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Optimization of copper adsorption by chemically modified fly ash using response surface methodology modeling

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ABSTRACT

Though copper is a necessary trace element but it can be toxic in higher concentration. Locally available fly ash was found to be low-cost adsorbent to remove copper from aqueous solution. Calcium oxide-treated fly ash was investigated in the study of scale up of copper removal. Response surface methodology (RSM) was used for the statistical optimization of the copper reduction process. A two-level-three-factor (2^3) full factorial central composite design with the help of Design Expert Version 7.0.0 (Stat Ease, USA) was used for the optimization of the copper adsorption process variables like: initial solution pH (3.5–5.5), initial copper concentration (15–50 mg/L), and contact time (45–90 min) and to evaluate the effects and interactions of process variables. The optimum reduction of copper was 99.16% at pH 3.98, 77.88 mg/L copper concentration, and 58.82 min of contact time. The percentage deviation between experimental and RSM model equation was 0.03%.

Keywords: Copper; Adsorption; Fly ash; Calcium oxide; Response surface methodology; Optimization

1. Introduction

Industrial wastewater contaminated with heavy metals has serious negative impacts on environment, because the heavy metals do not undergo biodegradation and cause bioaccumulation as well as biomagnifications.

Copper is present in maximum industrial effluents such as metal cleaning and plating baths, the fertilizer industry, electroplating, microelectronics, battery manufacture, metallurgical, etc. [1,2]. Though Copper is one of the important trace nutrients in all high plants and animals, but it may be harmful in high concentration. Marine life may be harmed due to high copper concentration in water [3,4]. The established methods of copper(II) removal from wastewaters are precipitation, ion exchange, electrolysis, reverse osmosis, adsorption using activated carbon, etc. but these processes have significant disadvantages. These methods require high capital and operating costs, high energy requirement, and also suffer from incomplete removal in some cases [5].

This study is focused on copper removal from aqueous solution using calcium oxide (CaO)-treated fly ash as an adsorbent. Fly ash is one of the residues generated in combustion and comprises the fine particles that rise with the flue gases. Primarily raw fly ash was unable to remove copper from aqueous solution in an effective percentage. Also raw fly ash increased the color intensity of copper solution, which caused trouble in spectrophotometrically copper concentration analysis. CaO was used to increase the sorption properties of low-cost fly ash converting fly ash to gypsum structures.

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Adsorption is a process where solute is removed from aqueous phase through the contact of solid adsorbent which has a special affinity for that particular solute [6].

The main advantage of adsorption process is cost effective, easily available sources, reformation of adsorbents and regeneration of metals from the adsorbents. Various types of natural and unreal adsorbents have been studied by various researchers for the removal of heavy metals. Different types of agro waste or plant-derived materials similar of rice husk, wheat shell, cereal chaff, sawdust, pine bark, etc. can be used to adsorb heavy metals [7–11].

Established batch adsorption studies demand the effect of individual parameters on the adsorption process has been investigated maintaining other process parameters such as initial solution pH, adsorbent dose, initial adsorbate concentration, temperature, agitation etc. constant at unspecified levels [12]. This approach cannot assure the combined effect of all the process parameters. For scale-up studies, formal batch process is time consuming, and requires a number of experiments to find out the optimum levels (which may be unreliable) thereby elevating the overall cost of the process.

These problems can be mitigated by optimizing all the process parameters collectively by statistical experimental design such as response surface methodology (RSM).

RSM is a combination of mathematical and statistical techniques used for better modernizing, and optimizing the processes and evaluate the relative significance of various process parameters even in the presence of complex parameter–parameter interactions [13,14].

The practical application of statistical methods for adsorption process demands less treatment time, minimum costs, and higher percentage yields [14].

Response surfaces, a graphical representation may be used to describe the individual and combined effect of the test variables on the response and determine the combined interaction between the test variables and their incidental effect on the response [15,16]. Design-Expert 7.0.0 software was used for this study. In this study, 2^3 full factorial central composite design was employed with 20 experiments including six replicates using RSM were employed.

