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Recovery of copper from synthetic solution by efficient technology: Membrane separation with response surface methodology

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Abstract

Heavy metals are toxic in nature as declared by the World Health Organisation. Excess concentration of heavy metals causes harmful affect and alters the physicochemical characteristics of surrounding environmental parameters. Copper is an important heavy metal present in the aquatic environment, including wide industrial applications, and is an essential factor in animal metabolism. To recover and reduce copper concentration from aqueous medium an attempted has been made with membrane technology. In this research work ultra filtration, nano filtration and reserve osmosis have been used. At optimum conditions 4.49 g/L initial concentration, 0.72 m^3/h inlet flow rate, 40 bar working pressure were obtained for maximum recovery (40.977 g/min) of copper at pH 6.8 with reverse osmosis. To achieve this, 27 experimental runs were developed according to central composite design and analysed. The value of $R^2 > 0.91$ for the obtained quadratic model indicates the high correlation between observed or the experimental value of response and response value predicted by the mathematical model. This implies that the experimental data correlated very well with the quadratic model chosen for the analysis.

Keywords: Copper concentration; Data analysis; Metal recovery; Working pressure; Toxicity

1. Introduction

Copper (Cu) is a naturally occurring element [1]. It is a transitional metal and occurs in nature in four oxidation states: elemental copper Cu (0) (solid metal), Cu (I) cuprous ion, Cu (II) cupric ion, and rarely Cu (III) [2]. Copper oxide is used in agriculture as a fungicide to protect coffee, cocoa, tea, banana, citrus, and other plants from major fungal leaf and fruit diseases such as blight, downy mildew, and rust [3]. It is also available as copper sulphate in salt and metal form and is highly soluble in water therefore it is easy to distribute in the environment and has been used as an aquatic herbicide and algaecide since 1950 [4]. Including it is a highly toxic in nature metal which is found as pollutant in water that mainly originates from chemical manufacturing and processing industries. Copper enters into the environment through sources such as natural and anthropogenic [5]. The contagion of air and water by copper is contributed from mining and metallurgy industries, electroplating industries etc [6]. It is a metal of choice for technologists and is an important engineering metal with a wide range of industrial applications such as in copper forming industries, plumbing, electroplating, in manufacture of wires for various industries namely electrical, electronics, automotive, electrical appliances, white goods etc., and in alloys such as brass, bronze and gunmetal [7]. Apart from industrial use copper is a necessary trace component required for humans for its function in the production of enzyme and bone development. But the excessive intake of copper causes headache, nausea and kidney failure [8].

To recover copper from different contaminated sources of air, water and soil, different methods have been suggested like chemical precipitations [9], adsorption [10], aqueous sodium alginate solution [11], ion-exchange [12], electrocoagulation [13,14] and membrane technology [15]. However, each recovery process itself requires resource consumption and generates some forms of impact [16]. Among these processes, membrane technology has shown good result for the removal of heavy

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Table 1
Membranes used in the experiments and their specifications.

Membrane type	Average working pressure (bar)	Internal diameter	Length (m)	Effective length (m)
AFC 99	30	12.5	1.20	1.10
AFC 30	20	12.5	1.20	1.10
FB 200	6	12.5	1.20	1.10

Table 2
Factors and levels of the experimental design for membrane separation.

Factors	Level 1(−1)	Level 2(0)	Level 3(1)
X_1 (Concentration (mg/L)	700	2500	4500
X_2 (Inlet flow rate (m^3/h))	0.36	0.62	0.72
X_3 (Working pressure (bar))	25	30	40

metal [17], nitrate containing wastewater [18], ammonia [19], pesticide [20], phenol [21], industries like distillery effluent [22], electroplating [23], pulp and paper industry [24] etc. Membrane separation processes are now being used as conventional treatment for water and industrial wastewater [25]. Recently membrane filtration has received considerable attention for the treatment of heavy metal (copper, zinc, lead etc) and valuable material (gold and silver) containing wastewater [26]. The separation of toxic metal ions using sorbents and membranes with doped ligands has also been introduced due to its high selectivity and removal efficiency, increased stability, and low energy requirements, and it is promising for improving the environmental quality [27]. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater.

Therefore an investigation has been made to recover the copper ion from water and wastewater by membrane technology and to prevent environmental degradation. The purpose of this study is to evaluate the performance of the RO, UF and NF processes in removing copper from water and wastewater. The effects of flow rate, initial metal concentration and working pressure were optimised by using response surface methodology.

2. Materials and method

2.1. Chemical

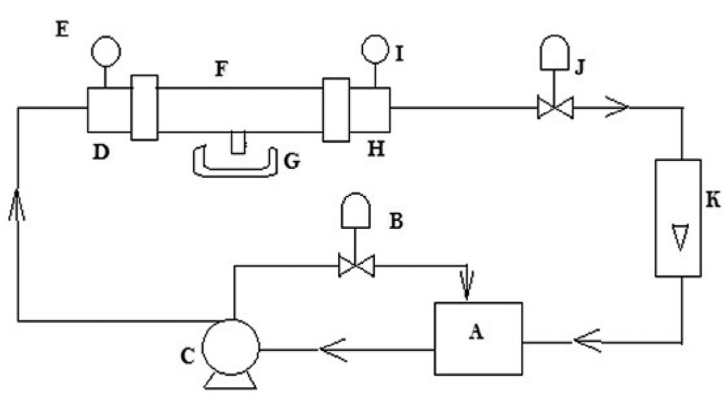
All laboratory grade chemicals – NaCN (sodium cyanide), NaOH (sodium hydroxide), HCL (hydrochloric acid) – were used without further treatment and were supplied by Himedia Laboratories Pvt., Mumbai, India. Stock solution of copper (1000 mg/L) was prepared in 1 L of deionised water by dissolving 3.929 g of copper sulphate ($CuSO_4{\cdot}5H_2O$) and used for all experiments with required addition of salt.

