

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Process optimization studies on copper adsorption onto 5Å molecular sieves using response surface methodology.

Srinivasa Rao V<sup>1\*</sup>, Ramachandra Murthy ChV<sup>2</sup>, Kalyani G<sup>1</sup> and Joga Rao H<sup>1</sup>.

<sup>1</sup>Department of Chemical Engineering, GMR Institute of Technology, Rajam, India

<sup>2</sup>Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam, India

### ABSTRACT

Adsorptive removal of Copper ( $\text{Cu}^{2+}$ ) from aqueous solution was investigated using 5Å molecular sieves as an adsorbent. A  $2^3$  full-factorial central composite design was successfully employed for batch experimental design and analysis of the results. The combined effects of pH, initial concentration, and adsorbent dosage on the  $\text{Cu}^{2+}$  adsorption were studied. An empirical model was developed and validated applying ANOVA analysis incorporating interaction effects of all parameters and optimized using response surface methodology (RSM). The results were analyzed statistically and the optimum conditions identified as: pH – 5.0, initial copper concentration - 55 mg/L and adsorbent dose - 15 g/L. The square model terms were highly significant ( $F = 25.19$  and  $P = 0.00$ ) than Linear ( $F = 12.81$  and  $P = 0.001$ ) and interactive ( $F = 0.27$  and  $P = 0.848$ ) model terms. Based on high 't'- and low 'P' value (< 0.05), both the linear terms and the squared terms i.e., pH ( $X_1$ ), initial copper concentration ( $X_2$ ) and adsorbent dosage ( $X_3$ ) shows significant effect; while in front of interaction effects are found to be in- significant effect on the percentage copper removal. 5Å Molecular sieves, when utilized under the optimum condition, may be a viable and effective treatment option for copper removal from industrial waste water.

**Keywords:** Molecular sieves; Adsorption; Optimization; Copper; Response surface methodology; Central Composite Design (CCD), Equilibrium

*\*Corresponding author*

## INTRODUCTION

Heavy metals discharged by the industries into the environment through various effluents are non-biodegradable and toxic even at very low concentration, resulting in their smooth entry into the food chain system [1-2]. In particular, pollution due to  $\text{Cu}^{2+}$  arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agro-chemicals [3]. The excess intake of  $\text{Cu}^{2+}$  by human being leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression [4-5]. The permissible limit of  $\text{Cu}^{2+}$  in drinking water according to World Health Organization (WHO) is 2.0 mg/L [5]. Therefore, removal of  $\text{Cu}^{2+}$  from contaminated water and wastewater is of paramount importance before their discharge into the environment.

Techniques for removal of heavy metals from wastewater include precipitation, ion exchange, adsorption, coagulation, evaporation and reverse osmosis [6]. Among these, adsorption is by and large considered as one of the best technique for the removal of heavy metals due to its high efficiency, easy handling, availability of different adsorbents, and cost-effectiveness [7-12]. Activated carbon is the most efficient classical way as it removes more than 99% of certain metal ions but the cost of its production is high and it cannot be regenerated and recycled [20]. However, it requires chelating agents to enhance the performance, leading to the increase in the treatment cost [13]. Therefore, exploitation of low-cost adsorbents for efficient removal of heavy metals has become a challenge before the scientists.

In the quest for efficient adsorbents for heavy metal removal, Molecular sieves may be better alternative because of their commercial availability and possibility of regeneration. Zeolites or Molecular sieves offer a variety of adsorption selectivity based on molecular size, molecular affinity for the sieve crystal surface, and shape of the molecule. In addition, they possess uniform and precise pore size. Using this type of system is exceptionally uncomplicated for diminishing impurities to practically indiscernible levels compared to other liquid separation systems; the results can be more accurate and repetitive. The ease of use and superior efficiency when compared to other adsorption systems makes the molecular sieve system as a most popular engineering solution. They have the advantage of a multiple purpose, highly porous, high capacity alkali metal alumino-silicates [14]. Zeolites have high cation exchange capacity (100–300 meq/100 g), depending upon the amount of  $\text{Al}^{3+}$  that replaces  $\text{Si}^{4+}$  in the structure [15]. Typical applications of molecular sieves are in drying of highly polar alcohols, drying of unsaturated hydrocarbons (ethylene, propylene, butadiene etc.), static dehydration of gas or air filled insulated glass units, gas drying, cracked gas drying and modern catalyst for many commercial chemical products synthesis such as catalytic cracking in petroleum refining. Molecular sieves possess high thermal stability, large inner surface area (600-1000  $\text{m}^2/\text{g}$ ) although its external surface area is small (1% of total surface area). They possess three-dimensional frame works, the pore volume is about 30% of the total volume. Due to the aforementioned characteristics and their homogeneous pore size distribution, they possess the ability to act as powerful adsorbents. Besides, they can also be regenerated and reused. In the past, natural zeolite and synthetic molecular sieves have been exploited for the adsorptive removal of heavy metals.