2. Experimental

2.1. Characteristics of the fly ash

Fly ash is generally a waste matter, generated from combustion method in industries with the flue gases. Fly ash consists of very fine particles and is light reddish brown in color. The characterization of used fly ash had been reported previously [17].

2.2. Preparation of the adsorbents

Fly ash was collected from local industry of Durgapur, India. Primarily, the fly ash was washed with distilled water and oven dried at 100 ± 5°C. Then fly ash was treated with 0.1(M) CaO solution for 24 h at 30°C. After that it was washed repeatedly with distilled water until the water becomes colorless. It was then oven dried at 100 ± 5°C for 24 h and was sieved to remove unwanted particles. The adsorbents mesh size was 1 mm. After that the CaO-modified fly ash was kept in an air tight glass bottle for further use for adsorption experiments.

2.3. Preparation of the adsorbate solution

A stock solution of copper was prepared using copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) dissolving in distilled water. Cu(II) stock solution (1,000 mg L^{-1}) was prepared by diluting 3.93 g of $CuSO_4{\cdot}5H_2O$ (obtained from Merck) in 1 L distilled water. Using this stock solution, different copper concentrations were prepared. For pH, adjustment was done with 0.1 (N) HCl and 0.1(N) NaOH solutions using a digital pH meter (ELICO).

2.4. Experimental setup

Then Copper solution was kept in conical flask and placed in incubator rotary shaker and 20 g/L adsorbent dose was added to the solution. Agitation speed (120 rpm) and adsorbent dose (20 g/L) was kept at fixed in this experiment.

After predefined time intervals, sample was collected and centrifuged at 6,000 rpm for 10 min and supernatant fractions were analyzed for the remaining copper concentration.

2.5. Analysis of Cu(II) concentration

Copper concentration was determined spectrophotometrically at 460 nm by using sodium diethyl dithiocarbamate (as the copper complexing agent); [18] 0.2 mL of 1% w/v solution and 20 mL 1.5(N) NH_3 solution were added to the 1 mL of supernatant solution after centrifugation [19]. By this method, copper concentration can be measured if that is less than 60 mg/L, if copper concentration is more than that then dilution is needed. Copper reduction by this process was obtained by using the following formula:

$$\%\ \text{reduction} = \{(C_0 - C_1)/C_0\} \times 100 \tag{1}$$

where, C_0 is initial copper concentration (mg/L) and C_1 is remaining copper concentration (mg/L).

Standard graph of copper concentration vs. optical density was used for the calculation of copper concentration. All OD was taken in UV 2300 Spectrophotometer.

2.6. Optimization of adsorption process

A two-level-three-factor (2^3) full factorial central composite design (CCD) was used for the study Design Expert Version 7.0.0 (Stat Ease, USA) was used for the optimization of the process parameters and to evaluate the impressions and interactions of process variables; initial pH 3.5–5.5, copper concentration 15–50 mg/L, and contact time 45–90 min were used.

The quadratic equation model for predicting the optimal point was expressed according to Eq. (2):

$$Y = \beta_{0+} \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \in \qquad (2)$$

where Y was the predicted response, X_i, X_j refers to the independent variables, β_0, β_i, β_{ii}, β_{ij} are the regression coefficients, and $\in$ is the statistical error.

Three factors were studied: pH of the solution, initial copper concentration, and contact time on percentage removal. The ranges and levels of variables investigated in the research are given in Table 1.

Percentage removal of copper was studied with a standard RSM design called the CCD. Twenty experiments were conducted consisting of factorial points (coded to the usual ± 1 notation), axial points (±α), and six replicates at the center points (0), and each of the experiment was conducted in duplicates in Table 2.

Design Expert Version 7.0.0 (Stat Ease, USA) was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the statistical regression equation and by analyzing the response surface contour plots.