2.2. Membrane modules and machines

Experiment has been conducted with Arm-field lab scale reverse osmosis having ultra-filtration unit (UF/RO). Three different membranes – AFC 99(RO), AFC 30(NF), and FB 200(UF) – of different average working pressure and similar dimensions are listed in Table 1. The FT18 is fully self-contained in a mobile cabinet having tubular module which can accommodate six 1.2 meter PCI membrane. The unit has a pack of both reverse osmosis, nanofiltration and ultrafiltration unit membranes. The arrangement is shown in Fig. 1.

2.3. Experimental design

The statistical method of factorial Design of Experiment eliminates systematic errors with an estimate of the experimental error and minimises the number of experiments [28]. In this study response surface methodology (RSM) was used to optimise the three-level factorial design and operating variables: concentration (X_1), inlet flow rate (X_2) and working pressure (X_3). Their ranges and levels are mentioned in Table 2. The independent variables range and levels were chosen after preliminary experiments. RSM is suitable for fitting a quadratic surface and it helps to optimise the interaction between effective parameters with a minimum number of experiments, which is given in Table 3. The response and the corresponding parameters are modelled with analysis of variance (ANOVA). It is



A-Feed Tank, B-Bypass Valve, C-Booster Pump, D-Short Piece, E-Upstream Pressure gauge, F-Hollow Fiber Module, G-Permeate Collector, H-Short Piece, I-Downstream Pressure gauge, J-Needle Valve, K-Rotameter

Fig. 1. Experimental setup of copper recovery.

Table 3
Full factorial design used for the membrane.

S.N.	X_1 [mg/L]	X_2 [g/min]	X_3 [bar]	Y [g/min]
1	4200	0.36	25	17.28
2	4200	0.36	30	20.71
3	4200	0.36	40	27.67
4	4200	0.62	25	16.12
5	4200	0.62	30	25.4
6	4200	0.62	40	35.1
7	4200	0.72	25	8.617
8	4200	0.72	30	30.02
9	4200	0.72	40	43.79
10	2500	0.36	25	14.95
11	2500	0.36	30	19.75
12	2500	0.36	40	25.64
13	2500	0.62	25	17.93
14	2500	0.62	30	23.21
15	2500	0.62	40	32.62
16	2500	0.72	25	18.26
17	2500	0.72	30	24.03
18	2500	0.72	40	34.81
19	700	0.36	25	16.5
20	700	0.36	30	19.96
21	700	0.36	40	27.65
22	700	0.62	25	18.99
23	700	0.62	30	22.77
24	700	0.62	40	33.23
25	700	0.72	25	15.27
26	700	0.72	30	22.13
27	700	0.72	40	33.58

used to calculate the statistical parameters by means of response surface methods. For statistical calculations, the levels for the three main variables were coded according to the following relationship

$$Y = f\left(x_1, x_2, x_3 \ldots\ldots\ldots x_n\right) \quad (1)$$

where Y is the response of the system and x_i is the variable of action called factors. The aim is to optimise the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors [29]. If the variance analysis indicates that overall curvature effect is significant, further experiments are carried out to develop a second order model. The second order model is defined as follows so as to facilitate calculations:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n}\sum_{j>1}^{n} b_{ij} x_i x_j \quad (2)$$

where Y is the predicted response, b_0 is the constant coefficient, b_i is the linear coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the interaction coefficient, and x_i, x_j are the coded values of the permeated mass flux variables. The quality of the fit polynomial model was expressed by the coefficient of determination R^2 and its statistical significance was checked by the F-test. Model terms were selected or rejected based on the P value (probability) with 99% confidence level. Three-dimensional plots were obtained based on the effects of the levels of three factors.

2.4. Experimental process

The membrane behaviour was established from the permeate flux and the rejection of the system. In order to value both aspects, different permeate samples were extracted by the designed experimental procedure. To determine suitable membrane type, from three different membranes, recovery process was carried out with each membrane. The experiments was done by using the different copper concentrations, at the average working pressure of each membrane, average inlet flow rate of 10 L/min, neutral pH range of 7.3 and constant temperature 30 °C. The permeate quality and permeate flux were taken as response variables. To determine the optimum pH selected membrane run for pH range from pH 3 to 11 and keeping all the other parameters (pressure, inlet flow rate and concentration) constant. Permeate quality and permeate flux were taken as response variables to check the optimum pH. For determining the optimum values of the other factors full factorial method of experimental design with three levels was done (Table 2). The combination of three factors, each with three levels, gives twenty seven different combinations of runs (Table 3).

