. Moreover, residuals for the percentage removal of copper ions had fallen in the permissible range of ± 10 . From the analysis of variance and percentage contribution, it was concluded that copper ion AOT concentration

and solution pH were highly significant operating parameters. The significance of square, as well as cross interaction parameters, were also identified on the percentage removal of copper ions.

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REFERENCES

- [1] Baghel R., Kalla S., Upadhyaya S., Chaurasia S.P., Singh K., [CFD Modeling of Vacuum Membrane Distillation for Removal of Naphthol Blue Black Dye from Aqueous Solution Using COMSOL Multiphysics](#), *Chemical Engineering Research and Design*, **158**: 77-88 (2020).

- [2] Baghel R., Upadhyaya S., Chaurasia S.P., Singh K., Kalla S., [Optimization of Process Variables by the Application of Response Surface Methodology for Naphthol Blue Black Dye Removal in Vacuum Membrane Distillation](#), *Journal of Cleaner Production*, **199**: 900–915 (2018).
- [3] Baghel R., Upadhyaya S., Singh K., Chaurasia S.P., Gupta A.B., Dohare R.K., [A Review on Membrane Applications and Transport Mechanisms in Vacuum Membrane Distillation](#), *Reviews in Chemical Engineering*, **34(1)**: 73–106 (2017).
- [4] Barakat M.A., [New Trends In Removing Heavy Metals from Industrial Wastewater](#), *Arabian Journal of Chemistry*, **4(4)**: 361–377 (2011).
- [5] Bilal M., Shah J. A., Ashfaq T., Gardazi S.M.H., Tahir A.A., Pervez A., Haroon H., Mahmood Q., [Waste Biomass Adsorbents for Copper Removal From Industrial Wastewater-A Review](#), *Journal of Hazardous Materials*, **263**: 322–333 (2013).
- [6] Camarillo R., Llanos J., García-Fernández L., Pérez Á., Cañizares P., [Treatment of Copper \(II\)-Loaded Aqueous Nitrate Solutions by Polymer Enhanced Ultrafiltration and Electrodeposition](#), *Separation and Purification Technology*, **70(3)**: 320–328 (2010).
- [7] Chang S. H., [Vegetable Oil as Organic Solvent for Wastewater Treatment in Liquid Membrane Processes](#), *Desalination and Water Treatment*, **52(1–3)**: 88–101 (2014).
- [8] Cui K. L., Yuan X. Z., Zeng G. M., Liang Y. S., Han Z. H., Zhang S., Peng X., [Application of Biosurfactant on The Construction of Reversed Micelle and the Optimization of its Microenvironment](#), *Zhongguo Huanjing Kexue/China Environmental Science*, **31(9)**: 1444–1450 (2011).
- [9] Durantini A.M., Darío Falcone R., Silber J.J., Mariano Correa N., [More Evidence on the Control of Reverse Micelles Sizes. Combination of Different Techniques as a Powerful Tool to Monitor AOT Reversed Micelles Properties](#), *Journal of Physical Chemistry B*, **117(14)**: 3818–3828 (2013).
- [10] Egorova K.S., Ananikov V.P., [Toxicity of Metal Compounds: Knowledge and Myths](#), *Organometallics*, **36(21)**: 4071–4090 (2017).
- [11] Ferreira G.F.D., Souza D.R.Q., Lima R., Lobato A.K.C.L., Silva A.C.M., Santos L.C.L., [Novel Glycerin-Based Microemulsion Formulation for Enhanced Oil Recovery](#), *Journal of Petroleum Science and Engineering*, **167**: 674–681 (2018).
- [12] Fu F., Wang Q., [Removal of Heavy Metal Ions from Wastewaters: A Review](#), *Journal of Environmental Management*, **92(3)**: 407–418 (2011).
- [13] Fuglestad B., Gupta K., Wand A.J., Sharp K.A., [Characterization of Cetyltrimethylammonium Bromide/ Hexanol Reverse Micelles by Experimentally Benchmarked Molecular Dynamics Simulations](#), *Langmuir*, **32(7)**: 1674–1684 (2016).
- [14] Goswami V., Upadhyaya R., Meher S.K., [Column Study for Adsorption of Methylene Blue Dye using Azadirachta indica Adsorbent](#), *Asian Journal of Water, Environment and Pollution*, **17(4)**: 47–52 (2020).
- [15] Halim S.F.A., Chang S.H., Morad N., [Extraction of Cu\(II\) Ions from Aqueous Solutions by Free Fatty Acid-Rich Oils as Green Extractants](#), *Journal of Water Process Engineering*, **33**(September 2019): 100997 (2020).
- [16] Hu H., Li X., Huang P., Zhang Q., Yuan W., [Efficient Removal of Copper From Wastewater by Using Mechanically Activated Calcium Carbonate](#), *Journal of Environmental Management*, **203**: 1–7 (2017).
- [17] Italiana C., Caselli M., Mangone A., Pellegrino T., Traini A., [Selective Transition Metal Extraction by Reverse Micelles](#), (2004).
- [18] Kalla S., Upadhyaya S., Singh K., Baghel R., [Experimental And Mathematical Study of Air Gap Membrane Distillation for Aqueous HCl Azeotropic Separation](#), *Journal of Chemical Technology and Biotechnology*, **94(1)**: 63–78 (2019).
- [19] Lépori C.M.O., Correa N.M., Silber J.J., Falcone R.D., [How the Cation 1-Butyl-3-Methylimidazolium Impacts the Interaction Between the Entrapped Water and the Reverse Micelle Interface Created with an Ionic Liquid-Like Surfactant](#), *Soft Matter*, **12(3)**: 830–844 (2016).
- [20] Martínez-Quiroz M., López-Maldonado E.A., Ochoa-Terán A., Oropeza-Guzman M.T., Pina-Luis G.E., Zeferino-Ramírez J., [Innovative Uses of Carbamoyl Benzoic Acids in Coagulation-Flocculation's Processes of Wastewater](#), *Chemical Engineering Journal*, **307**: 981–988 (2017).