3. Results and discussion

3.1. Response surface estimation for maximum removal of copper

An empirical relationship between the response and the independent variables had been expressed by the following quadratic model.

$$\begin{aligned} R_1 = {} & 47.69740 + 11.50986A + 0.86072B - 0.16982C \\ & -0.053857AB + 0.025889AC - 0.00125079BC \\ & -1.10821A^2 - 0.00367638B^2 + 0.0013936C^2 \end{aligned} \qquad (3)$$

where A is pH, B is copper concentration in mg/L, and C is time in min.

The percentage removal of copper was taken as the response of the system.

The design expert 7.0.0 software was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the analysis of variance, to determine the significance of each term in the equations fitted and to figure out the goodness of fit (Table 3). Response surfaces were drawn for the experimental results to find out the effect of different variables on the percentage removal of copper to estimate the individual and cumulative effects of these variables and the mutual interactions between these variables.

The F value (237.30) with a low probability ($p < 0.0001$) showed that the model was significant. The multiple correlation co-efficient (R^2) also manifested the goodness of the model (Table 4). Moreover, R^2 value is 0.9953 implied that more than 99% of the data deviation may be explain by the originated quadratic model and the predicted R^2 values were in agreement with adjusted R^2, which means all the terms depicted in the model were significant. The nonsignificant lack 0.9953 (more than 0.05) showed that the quadratic model was effective for this study [20,21].

Table 1
Experimental range and levels of independent process variables

Independent variables	Range and levels(coded)				
	–α	–1	0	+1	+α
pH (A)	2.82	3.50	4.50	5.50	6.18
Initial copper concentration, mg/L (B)	3.07	15	30.00	50	61.93
Time, min (C)	29.65	45.00	67.50	90.00	105.34

Table 2
The 2^3 factorial experimental setup and percentage removal response

Run	Initial solution pH (*A*)	Initial copper concentration (C_0), mg/L (*B*)	Time, min (*C*)	Final copper concentration (C_1), mg/L	Response (% removal)
1	5.50	15	90	1.155	92.3
2	4.50	32.50	67.50	2.057	93.67
3	4.50	61.93	67.50	0.619	99
4	4.50	32.50	67.50	2.015	93.8
5	3.50	15	90	2.07	86.2
6	3.50	15	45	2.6775	82.15
7	4.50	32.50	67.50	2.6	92
8	3.50	50	90	1.4	97.2
9	4.50	32.50	67.50	2.08	93.6
10	6.18	32.50	67.50	2.37	92.7
11	4.50	32.50	105.34	0.358	98.9
12	4.50	3.07	67.50	0.577	81.2
13	5.50	15	45	2.1	86
14	5.50	50	45	2.4	95.2
15	5.50	50	90	0.195	99.61
16	4.50	32.50	67.50	2.24	93.1
17	2.82	32.50	67.50	4.03	87.6
18	4.50	32.50	67.50	2.129	93.45
19	3.50	50	45	2.4	95.2
20	4.50	32.50	29.66	2.711	91.66

Table 3
Analysis of variance for the response surface quadratic model for copper removal

Source	Sum of squares	Degree of freedom (*df*)	Mean square	*F* value	Probablity > *F*
Model	513.86	9	57.10	237.30	<0.0001
Residual	2.41	10	0.24		
Lack of fit	0.18	5	0.036	0.082	0.9921
Pure error	2.22	5	0.44		
Cor. total	516.27	19			

Table 4
Regression analysis by using central composite design

Model Term	Coefficient estimate	Standard error	*F* value	*P* value
A	1.53	0.13	133.41	<0.0001
B	5.16	0.13	1512.43	<0.0001
C	2.12	0.13	254.82	<0.0001
AB	–0.94	0.17	29.54	0.0003
AC	0.58	0.17	11.28	0.0073
BC	–0.49	0.17	8.06	0.0176
A^2	–1.11	0.13	73.56	<0.0001
B^2	–1.13	0.13	75.93	<0.0001
C^2	0.71	0.13	29.81	0.0003

$R^2 = 0.9953$; adjusted $R^2 = 0.9911$; predicted $R^2 = 0.9911$.