3. Result and discussion

3.1. Selection of membrane

The experiment was carried out to determine the best suitable membrane for the copper recovery with NF, UF and RO. The experiments were run at similar inlet flow rate 10 L/min, pH 7.3, feed concentration 4500 mg/L and average working pressures taken as mentioned in Table 1. Before analysing the copper recovery potential, it important to know the copper concentration in permeates. This can be done by measuring the absorbance of different copper concentrations prepared in the laboratory using the photospectrometer at a wavelength of 580 nm. The absorbance values will be plotted against the concentration of copper, as shown in Fig. 2. The copper concentration (mg/L) with absorption value (580 nm) by NF, UF and RO is mentioned in Table 4 and the result obtained in terms of permeated flux is mentioned in Table 5. The percentage recovery of copper concentration was calculated from Eq. (3); it can be seen from Table 5 that for the permeate from the Ultra filtration FB 200 module, copper recovery was 96.86%, and colour of the copper solution is visible which makes it unfit for the copper recovery. The permeates from nano filtration AFC 30 module was 97.56% and reverse osmosis AFC 99 module was 99.8%, both have nearly similar flow rates; however considering the copper recovery potentials RO shows better than NF. Moreover the end use requirement of the wastewater for potable/drinking water purpose makes the RO membrane preferable than others. Average values of the membranes are shown below with their percentage recovery.

$$\text{Percentage recovery} = \left[1 - C_{\text{permeate}} / C_{\text{inlet}}\right] \quad (3)$$

3.2. Optimisation of pH

The pH of sample has a significant role in reduction and recovery of copper. The input parameters are held constant at

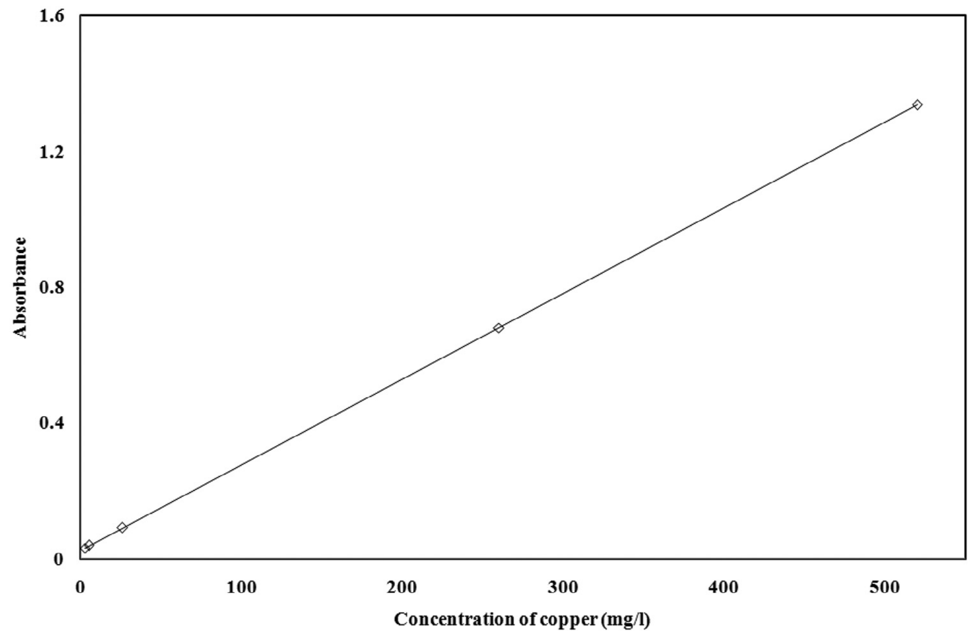


Fig. 2. Absorbance of copper at wavelength of 580 nm.

feed concentration of 3500 mg/L, inlet flow rate of 0.36 m^3/h, and working pressure of 40 bar to investigate the variations in permeate flux at different pH ranges. The adjustment of pH was carried out with 1 M sodium hydroxide and 1 N hydrochloric acid. The copper recovery with respect to different pH is mentioned in Table 6 and variation in permeated mass flux was represented in Fig. 3. As shown in Table 6 recovery of copper increases or decreases with pH. The maximum permeated flux of 151.0901 g/min and copper recovery of 0.99989 were observed at pH 6.8, which is considered as the optimum pH for further analysis. From the result it is crystal clear that the optimum pH is around the neutral range, hence the excessive alkalinity and acidity faced have to be brought down to the state of neutrality by adding appropriate acid and base solution respectively. The permeate flux increases starting from the very acidic pH to the neutral point where it reaches maximum and decreases as the alkalinity increases. It may be due to the fact that speciation of metals differs at different pH ranges, as shown in Fig. 4. In this experiment copper metal valence state exists at different pH ranges. From Fig. 4 it can be observed that the copper recovery increases with increasing the pH of aqueous phase, the optimum pH is 6.8 at which the $CuSO_4$ started to disappear and converted to $Cu_3SO_4(OH)_4$ complex. The pH range easily tells us what kind of copper ion can be found at different pH ranges and helps for monitoring of copper in industrial effluent discharges. For optimum yield the pH of the sample needs to be adjusted before running the membrane.

Table 4
Absorbance of different membranes with copper concentration (580 nm).

Absorbance (580 nm)	Membrane type	Concentration (mg/L)
0.38	UF	146.36
0.37	UF	144.22
0.35	UF	135.17
0.34	NF	130.20
0.30	NF	113.86
0.29	NF	109.90
0.28	RO	107.74
0.12	RO	45.46
0.13	RO	49.31

3.3. *Second order polynomial equation and data analysis*

The RSM (Design Expert 6.0.8 software) was used to analyse the relationship of three variables (initial concentration, flow rate and working pressure) and process responses (permeated mass flux). The regression equation coefficients were calculated and the data were fitted with second order polynomial equation. The final empirical models in terms of coded and actual factors after excluding the insignificant terms for permeated mass flux (Y) are mentioned in Eq. (4)

Table 5
Comparative parameters for membrane selection.