Adsorption process is dependent on several factors *viz.* adsorbent dosage, adsorbent particle size, contact time, temperature, initial solution concentration, pH, and ionic strength of solution.

This study aims at investigating the feasibility of molecular sieves for the removal of  $\text{Cu}^{2+}$  from aqueous solution. Central composite design (CCD) based response surface methodology (RSM) was employed to investigate the individual effects of the initial  $\text{Cu}^{2+}$  concentration, pH, and adsorbent dosage and their interactions, which are considered as the most critical parameters affecting the removal of  $\text{Cu}^{2+}$  from aqueous solution. RSM is an effective statistical technique used to design complex experiments and analyze the effects of independent variables on the system response. The main objective is the determination of optimum conditions within the operating specifications [16-19].

## MATERIALS AND METHODS

### Adsorbent

Molecular sieves of pore size 5Å, 1.5mm cylindrical pellets were used as adsorbent, and their Physical properties are listed in Table 1. Laboratory grade Molecular sieves were used directly as received from the supplier (Merck, Mumbai) in conducting the experiments.

**Table 1: Physical properties of molecular sieves used in the experiments**

Properties	Technical data (units)
Shape	Pellets
Mean Particle Diameters	1.5 mm
Nominal Pore Size	5Å
Bulk Density	44 lb/Ft <sup>3</sup>
Average Crushing Strength Under Increasing Pressure	12(lb)
Equilibrium Water Capacity (Theoretical)	21.7% w/w
Water Content (as shipped)	1.5% w/w (max.)
Heat of Adsorption (max.)	1,800 Btu/lb H <sub>2</sub> O
Specific Heat (approx.)	0.23 Btu/lb/°F
Recommended Temp. of Regeneration (°F)	400 – 600

### Synthetic effluent preparation

An accurate weight of 3.9291 g of CuSO<sub>4</sub>.5H<sub>2</sub>O (S. D. Fine-chem. Ltd, Boisar) was dissolved in 1L of distilled water to produce 1000 mg/L of copper of the synthetic standard solution. The sample copper solution for all the experiments was prepared by diluting this stock solution with distilled water to achieve the desired concentration levels. Every time the stock and standard solution have been prepared; the solutions were shaken enough to ensure that each solution was homogeneous. All chemicals were used without further purification.

### Batch adsorption experiment and copper analysis

Batch experiments were conducted in a series of 250 ml conical flasks containing 100mL of known (concentration) copper solutions. Predetermined concentrations of adsorbents were added to these flasks as per the experimental design. The required pH (Systronics, Ahmadabad.) was adjusted using 0.1N H<sub>2</sub>SO<sub>4</sub> or 0.1N NaOH (Fisher scientific India Pvt. Ltd. Mumbai). All the experiments were performed in an orbital shaker (REMI-CIS-24 plus, 230V, 50Hz), maintained at 28°C and 200 rpm. Based on the results from preliminary kinetic studies, stirring time of 130 min. was selected as the equilibrium time. Upon completion of the experiments, the separation of the liquid from the solid phase was followed by filtration of the supernatant using Whatman<sup>®</sup> 42(2.5µm) filter paper. Copper ion concentrations were measured using atomic absorption spectrophotometer (AAS) (Perkin Elmer Analyst 400 model, India) at λ<sub>max</sub>= 327.4 nm. Experiments were performed according to the central composite design (CCD) matrix given in Table 3. The response was expressed as % removal of copper (RE %) using the following equation:

$$RE (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

Where, C<sub>o</sub> and C<sub>e</sub> are the initial and final or equilibrium concentrations of copper in the solution (mg/L), respectively. All the experimental analyses were carried out in duplicate and the mean values were reported. Adsorption equilibrium time was determined through experiments with known initial copper concentration (26.50 and 96.14 mg/L), at the initial solution pH of 5.5 and at room temperature. The kinetics showed that the equilibrium could be reached, for copper adsorption by 130 min. (Fig. 1).