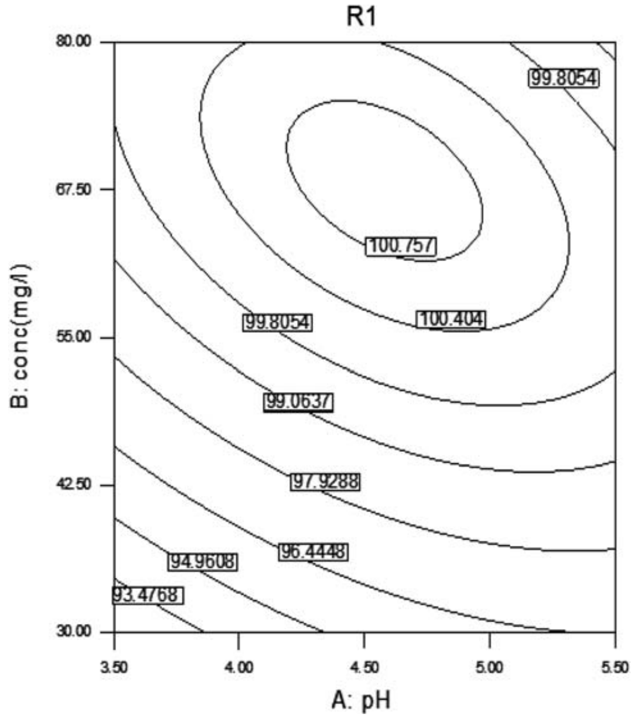

Fig. 1. The contour plot shows the relationship between pH and initial copper concentration with the R1.

3.2. *Effect of initial solution pH and initial copper concentration*

The effect of different levels of initial solution pH and initial copper concentration on adsorption using the CaO-modified fly ash can be predicted from the contour plot as shown in Fig. 1. The potential destinations were: within range (for three independent variables pH, initial copper concentration and time), and maximum (for responses only) and set to an exact value (factors only). From the contour plot, it can be observed that copper removal percentage increased with increase of pH and initial copper concentration. As copper concentration increase in the solution, it leads to an increase in the concentration gradient and thereby increasing the driving force [22,23].

The solution pH affected the chemistry of copper ions and the activity of ions on surface of fly ash [24–26]. The surface of treated fly ash was positively charged at lower pH values than 3.5 and due to competition between copper cations and H^+ ions, restrained the approach of positively charged copper cations to the surface of the fly ash [27]. In the pH range of 3.5–5.5, these surfaces were negatively charged and the reduction process of copper was then carried on because of electrostatic attraction between the negatively charged treated fly ash surface and the positively charged copper cations [28,29].

The adsorption of copper ions at the solid–solution interface depends strongly on the adsorbed hydroxo, sulfato, carbonato, and other metal species, and not on the free copper concentration in the solution [30]. The distribution and accurate nature of the copper hydroxide ions depend on the concentration of the ligands, i.e. solution pH and copper concentration in the solution. The adsorption increase of Cu(II) at higher pH is generally assigned to the abundance of OH^- that results in an increased hindrance to the diffusion species [31,32].

3.3. *Effect of initial copper concentration and time*

The combined effect of initial copper concentration and contact time on copper reduction is shown in the contour plot of Fig. 2. The number of copper cations adsorbed at higher concentrations was more than that removed from less-concentrated solutions. With increasing copper concentrations, the mass transfer driving force increased and raised the copper cations adsorption on the surface of chemically modified fly ash. After a certain time, there were no free binding sites on modified fly ash surface and the reduction reached to equilibrium. From the results, it was observed that an optimum removal efficiency of 99.16% was achieved at combined effect of pH 3.98, 77.88 mg/L initial copper concentration, and 58.82 min of contact time.