Membrane type	Average working pressure (bar)	Inlet flow rate (L/min)	pH	Recovery potential	Colour visibility	Permeate flow rate (mL/min)
AFC 99 (RO module)	40	10	7.3	0.998	Colourless	23.34
AFC 30 (NF Module)	20	10	7.3	0.9756	Colourless	30.27
FB 200 (UF module)	6	10	7.3	0.9686	Visible	60.57

Table 6
Optimisation of pH from reverse osmosis.

S. No.	pH	Permeate mass flux (g/min)	Copper recovery (mass %)
1	3.5	106.01	0.99965
2	5	104.16	0.99974
3	6.8	151.09	0.99989
4	7.9	106.79	0.99983
5	10	93.09	0.99965
6	12	86.98	0.99961

$$\text{Permeated mass flux } (Y) = 25.921 + 1.086X_1 + 2.599X_2 + 8.051X_3 + 0.839X_1^2 - 0.842X_2^2 - 1.751X_3^2 + 0.725X_1X_2 + 1.613X_1X_3 + 2.735X_2X_3 \quad (4)$$

Positive sign in front of the terms indicates synergistic (acting together) effect, whereas negative sign indicates antagonistic (resistance) effect. To determine the significance of the quadratic model analysis of variance was performed and the result is mentioned in Table 7. Based on the statistical analysis

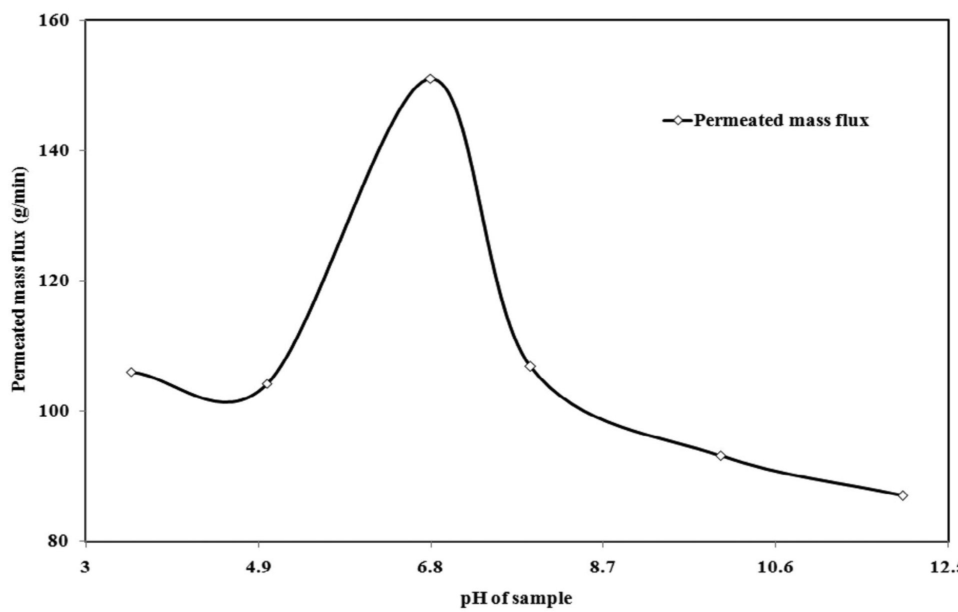


Fig. 3. Effect of pH on permeated mass flux at feed concentration of 3500 mg/L, inlet flow rate of 0.36 m3/h, and working pressure of 40 bar.

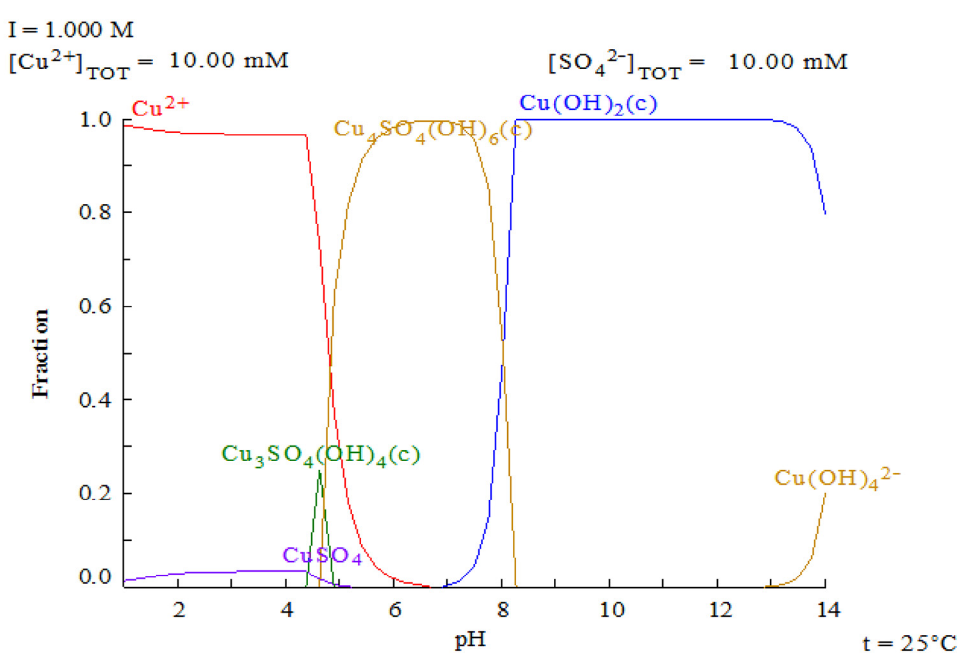


Fig. 4. Effect of pH on the complex formation and copper ion species.