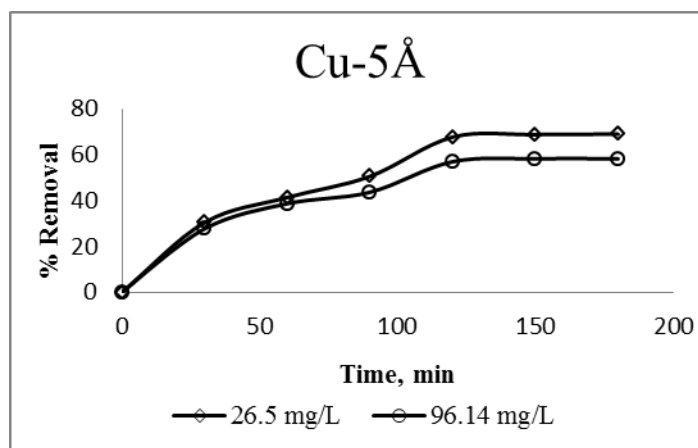


Figure 1: Time course profiles of Copper adsorption.

### Factorial experimental design and optimization of parameters

Based on the preliminary studies and literature, pH ( $X_1$ ), initial Copper concentrations ( $X_2$ ) and adsorbent dose ( $X_3$ ) were chosen as independent variables and the copper removal efficiency (RE %) as the dependent response variable. Independent variables, experimental range and levels of copper removal are given in Table 2. A  $2^3$ -full factorial CCD experimental design [34], with six replicates at the center point and thus a total of 20 experiments were employed in this study. The center point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property. Independent variables, experimental range and levels of copper removal are given in Table 3. For statistical calculations, the variables  $X_i$  were coded as  $x_i$  according to the following relationship:

$$X_i = \frac{x_i - x_0}{\Delta x} \times 100 \quad (2)$$

Where,  $X_i$  is the coded value of variable  $i$ ,  $x_i$  the uncoded real value of an independent variable,  $x_0$  the value of  $X_i$  at the center point, and  $\Delta x$  is the step change between levels 0 and 1. The behavior of the system can be explained by the following quadratic equation,

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (3)$$

The optimum values of the test variables were obtained using the numerical point prediction tool in MINITAB (Version 16, PA, USA). The optimum values of the process variables were first obtained in coded units and then converted to uncoded, i.e. real, units using Equation (1). Furthermore, for the sake of verification of the optimized conditions, the models were also optimized using a Monte-Carlo optimization technique, as mentioned elsewhere [32]. The experimental design of the batch experiments and results for the adsorption of copper are presented in Table 3.

## RESULTS AND DISCUSSION

### Development of regression model equation

Central Composite Design (CCD) was used to develop a correlation between the % removal and variables affecting the adsorption of copper from aqueous solution onto 5Å molecular sieves. The complete experimental range and levels of independent variables are given in Table 2. The output data given by MINITAB (Based on the range of variables chosen) are shown in Table 3; and runs 15-20 are at the center point were used to determine the experimental error. The quadratic model was selected as suggested by the software. Experiments were planned to obtain a quadratic model consisting of  $2^3$  trials plus a star configuration ( $\alpha = \pm 1.682$ ) and three replicates at the center point. The design of this experiment is given in Table 3, together with the experimental and predicted results. The maximum adsorption of copper was found to be 97.05 and at the optimal conditions suggested by the design. The model expressed by Eq. (4) where, the

variables take their coded values, represents % removal of copper (Y) as a function of initial copper solution pH ( $X_1$ ), copper solution concentrations ( $X_2$ ) and adsorbent dose ( $X_3$ ).

$$Y = 94.612 - 2.389X_1 - 1.899X_2 + 1.794X_3 - 2.821X_1^2 - 1.537X_2^2 - 4.075X_3^2 + 0.521X_1X_2 - 0.062X_2X_3 + 0.413X_1X_3 \quad (4)$$

The predicted value of the %removal of adsorption of copper onto adsorbent using the above equation is given Table 3, along with the experimental value. The coefficients of the regression models calculated are listed in Table 4 for the adsorption of copper, which contains three linear, three square and three interaction terms. The significance of each coefficient was determined by student's t test and 'p' values, which were also listed in Table 4. The efficiency of the model in predicting the % removal of adsorption was evaluated by the coefficient of determination ( $R^2$ ), standard error, t-values, p-values and Fisher's 'F' test value. The  $R^2$  value provides a measure of variability in the observed response that can be explained by the experimental process variables and their interactions. The  $R^2$  was found to be 0.919 for copper, which indicates high correlation between the observed and predicted values.