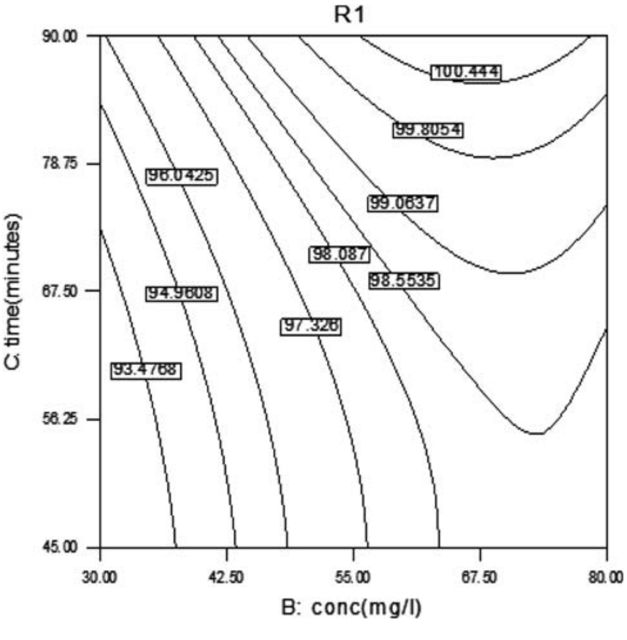

Fig. 2. The contour plot shows the relationship between initial copper concentration and time with the R1.

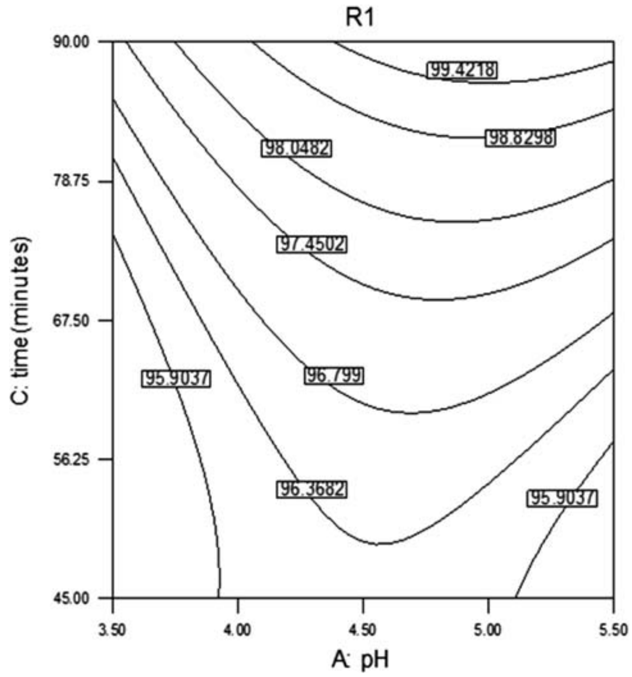

Fig. 3. The contour plot shows the relationship between pH and the time with the R1.

3.4. Effect of initial solution pH and contact time

The combined effect of initial solution pH and contact time on copper removal is shown in the contour plot of Fig. 3. It was observed that percentage copper removal increased with increasing pH as well as the time. The optimum copper removal 99.16% was obtained from pH 3.98 and contact time 58.82 min, when copper solution concentration was fixed at 77.88 mg/L. It was apparent from contour plots that both the independent variables had a strong influence on the copper adsorption process. As contact time increased percentage reductions of copper also increased until it reached equilibrium [33]. From the results, it was observed that a maximal removal efficiency of 99.16% was achieved at initial pH 3.98, 77.88 mg/L initial copper concentration, and 58.82 min contact time. After this adsorption study, the remaining copper concentration was 0.65 mg/L of the adsorbate solution.

3.5. Optimization using the desirability functions

In numerical optimization, the desired goal for each factor and response from the menu was chosen. The potential goals were: maximize, minimize, target, within range, none (for responses only), and adjust to a precise value (factors only). A minimum and a maximum level must be furnished for each parameter included in the copper reduction study. There may be two or more maximum level because of curvature in the response surfaces and their combination in the desirability function. Beginning from different points in the design improved the probabilities for finding out the "best" local maximum [25,34]. A multiple response method was applied for optimization of any combination of four goals, namely initial solution pH, initial copper concentration, contact time, and percentage removal of copper. The numerical optimization found a point that maximizes the desirability function in the copper reduction study. Level of initial solution pH (3.5–5.5), initial copper concentration (15–50 mg/L), and contact time (45–90 min) were in between the range and maximum percentage removal of copper (99.99%) were set for maximum desirability. The grandness of each goal was changed in relation to the other goals. Fig. 4 showed a ramp desirability that was generated from nine optimum points via numerical optimization.