Table 7
Analysis of variance.

Source	Sum of squares	DF	Mean square	F value	Prob > F	Remark
Model	1516.462	9	168.496	20.750	<0.0001	Significant
X_1	15.717	1	15.717	1.936	0.1821	
X_2	118.636	1	118.636	14.610	0.0014	Significant
X_3	1123.810	1	1123.810	138.397	<0.0001	Significant
X_1^2	3.036	1	3.036	0.374	0.549	
X_2^2	2.573	1	2.573	0.317	0.5809	
X_3^2	14.011	1	14.011	1.725	0.2065	
X_1X_2	5.712	1	5.712	0.703	0.4133	
X_1X_3	27.461	1	27.461	3.382	0.0835	
X_2X_3	99.210	1	99.210	12.218	0.0028	Significant
Residual	138.044	17	8.120			
Cor Total	1654.506	26				

the value of "P > F" with less than 0.0500 is preferable. As shown, Model F-value of 20.75 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In this case X_2, X_3 and X_2X_3 are significant model terms at 99% confidence level. The quality of the model developed was evaluated based on the correlation coefficient value (R^2) of 0.91 and the value varies from 0.0 to 1.0, with higher values being preferable. This result indicates that the fitted model could explain 91.70% of the variability. The accuracy and general ability of the polynomial model were reliable [30]. In addition, Pred-R^2 (0.76) is in reasonable agreement with the AdjR^2 (0.87). "Adeq Precision" measures the signal to noise ratio and a ratio greater than 4.0 is desirable in a model. The ratio obtained was 14.53; it indicated that an adequate signal was proved in this model.

Data were also analysed to check the normality of the residuals. A normal probability plot or a dot diagram of these residuals is shown in Fig. 5(a). It can be observed that the actual values are distributed close to the straight line (y = x) with relatively high values of R^2. Fig. 5(b) shows the relationship between the actual and predicted values of Y for permeated mass flux by RO. It can be seen (Fig. 5(b)) that the developed model is adequate because the residuals for the prediction of each response are minimum and the data points lie close to the diagonal line.

3.4. *Effect of input parameters*

The Central Composite Design (CCD) was used to study the effects of the variable working pressures (25–40 bar), flow rate (0.36–0.72m^3/h) and initial concentration (700–4500 mg/L) towards the permeated mass flux (response). Experiments according to the design were carried out and relevant results are shown in Fig. 6(a)–(c).

From Fig. 6(a) it can be observed that permeate flow rate proportionally increases with inlet flow rate, concentrations and working pressures. The reasons for permeate flow rate increase with inlet flow rate may be due to the increase of the stress exerted on the wall of the tubular membrane, which is proportional to the flow velocity and has a positive impact on permeate flow rate and also the reduction of concentration polarisation effect (mass transfer phenomena) by the high velocity flow (usually flow at high velocity has turbulent nature) [31]. Concentration polarisation is the concentration gradient of material on the high pressure side of the membrane surface created by the less immediate re-dilution of solutes left behind as water permeates through the membrane. The material concentration in this boundary layer exceeds the concentration of the bulk water. This phenomenon impacts the permeate flux quantity by increasing the osmotic pressure at the membrane's surface and increasing the probability of scale development. Increasing the velocity (turbulence) of the flowing stream helps to reduce the concentration polarisation [32].

Applied pressure affects both the permeate flux and solute rejection of RO membranes. As osmosis is the flow of water across a membrane from the dilute side towards the concentrated solution side, reverse osmosis technology involves application of pressure to the feed stream to overcome the natural osmotic pressure [33]. Pressure in excess of the osmotic pressure is applied to the concentrated solution and the flow of water is reversed. From Fig. 6(b) it can be observed that

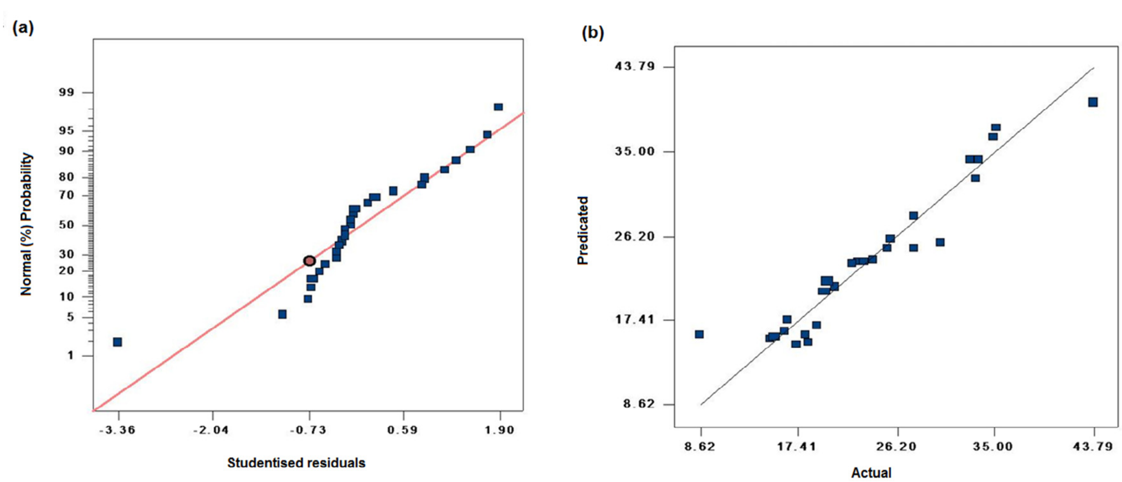


Fig. 5. The normality of the residuals: (a) normal probability; (b) actual and predicted.