**Table 2: Experimental variables and levels investigated by central composite design**

Variables	Cu- Coded levels				
	-1.682	-1	0	1	1.682
pH ( $X_1$ )	3	3.8	5	6.2	7
Initial Conc. ( $X_2$ , mg/L)	10	28.25	55	81.75	100
Adsorbent dosage ( $X_3$ , g/L)	5	9	15	21	25

**Table 3: Experimental design matrix and results for adsorption of Copper**

Run	Independent variables			% RE of Copper	
	$X_1$	$X_2$	$X_3$	Observed	Predicted
1	-1	-1	-1	91.07	89.55
2	1	-1	-1	83.36	83.85
3	-1	1	-1	84.19	83.88
4	1	1	-1	81.48	80.27
5	-1	-1	1	93.36	92.43
6	1	-1	1	88.32	86.49
7	-1	1	1	91.04	88.42
8	1	1	1	85.18	84.56
9	-1.682	0	0	88.48	90.65
10	1.682	0	0	81.76	82.61
11	0	-1.682	0	92.23	93.46
12	0	1.682	0	85.27	87.07
13	0	0	-1.682	79.58	80.07
14	0	0	1.682	83.56	86.10
15	0	0	0	97.05	94.61
16	0	0	0	95.50	94.61
17	0	0	0	94.98	94.61
18	0	0	0	92.50	94.61
19	0	0	0	94.27	94.61
20	0	0	0	93.89	94.61

A consistent model predicts the response with reasonable accuracy when compared to the experimental data. Fig. 2 show the parity plot of copper, which compares the experimental value with the predicted values obtained from the model which indicates the good agreement between the two. The data points cluster around the diagonal line in Fig. 2 confirm the good fit of the model, because the deviations between the experimental and predicted values are less.

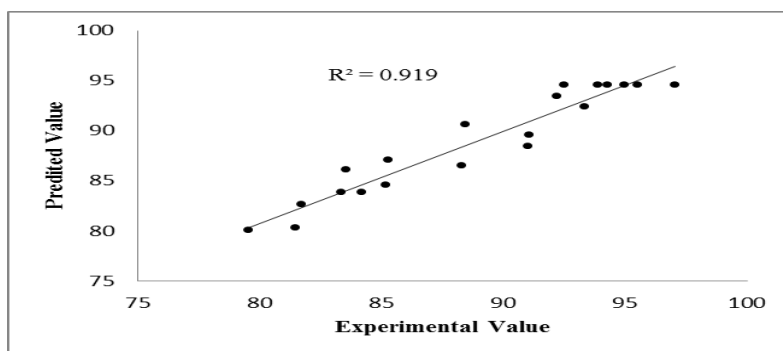


Figure 2: Parity plot for the experimental and predicted value of copper removal efficiency (%).

**Effect of initial copper concentration, adsorbent dose and pH on % removal of copper**

In order to study the combined effect of the factors, experiments were performed for different combinations of the physical parameters using statistically designed experiments (Table 3). The initial copper concentration range was studied between 10-100 mg/L; adsorbent dose was taken in between 5-25 g/L and the initial solution pH in the range 3-7.

Apart from the linear effect of the parameters on % removal of copper, the RSM also gives insight into the squared and interaction effects of the parameters. These analyses were performed by means of Fisher’s *F*-test and Student *t*-test. The ANOVA of the regression model demonstrated that it is highly significant (Table 5), as evident from the *F*-value (12.76) and the low probability value ( $P = 0.000$ ). Values of  $P < 0.05$  indicated that the model terms are highly significant (at 95% confidence interval). In addition, the lack of fit of the model was insignificant ( $P = 0.147$ ). “*F*-value of Lack-of-fit” (2.73), implies the significance of the model correlation between the variables and process response for copper removal. For all the parameters (Table 5), the squared variable effects, were more significant ( $F= 25.19$ ) than the linear parameter effects ( $F= 12.81$ ) on %copper removal; while the interaction effects are not significant ( $F= 0.27$ ). The Student *t*-test was used to determine the significance of the regression coefficients of the parameters. In general, the larger the magnitude of ‘*t*’ and smaller the value of ‘*P*’; the more significant is the corresponding Coefficient term [33]. From the Table 4, it is evident from the results that the squared effects of all independent variables for copper were also highly significant, because of their *P*-values were less than 0.05; the *P* values for pH ( $X_1$ ), concentration ( $X_2$ ) and adsorbent dosage ( $X_3$ ) were found to be 0.0, 0.02 and 0.0 respectively. In addition, the linear effects of pH ( $X_1$ ), concentration ( $X_2$ ) and adsorbent dosage ( $X_3$ ) are also significant( $P<0.05$ ) and are able to influence the %removal of copper. The magnitude of *t*-value gives the positive or negative influence on the dependent variable. The coefficient of adsorbent dosage ( $X_3$ ) showed the greatest linear positive effect and the negative effect by the other two variables, i.e. pH ( $X_1$ ) and concentration ( $X_2$ ) (Table 4) on copper removal. All the squared terms, pH ( $X_1$ ), concentration( $X_2$ ) and adsorbent dosage ( $X_3$ ) shows a negative influence on the adsorption of copper. All interaction effects between process variables were found to be statistically insignificant (*P*-values were  $>0.05$ ).