- [21] Mousavi S.J., Parvini M., Ghorbani M., [Adsorption of Heavy Metals \(Cu²⁺ and Zn²⁺\) on Novel Bifunctional Ordered Mesoporous Silica: Optimization by Response Surface Methodology](#), *Journal of the Taiwan Institute of Chemical Engineers*, **84**: 123–141 (2018).
- [22] Neto A.A.D., Fernandes M.R., Neto E.L.B., Dantas T.N.C., Moura M.C.P.A., [Alternative Fuels Composed by Blends of Nonionic Surfactant with Diesel and Water: Engine Performance and Emissions](#), *Brazilian Journal of Chemical Engineering*, **28(3)**: 521–531 (2011).
- [23] Noah N.F.M., Jusoh N., Othman N., Sulaiman R.N.R., Parker N.A.M.K., [Development of Stable Green Emulsion Liquid Membrane Process via Liquid–Liquid Extraction to Treat Real Chromium from Rinse Electroplating Wastewater](#), *Journal of Industrial and Engineering Chemistry*, **66**: 231–241 (2018).
- [24] Orellano M.S., Porporatto C., Silber J.J., Falcone R.D., Correa N.M., [AOT Reverse Micelles as Versatile Reaction Media for Chitosan Nanoparticles Synthesis](#), *Carbohydrate Polymers*, **171**: 85–93 (2017).
- [25] Pandit P., Basu S., [Removal of Organic Dyes from Water by Liquid-Liquid Extraction Using Reverse Micelles](#), *Journal of Colloid and Interface Science*, **245(1)**: 208–214 (2002).
- [26] Pandit P., Basu S., [Removal of Ionic Dyes from Water by Solvent Extraction Using Reverse Micelles](#), *Environmental Science and Technology*, **38(8)**: 2435–2442 (2004).
- [27] Peng X., Xu H., Yuan X., Leng L., Meng Y., [Mixed Reverse Micellar Extraction and Effect of Surfactant Chain Length on Extraction Efficiency](#), *Separation and Purification Technology*, **160**: 117–122 (2016).
- [28] Sankaran R., Bong J.H., Chow Y.H., Wong F.W.F., Ling T.C., Show P.L., [Reverse Micellar System in Protein Recovery-A Review of the Latest Developments](#), *Current Protein & Peptide Science*, **20(10)**: 1012–1026 (2019).
- [29] Senske M., Xu Y., Bäumer A., Schäfer S., Wirtz H., Savolainen J., Weingärtner H., Havenith M., [Local Chemistry of the Surfactant's Head Groups Determines Protein Stability in Reverse Micelles](#), *Physical Chemistry Chemical Physics*, **20(13)**: 8515–8522 (2018).
- [30] Siu P.C.C., Koong L.F., Saleem J., Barford J., McKay G., [Equilibrium and Kinetics of Copper Ions Removal from Wastewater by ion Exchange](#), *Chinese Journal of Chemical Engineering*, **24(1)**: 94–100 (2016).
- [31] Solomon F., [Impacts of copper on aquatic ecosystems and human health](#), *Mining.Com Magazine*, January, **9-11**: 25–28 (2009).
- [32] Tanda B.C., Oraby E.A., Eksteen J.J., [Recovery of Copper from Alkaline Glycine Leach Solution Using Solvent Extraction](#), *Separation and Purification Technology*, **187**: 389–396 (2017).
- [33] Upadhyaya S., Singh K., Chaurasia S.P., Baghel R., Singh J.K., Dohare R.K., [Sensitivity Analysis and Taguchi Application in Vacuum Membrane Distillation](#), *Membrane Water Treatment*, **9(6)**: 435–445 (2018).
- [34] Upadhyaya S., Singh K., Chaurasia S.P., Dohare R.K., Agarwal M., [Mathematical and CFD Modeling of Vacuum Membrane Distillation for Desalination](#), *Desalination and Water Treatment*, **57(26)**: 11956–11971 (2016a).
- [35] Upadhyaya S., Singh K., Chaurasia S. P., Dohare R. K., Agarwal M., [Recovery and Development of Correlations for Heat and Mass Transfer in Vacuum Membrane Distillation for Desalination](#), *Desalination and Water Treatment*, **57(55)**: 26886–2689 (2016b).
- [36] Verma S.P., Sarkar B., [Rhamnolipid Based Micellar-Enhanced Ultrafiltration for Simultaneous Removal of Cd\(II\) and Phenolic Compound from Wastewater](#), *Chemical Engineering Journal*, **319**: 131–142 (2017).