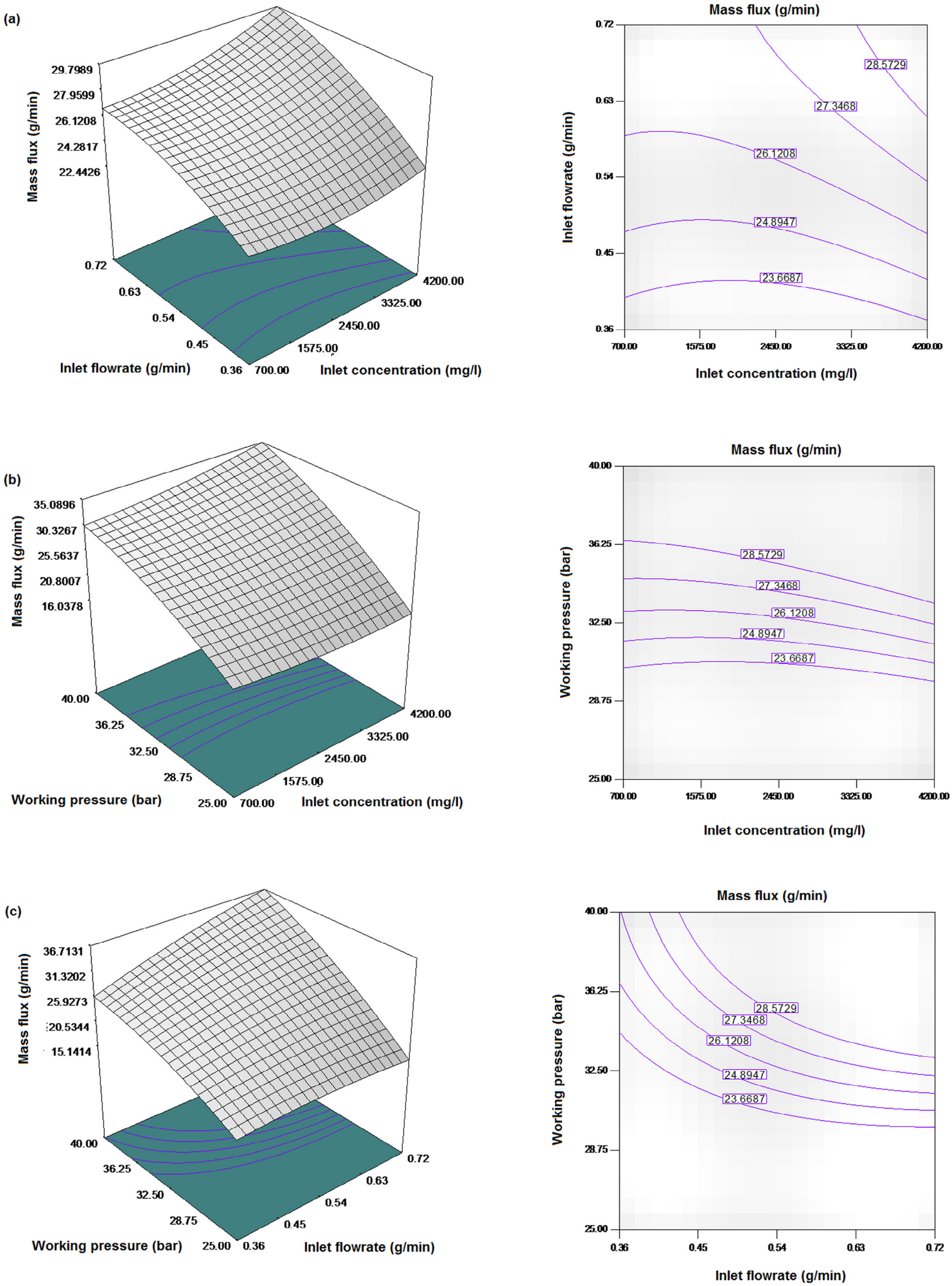


Fig. 6. Three dimensional surface and contour plot of (a) initial concentration, (b) flow rate and (c) working pressure with respect to permeated mass flux at optimum condition.

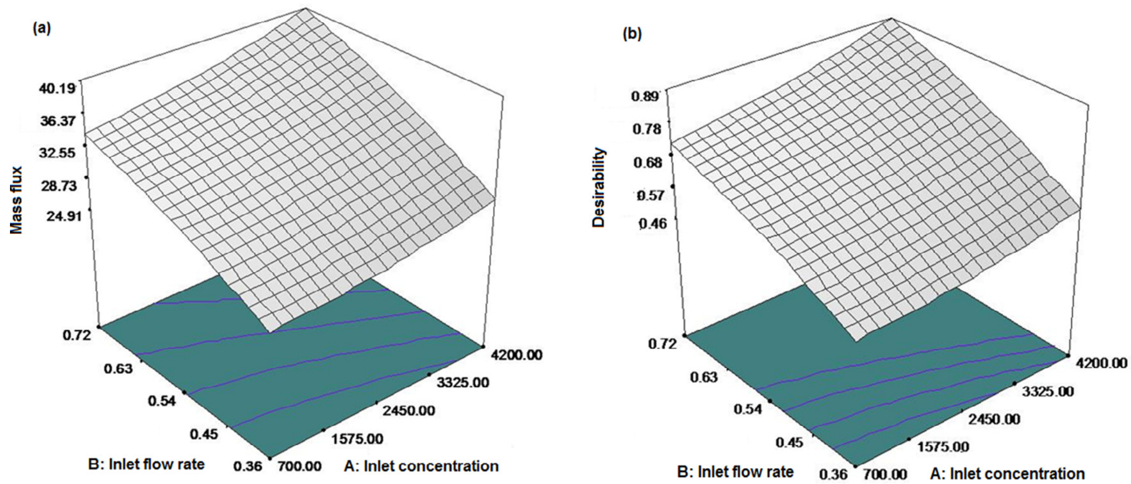


Fig. 7. Optimisation of parameters: (a) permeated mass flux; (b) desirability.