Table 4: Estimated regression coefficients and corresponding *t*- and *P*- values of the models.

Factor	% RE of Copper		
	Coefficient	't' – value	'P' – value
Constant	94.612	109.932	0
$X_1$	-2.389	-4.184	0.002
$X_2$	-1.899	-3.325	0.008
$X_3$	1.794	3.141	0.01
$X_1^2$	-2.821	-5.076	0
$X_2^2$	-1.537	-2.765	0.02
$X_3^2$	-4.075	-7.33	0
$X_1X_2$	0.521	0.699	0.501
$X_2X_3$	-0.062	-0.083	0.935
$X_1X_3$	0.413	0.554	0.592

**Table 5: Analysis of variance (ANOVA) for response surface quadratic model for adsorption of copper.**

Source	Sum of squares	Degree of freedom	Mean square	F value	P value
Regression	511.243	9	56.805	12.76	0.000
Linear	171.139	3	57.046	12.81	0.001
X <sub>1</sub>	77.97	1	77.97	17.51	0.002
X <sub>2</sub>	49.231	1	49.231	11.06	0.008
X <sub>3</sub>	43.937	1	43.937	9.87	0.01
Square	336.535	3	112.178	25.19	0.000
X <sub>1</sub> <sup>2</sup>	78.614	1	114.721	25.76	0.000
X <sub>2</sub> <sup>2</sup>	18.666	1	34.047	7.65	0.02
X <sub>3</sub> <sup>2</sup>	239.255	1	239.255	7.65	0.000
Interaction	3.569	3	1.19	0.27	0.848
X <sub>1</sub> X <sub>2</sub>	2.174	1	2.174	0.49	0.501
X <sub>1</sub> X <sub>3</sub>	0.031	1	0.031	0.01	0.935
X <sub>2</sub> X <sub>3</sub>	1.364	1	1.364	0.31	0.592
Residual Error	44.52	10	4.453	–	–
Lack of fit	32.603	5	6.521	2.73	0.147
Pure Error	11.927	5	2.385	–	–
Total	555.772	19			

The response surface plots based on Equation (1), is more useful in understanding both the main and interaction effects of these variables, depicted in Fig. 3. The response surface graphs demonstrate the interaction of the process variables and determine the optimum level of each variable for maximum response. The contour plots are used to get a better understanding of the influence of independent variables and their interaction on the dependent variable. It represents the interactive effect of any two variables on the response variable, when the remaining variables kept constant. The shape of the surface plots indicates an interaction between the variables. The elliptical shape of the response surface curve indicates good interaction of two variables. Fig. 3 (a-c) are plotted between pH and initial concentration, pH and adsorbent dose, adsorbent dose and initial copper concentration, respectively. The response surface plot (Fig. 3a to 3c) had a clear peak, which indicated that the optimum conditions falls inside the design boundary. The maximum % removal of copper is indicated by the surface confined to the smallest curve of the plot with the other variable maintained at hold value [25]. For model design one variable is held at its intermediate level to check the interaction effect of the other two variables. It is evident from the elliptical nature of the contours that interaction between the individual variables is significant as shown in Fig. 3a to 3c. It is clear from the Fig. 3a that the combined effect of pH and the initial concentration on % removal, at constant adsorbent dose (15 g/L) is significant. It can be seen that the maximum removal efficiency of copper (>90%) was determined at a constant adsorbent dose (15g/L).