3.6. Comparison between theoretical and experimental data

The CCD equation of actual factors was solved by partial differential calculus for obtaining the optimum value of A, B, and C [35].

$$\begin{aligned} R_1 = {} & 47.69740 + 11.50986A + 0.86072B - 0.16982C \\ & -0.053857AB + 0.025889AC - 0.00125079BC \\ & -1.10821A^2 - 0.00367638B^2 + 0.0013936C^2 \end{aligned} \tag{4}$$

$$\begin{aligned} \partial R_1/\partial A = {} & 11.50986 - 0.053857B + 0.025889C \\ & - 2.21642A \end{aligned} \tag{5}$$

$$\partial^2 R_1/\partial A^2 = -2.21642 \tag{6}$$

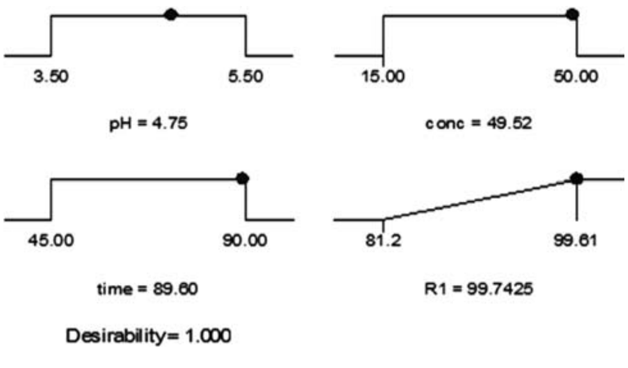

Fig. 4. Desirability ramp for optimization of three goals, namely initial solution pH, adsorbent dose, and time of maximum removal of copper (R1).

Table 5
Comparison between experimental and theoretical responses

Run	Initial solution pH (*A*)	Initial copper concentration, mg/L (*B*)	Time, min (*C*)	Experimental Response (% removal)	Theoretical response
1	5.50	15	90	92.3	92.25
2	4.50	32.50	67.50	93.67	93.27
3	4.50	61.93	67.50	99	98.77
4	4.50	32.50	67.50	93.8	93.27
5	3.50	15	90	86.2	86.13
6	3.50	15	45	82.15	82.08
7	4.50	32.50	67.50	92	93.27
8	3.50	50	90	97.2	97.36
9	4.50	32.50	67.50	93.6	93.27
10	6.18	32.50	67.50	92.7	92.72
11	4.50	32.50	105.34	98.9	98.83
12	4.50	3.07	67.50	81.2	81.41
13	5.50	15	45	86	85.86
14	5.50	50	45	95.2	95.29
15	5.50	50	90	99.61	99.71
16	4.50	32.50	67.50	93.1	93.27
17	2.82	32.50	67.50	87.6	87.56
18	4.50	32.50	67.50	93.45	93.27
19	3.50	50	45	95.2	95.27
20	4.50	32.50	29.66	91.66	91.70

$$\partial R_1/\partial B = 0.86072 - 0.053857A - 0.00735B - 0.00125C \tag{7}$$

$$\partial^2 R_1/\partial B^2 = -0.00735 \tag{8}$$

$$\partial R_1/dC = -0.16982 + 0.025889A - 0.00125B + 0.0027872C \tag{9}$$

$$\partial^2 R_1/\partial C^2 = +0.0027872 \tag{10}$$

Eqs. (4), (6), and (8) are first-order partial differential equations and these equations were equated with zero for solving, we get
A (pH) = 3.98,
B (conc.) = 77.88 mg/L, and
C (time) = 58.82 min.

Eqs. (5), (7), and (9) are second-order partial differential equations.