working pressure is directly proportional to the permeate flow rate. Besides the slope of the graphs for this case are steeper than the permeate flow rate Vs inlet flow rate graphs; this shows that working pressure has more effect on the permeate flow rate than inlet flow rate. Increasing the applied/feed pressure also results in increased solute rejection (copper salt recovery). This may be due to RO membranes being imperfect barriers to dissolved salts in the feed. As feed pressure is increased, the solute passage is increasingly over come as the solution is pushed through the membrane at a faster rate than solute can be transported. However, there is an upper limit to the amount of solute that can be excluded via increasing feed pressure. Above a certain pressure level, solute rejection no longer increases and some solute flow remains coupled with water flowing through the membrane [34].

In Fig. 6(c) the slope of the lines on these graphs are in a slight deviation from horizontal line which indicates that the effect of feed copper concentration on permeate flow rate is not as significant as the above two parameters. In addition the trend of the curves for all cases is increasing to some extent and then decreasing except some lines which may due to reading or any errors incorporated like experimental leaks and pressure oscillations in factor adjustment [30]. This shows that until to some critical concentration the increasing of feed copper concentration has a little positive effect on the permeate flux but above that critical concentration it has a negative effect on the permeate flux. The reason for this can be the fast clogging of the membrane pores by the copper particles; because in that case inter particle interaction between the copper particles is relatively low, which may lead them to occupy any available free space easily and quickly. So the increase in concentration in such cases will have a positive impact on permeate flow rate by increasing inter particle interaction, which reduces quickly, and easily clogging of membrane pores. But after some critical concentration the dominating factor on the permeate flow rate quantity will not be the clogging or unclogging of the membrane pore rather it will be the concentration polarisation effect that becomes dominant [35]. If permeate flux is increased (and feed pressure remains constant), the copper salts in the residual feed become more concentrated and the natural osmotic pressure will increase until it is as high as the applied feed pressure. This can negate the driving effect of feed pressure, slowing or halting the reverse osmosis process and causing permeate flux and percentage recovery to decrease and even stop [36].

The optimum condition for maximum permeated mass flux and desirability is shown in Fig. 7(a) and (b). Finally it can be concluded that at optimum conditions of 4499.99 mg/L initial concentration, 0.72 m^3/h inlet flow rate, and 40 bar working pressure, 40.98 g/min maximum permeated flux was observed. The desirability of study was found to be 0.92.

4. Conclusion

A systematic experimental design based on the response surface methodology was used to determine the optimal condition for copper recovery. The results showed that the three factors considered in this study played an important role on recovery process. The optimum conditions 4499.99 mg/L initial concentration, 0.72 m^3/h inlet flow rate, 40 bar working pressure were obtained for maximum recovery (40.98 g/min) of copper at pH 6.8. Among ultra filtrations and nano filtrations reverse osmosis has shown maximum performance of 99.80% at 40 bar working pressure, 10 L/min flow rate, pH 7.3 and 23.24 mL/min permeated flow. A second-order polynomial equation was adequate to predict the permeability as the response. An R^2 value of 0.91 ensures a sufficient adjustment of the model with the experimental data. Lastly, the outcome of this research study is that reverse osmosis technology is suitable for metal recovery and reduction from ground, surface, domestic and industrial wastewater. The response surface methodology (RSM) was an appropriate method to optimise the operating parameters.

References

[1] L. Kiaune, N. Singhasemanon, Pesticidal copper (I) oxide: environmental fate and aquatic toxicity, Rev. Environ. Contam. Toxicol. 213 (2011) 1–26, doi:10.1007/978-1-4419-9860-6_1.

[2] P.G. Georgopoulos, A. Roy, M.J. Yonone-Lioy, R.E. Opiekun, P.J. Lioy, Copper: environmental dynamics and human exposure issues, J. Toxicol. Environ. Health B Crit. Rev. 4 (2001) 341–394.

[3] HSDB (Hazardous Substances Data Bank), U.S. National Library of Medicine, 2008. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. (Accessed 8 July 2008).

[4] EPA (Environmental Protection Agency Office of Pesticide Programs), Wisconsin Department of Natural Resources, Box 7921 Madison, WI 53707-7921, 2012.

[5] C. Reimann, P. DeCaritat, Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors, Sci. Total Environ. 337 (1) (2005) 91–107.

[6] S. Das. Batch study removal of copper ions from water by using ion exchange resin (Doctoral dissertation), National Institute of Technology, Rourkela, 2014.

[7] D.T. Burns, N. Chimpalee, M. Harriott, Applications of a slotted tube atom trap and flame atomic absorption spectrophotometry: determination of antimony in copper based alloys, Fresenius J Anal. Chem. 349 (7) (1994) 527–529.

[8] M. Robson, Methodologies for assessing exposures to metals: human host factors, Ecotoxicol. Environ. Saf. 56 (1) (2003) 104–109.