It can be seen from the Fig. 3a, 3b that the percentage removal increases very sharply with the increase in pH from 3 to 5; the less removal observed at low pH may be due to the availability of the high H<sup>+</sup> ion concentration and their higher mobility in the solution. Therefore adsorption of hydrogen ions is higher as compared to Cu<sup>2+</sup> ions [21]. Besides, it was explained that at lower pH value, the surface of the adsorbent is surrounded by H<sup>+</sup> ions, thereby preventing the metal ions from approaching the binding sites of the adsorbent [22]. This means that at the higher H<sup>+</sup> concentration, the adsorbent surface becomes more positively charged such that the attraction between adsorbent and metal cations is reduced [23]. In contrast, as the pH increases, more negatively charged surface becomes available, thus facilitating greater copper removal. It is commonly agreed that adsorption of metal cations increases with increasing pH as the metal ionic species become less stable in the solution. However, when the pH was greater than 5, there was a decrease in the adsorption capacity [26]. This may be due to the occurrence of copper precipitation. At this stage there are three species present in solution, Cu<sup>2+</sup> in very small quantities, Cu(OH)<sup>+</sup> and Cu(OH)<sub>2</sub> in large quantities [35]. These species might be adsorbed on the surface of adsorbent by ion exchange mechanism with the functional groups present in adsorbent or by hydrogen bonding.

The %removal of copper increased when the initial concentration was increased from 10 to 55 mg/L (Fig. 3a, 3c). The trend is the resultant of the progressive increase in the electrostatic interaction between the copper ions and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorption

sites were being covered as the metal ions concentration increases [31]. Besides, higher initial concentrations lead to an increase in the affinity of the copper ions towards the active sites [29]. However, a further increase in the initial concentration (>55mg/L) resulted in a decrease in %removal of copper. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species, at higher concentrations [30]. This indicates that the initial Copper concentration is an effective parameter to maximize the adsorption capacity.

The %removal of copper increased when the adsorbent dose was increased from 5 to 15g/L (Fig. 3b, 3c). This was due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at a higher dosage. It is plausible that with a higher dosage of adsorbent, there would be greater availability of exchangeable sites for metal ions [24]. Besides, the reduction in adsorbent dosage in the suspension at a given metal concentration enhances the metal/adsorbent ratio, and thus increases the metal uptake per unit adsorbent, as long as the latter is not saturated [35]. However, a further increase in adsorbent dosage (> 15 g/L) resulted in a decrease in %removal of copper. These results may be due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [27]. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal [28]