Eqs. (5) and (7) showed negative values indicating absence of local maximum and applicability of maximization and Eq. (9) showed positive values indicating the local minimum and applicability of minimization of process time.

Using the CCD equation optimum theoretical response was calculated at *A* (pH) = 3.98, *B* (conc.) = 77.88 mg/L, and *C* (time) = 58.82 min. The theoretical response (% reduction) was 99.16% and the remaining copper concentration was 0.65 mg/L of the adsorbate solution (theoretically).

Experimental reduction (R_1) was 99.19% obtained at *A* (pH) = 3.98, *B* (conc.) = 77.88 mg/L, and *C* (time) = 58.82 min. After this adsorption study, the remaining copper concentration was 0.63 mg/L of the adsorbate solution.

The percentage deviation of experimental and theoretical was 0.030%.

Using the CCD equation theoretical response was calculated at 20 different sets of the A, B, and C values. Table 5 showed the comparison between experimental data and theoretical data.

3.7. SEM analysis of the fly ash

Scanning electron microscopy analysis was performed for the surface morphology of the treated fly ash sample at 600× resolution before (Fig. 5) and after adsorption by the treated fly ash (Fig. 6). It was observed that surface of the adsorbent became quite smoother after copper adsorption by the treated fly

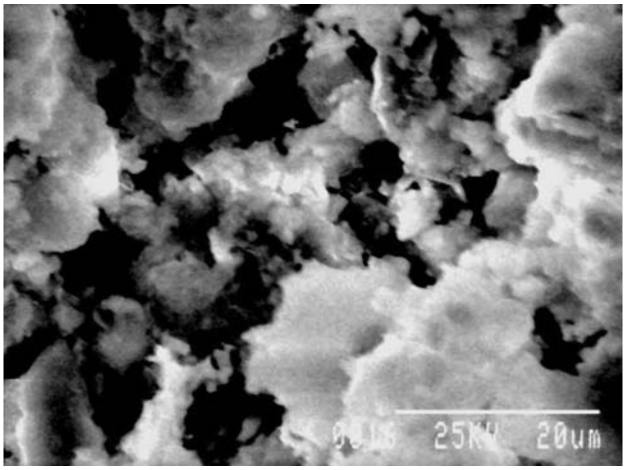

Fig. 5. Treated fly ash at 600× resolution.

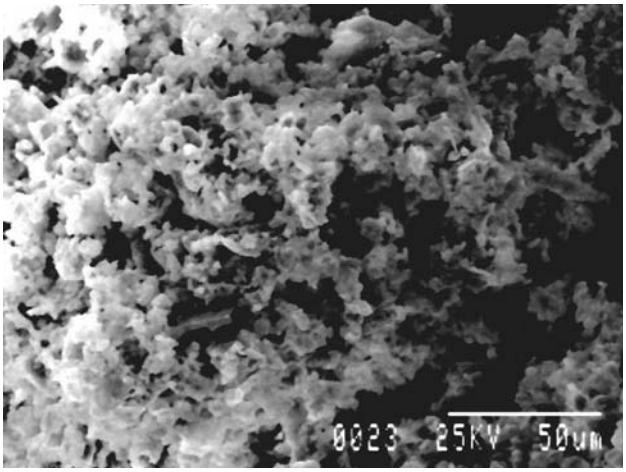

Fig. 6. Treated fly ash + copper after adsorption at 600× resolution.

ash. Hitachi scanning microscope (S-530) was used for this analysis.

4. Conclusion

The present study was taken with the aim of scale-up of the copper adsorption process using the CaO-modified fly ash and to investigate the combined effect of various process parameters on copper removal using RSM. The initial solution pH, initial copper concentration, and contact time significantly influenced the copper removal efficiency. Optimization conditions for the maximum removal efficiency of copper were obtained by applying a desirability function in RSM. Based on the statistics analysis, the optimum conditions were obtained from pH 3.98, initial copper concentration 77.88 mg/L, contact time 58.82 min, and the copper removal was 99.16%. The CaO-treated fly ash can be used for effective reduction of copper at low cost.

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