[9] A. Janin, F. Zaviska, P. Drogui, J.F. Blais, G. Mercier, Selective recovery of metals in leachate from chromated copper arsenate treated wastes using electrochemical technology and chemical precipitation, Hydrometallurgy 96 (4) (2009) 318–326.

[10] N. Feng, X. Guo, S. Liang, Adsorption study of copper (II) by chemically modified orange peel, J. Hazard. Mater. 164 (2) (2009) 1286–1292.

[11] F. Wang, X. Lu, X.Y. Li, Selective removals of heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) from wastewater by gelation with alginate for effective metal recovery, J. Hazard. Mater. 308 (2016) 75–83.

[12] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage. 92 (3) (2011) 407–418.

[13] D. Salari, A. Niaei, A. Khataee, M. Zarei, Electrochemical treatment of dye solution containing CI Basic Yellow 2 by the peroxi-coagulation method and modeling of experimental results by artificial neural networks, J. Electroanal. Chem. 629 (1) (2009) 117–125.

[14] S. Fogarasi, F. Imre-Lucaci, Á. Imre-Lucaci, P. Ilea, Copper recovery and gold enrichment from waste printed circuit boards by mediated electrochemical oxidation, J. Hazard. Mater. 273 (2014) 215–221.

[15] D.J. Son, W.Y. Kim, C.Y. Yun, D. Chang, D.G. Kim, S.O. Chang, et al., Combination of electrolysis technology with membrane for wastewater treatment in rural communities, Int. J. Electrochem. Sci. 9 (2014) 4548–4557.

[16] R.S. Rubin, M.A.S. de Castro, D. Brandão, V. Schalch, A.R. Ometto, Utilization of life cycle assessment methodology to compare two strategies for recovery of copper from printed circuit board scrap, J. Clean. Prod. 64 (2014) 297–305.

[17] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arabian J. Chem. 4 (4) (2011) 361–377.

[18] M. Shrimali, K.P. Singh, New methods of nitrate removal from water, Environ. Pollut. 112 (3) (2001) 351–359.

[19] X. Tan, S.P. Tan, W.K. Teo, K. Li, Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J. Memb. Sci. 271 (1) (2006) 59–68.

[20] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, et al., Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination 202 (1) (2007) 156–181.

[21] A. Bodalo, E. Gomez, A.M. Hidalgo, M. Gómez, M.D. Murcia, I. López, Nanofiltration membranes to reduce phenol concentration in wastewater, Desalination 245 (1) (2009) 680–686.

[22] U.K. Rai, M. Muthukrishnan, B.K. Guha, Tertiary treatment of distillery wastewater by nanofiltration, Desalination 230 (1) (2008) 70–78.

[23] A.G. Boricha, Z.V.P. Murthy, Preparation, characterization and performance of nanofiltration membranes for the treatment of electroplating industry effluent, Sep. Purif. Technol. 65 (3) (2009) 282–289.

[24] Z.B. Gonder, S. Arayici, H. Barlas, Advanced treatment of pulp and paper mill wastewater by nanofiltration process: effects of operating conditions on membrane fouling, Sep. Purif. Technol. 76 (3) (2011) 292–302.

[25] J. Radjenovic, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Water Res. 42 (14) (2008) 3601–3610.

[26] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: a review, J. Hazard. Mater. 158 (2) (2008) 228–256.

[27] I. Zawierucha, C. Kozlowski, G. Malina, Immobilized materials for removal of toxic metal ions from surface/groundwaters and aqueous waste streams, Environ. Sci. Process. Impacts 18 (4) (2016) 429–444.

[28] D.C. Montgomery, Design and Analysis of Experiments, third ed., Wiley, New York, 2001.

[29] K.J. Cronje, K. Chetty, M. Carsky, J.N. Sahu, B.C. Meikap, Optimization of chromium (VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride, Desalination 275 (1) (2011) 276–284.

[30] H. Zheng, C.H.E.N. Jingjing, W.A.N.G. Biyu, Z.H.A.O. Suying, Recovery of copper ions from wastewater by hollow fiber supported emulsion liquid membrane, Chin. J. Chem. Eng. 21 (8) (2013) 827–834.

[31] Q. Guan, H. Wang, J. Li, X. Li, Y. Yang, T. Wang, Optimization of an electrocatalytic membrane reactor for phenolic wastewater treatment by response surface methodology, J. Water Sustain. 3 (1) (2013) 17–28.

[32] L. Feini, G. Zhang, M. Qin, H. Zhang, Performance of nanofiltration and reverse osmosis membranes in metal effluent treatment, Chin. J. Chem. Eng. 16 (3) (2008) 441–445.

[33] A.L. Ahmad, B.S. Ooi, A study on acid reclamation and copper recovery using low pressure nanofiltration membrane, Chem. Eng. J. 156 (2) (2010) 257–263.

[34] L. Cifuentes, I. García, P. Arriagada, J.M. Casas, The use of electrodialysis for metal separation and water recovery from $CuSO_4$–H_2SO_4–Fe solutions, Sep. Purif. Technol. 68 (1) (2009) 105–108.

[35] M.G. Khedr, Membrane methods in tailoring simpler, more efficient, and cost effective wastewater treatment alternatives, Desalination 222 (2008) 135–145.

[36] K.K. Tetala, D.F. Stamatialis, Mixed matrix membranes for efficient adsorption of copper ions from aqueous solutions, Sep. Purif. Technol. 104 (2013) 214–220.