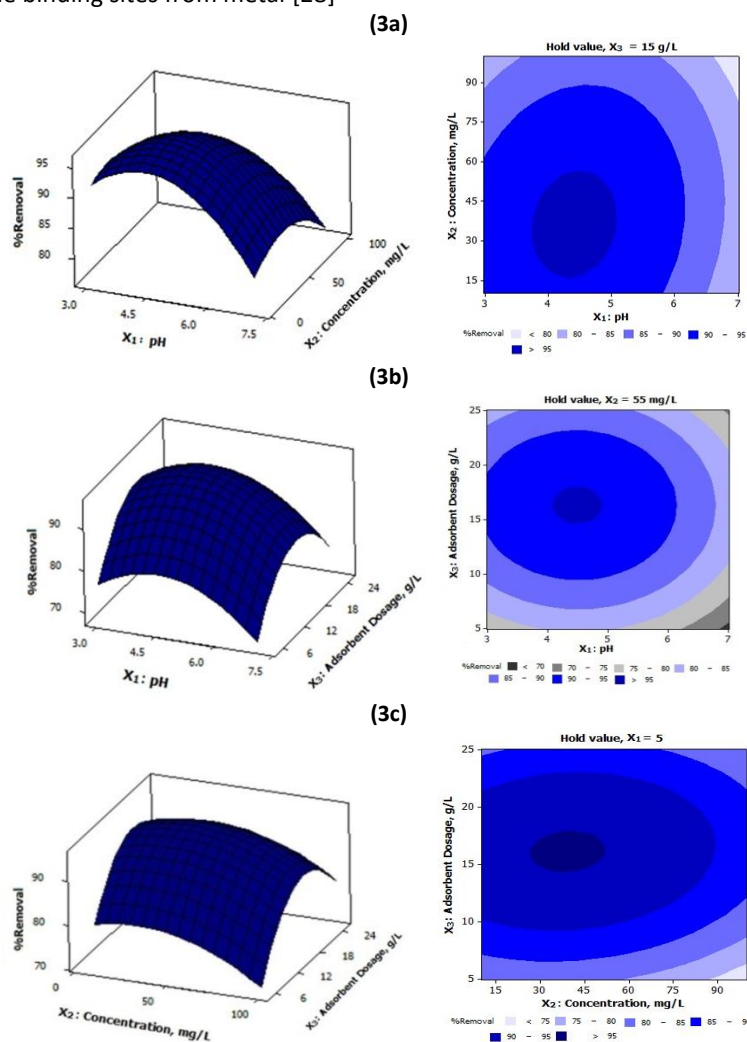


Figure 3: Response surface and contour plots showing (a) the effect of pH ( $X_1$ ), initial Copper concentration ( $X_2$ ) and their mutual interaction on % removal of Copper, with constant adsorbent dose ( $X_3$ ); (b) the effect of  $X_1$ ,  $X_3$  and their mutual interaction on % removal of Copper, with constant level of  $X_2$ ; (c) the effect of  $X_2$ ,  $X_3$  and their mutual interaction on % removal of Copper, with constant level of  $X_1$ .



### Optimization and confirmation experiment

One of the main aims of this study was to find the optimum process parameters to maximize the % removal of copper from the mathematical model equations developed in this study. The quadratic model equations were optimized using response optimizer to maximize % removal of copper within the experimental range studied. The optimum adsorption conditions determined for copper were pH - 5.0, initial copper concentration-55 mg/L and adsorbent dosage-15 g/L. The optimum values for copper removal were calculated from the regression model equation (1) using a Monte-Carlo technique and were in good agreement with the values obtained from MINITAB. Under optimal conditions, the model predicted a removal of copper is 94.61%. In order to confirm the validity of the statistical experimental strategy, batch experiments were performed under optimal conditions in duplicate. The calculated optima are in close agreement with the observed values of the Copper removal was 95.50%. The composite desirability value ( $D$ ) of predicted yield at optimized levels of variables was found to be close to 1 for copper ( $D=0.999$ ). The result shows that the regression models developed in this study resulted in good agreement between actual and predicted responses for the copper using 5Å molecular sieves as the adsorbent.

### CONCLUSIONS

The present work was focused on the optimization of key process parameters for improvement of copper removal from industrial wastewater using statistical methodology. The statistical design of the experiments was applied for optimizing the conditions of maximum removal of copper onto 5Å molecular sieves. The result data from ANOVA demonstrates that both the model was highly significant. Similarly, the experimental results showed for the copper removal, among all the variables, the squared effect of initial metal concentration had the greatest influence (copper:  $t = -2.765$ ,  $P = 0.02$ ), while in terms of linear effects, the adsorbent dose had the greatest influence (copper:  $t = 3.141$ ,  $P = 0.01$ ); thus demonstrating that the model terms are highly significant at 99% confidence interval. Accurate prediction of the maximum value of the experimental responses indicated that the quadratic model had been adequately selected (for copper adsorption) to describe the response surface within the experimental region. The RSM results indicated that (at the optimum conditions for maximizing copper removal) the predicted copper, removal efficiency was 94.61%. The predicted values were close to the experimental values of copper removal efficiency of 95.50%, obtained from the confirmation experiment. 5Å molecular sieves, when used under the optimum condition, may be a feasible and efficient treatment option for copper removal from industrial waste water.

### REFERENCES

- [1] Shi WY, Shao H.B, LiH, Shao MA, Du S, Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *J. Hazard. Mater.* 2009; 170:1–6.
- [2] Xuea Y, Houa H, Zhu S, Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag. *J. Hazard. Mater.* 2009; 162:391–401.
- [3] Xuejiang Wang, Xia Liang, Yin Wang, Xin Wang, Mian Liu, Daqiang Yin, Siqing Xia, Jianfu Zhao, Yalei Zhang, Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation. 2011.
- [4] Aman T, Kazi AA, Sabri MU, Bano Q, Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. *Colloids Surf. B Biointerfaces.* 2008; 63:116–121.
- [5] Gamze Turan N, Sermin Elevli, Başak Mesci, Adsorption of copper and zinc ions on illite: Determination of the optimal conditions by the statistical design of experiments. *Applied Clay Science.* 2011; 52:392–399.
- [6] Yi FC, Fu YB, Li YX, Composition and characterization of palygorskite in Guanshan with simulative Sr and Cs radio nuclides adsorpted. *Journal of China University of Mining & Technology.* 2007; 36(2): 271–276 (In Chinese).
- [7] Bhattacharya AK, Mandal SN, Das SK, Adsorption of Zn (II) from aqueous solution by using different adsorbents. *Chem. Eng. J.* 2006; 123:43–51.
- [8] Cheremisinoff P.N, *Handbook of Water and Wastewater Treatment Technology.* Marcel Dekker Inc., New York, 1995.
- [9] Ijagbemi CO, Baek MH, Kim DS. Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions. *J. Hazard. Mater.* 2009; 166:538–546.

- [10] Lin SH, Juang RS, Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *J. Hazard. Mater.* 2002; 92:315–326.
- [11] McKay G, Use of Adsorbents for the Removal of Pollutants from Wastewater, CRC Press, Tokyo, 1996.
- [12] Rousseau RW, Handbook of Separation Process Technology, Wiley-Interscience, New York, 1987.
- [13] Oliveira EA, Montanher SF, Andrade AD, Nobrega JA, Rollemberg MC, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. *Process. Bioche.* 2005; 40:3485–3490.
- [14] Krobba A, Nibou D, Amokrane A, Mekatel, Adsorption of copper (II) onto molecular sieves NaY, *Desalination and Water Treatment.* 2012; 37:31–37.
- [15] Pal DK, Wani SP, Sahrawat KL, Zeolitic soils of the Deccan basalt areas in India: their pedology and edaphology, *Current Science*, 2013; Vol. 105, No. 3.
- [16] Batalon JT, Madamba PS, Optimization of coir dust compaction using the response surface methodology approach. *J. Agric. Eng. Res.* 2001; 78:167–175.
- [17] Can MY, Yildiz E, Phosphate removal from water by fly ash: factorial experimental design. *J. Hazard. Mater.* 2006; B135:165–170.
- [18] Mallick N, Gupta S, Panda B, Sen R, Process optimization for poly(3- hydroxybutyrate-co-3-hydroxyvalerate) co-polymer production by *Nostocmuscorum*. *Biochem. Eng. J.* 2007; 37:125–130.
- [19] Ren J, Lin WT, Shen YJ, Wang JF, Luo XC, Xie MQ, Optimization of fermentation media for nitrite oxidizing bacteria using sequential statistical design. *Bioresour. Technol.* 2008; 99:7923–7927.
- [20] Umar Farooq, Janusz Kozinski A, Misbahul Ain Khan, Makshoof Athar, Biosorption of heavy metal ions using wheat based biosorbent *Bioresource Technology.* 2010; 101:5043–5053 .
- [21] Ajmal Rao M, Ahmad RAK, Ahmad R, Adsorption studies on Citrus reticulate (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. *Hazardous Materials.* 2000; 79:117-131.
- [22] Wong KK, Lee CK, Low KS, Haron MJ, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous Solutions. *Chemosphere.* 2003; 50:23-28.
- [23] Saeed A, Muhammed Iqbal, WaheedAkhtar M, Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *Hazardous Materials.* 2004; 117:65-73.
- [24] Babel S, Kurniawan TA, Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere.* 2004; 54:951-967.
- [25] Fourest E, Roux JC, Heavy metal biosorption by Fungalmycelial by-products: Mechanism and Influence of pH. *Applied Microbiology Biotechnology.* 1992; 37:399-403.
- [26] Mashitah MD, Zufadhly Z, Bhatia S, Ability of *Pycnoporoussanguineus* to remove copper ions from aqueous solution. *Artificial Cells, Blood Substitues and Immobilized Biotechnology.* 1999; 27 (5&6):429-433.
- [27] Garg VK, Gupta R, Yadav AB, Kumar R, Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresource Technology,* 2003; 89:121-124.
- [28] Pons MP, Fuste CM, Uranium uptake by immobilized cells of *Pseudomonas* strain EPS 5028. *Applied Microbiology Biotechnology.* 1993; 39:661-665.
- [29] Al-Asheh, Banat R, Al-Omari Z, Duvnjak, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater. *Cleaner Production.* 2003; 11:321-326.
- [30] Khalid N, Ahmad S, Toheed A, Ahmed J, Potential of rice husks for antimony removal. *Applied Radiation and Isotopes.* 2000; 52:31-38.
- [31] Laraous S, Meniai AH, Bencheikh Lehocine M, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination.* 2005; 185:483-490.
- [32] Ravikumar K, Pakshirajan K, Swaminathan T, Balu K, Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent, *ChemEng J.* 2005; 105: 131–138.
- [33] Montgomery DC, Design and Analysis of Experiments, 3rd edn. Wiley, New York, 1991.
- [34] Myers RH, Montgomery DC, Response surface methodology, 2nd ed. John Wiley & Sons Inc. 2002.
- [35] Elliot HA, Huang CP, *Water Resources.* 1981; 15:849.