Adsorption of Cu^{2+} from aqueous solution onto modified glass beads with 3-aminopropyltriethoxysilane

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ABSTRACT

The discharge of heavy metals into the aquatic ecosystem is a main concern over the last few decades. These pollutants are introduced into aquatic systems as a result of various industrial operations. This study investigates the efficiency of the modified glass beads with APTES ligand for removal of Cu^{2+} from the aqueous solution. Response surface methodology based on Box-Behnken was used to assess the effect of independent variables, including flow rate, solution pH, initial concentration and glass beads size on the response function and prediction of the best response value.
Atomic absorption spectroscopic analysis of eluents of a column of the modified glass beads showed that Cu^{2+} ion was more than 90% entrapped on a column of glass beads. The isotherm evaluations indicate that the equilibrium data for Cu^{2+} adsorption could be fitted with the Langmuir model. Experimental data were also evaluated in terms of adsorption kinetics using the pseudo-first-order and pseudo-second-order kinetic models. The results also showed that the adsorption process of the Cu^{2+} well suited with the pseudo-second-order kinetics model. All the results demonstrated that modified glass beads successfully absorbed heavy metals from aqueous solution.

Key words: Heavy metals; Modified glass beads; Response Surface Modeling; Box–Behnken experimental design

INTRODUCTION

Heavy metals are the most significant pollutants that can have a direct and indirect effect on humans, the environment and animals [1,2]. Among the heavy metals, cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), copper (Cu), and zinc (Zn) are the most hazardous. Copper is considered as one of the most toxic metals and poses a potential threat to the human health and the environment, even at low concentrations. It has been well reported that the accumulation of copper in the human body causes brain, skin, pancreas and heart diseases [3, 4]. The permissible limit of copper is 2.5 mg L^{-1} in water. Wastewater from various industries, such as electroplating, plastic, metal, finishing, pigments, and mining contains copper [5]. Therefore, these needs have led to the development of various technologies for effective removal of Cu^{2+} from aqueous solution for the protection of the environment and public health [6,7]. Likely methods that can be used to remove metals from the water resources are electrochemical and chemical precipitations, ion exchange, evaporation, membrane technologies,

coagulation–flocculation, chelation, solvent extraction, reverse osmosis, biosorption, and adsorption [8-11]. Although these methods are effective in removing heavy metal, they are expensive to operate, non-reusable, or they cause membrane fouling or secondary contamination [12]. However, amongst the mentioned methods, the adsorption techniques offer flexibility in design, generation of high-quality treated effluent, low maintenance cost, high efficiency and ease of operation [13]. As a very popular class of designs for fitting a response surface, Box-Behnken design (BBD) provides efficient solutions compared, reducing the number of required experiments by confounding higher-order interactions, decrease of time and expenses as well as a saving in the consumption of reagents and materials, which becomes more significant as the number of factors increases [14-18]. In order to achieve selectivity, modification and impregnation techniques have long been used to bring about the selective removal of particular metals. The application of these techniques for the adsorption of metals should gain attention due to their high mechanical strength and

being widely used in various applications. In fact, a number of new materials have been successfully prepared from the glass beads by employing the surface modification [19-21], and these achievements prompted us to immobilize HCl and ATES ligand on the surface of glass beads. In this study, glass beads modified with 3-aminopropyltriethoxysilane, was filled in a packed bed column for the separation and enrichment of Cu^{2+} prior to their analysis by flame atomic absorption spectrophotometer (Perkin Elmer, AAnalyst200). In addition, the effects of flow rate, pH of solution, influent concentration, glass bead sizes on the removal efficiency of the selected metals were investigated.

MATERIALS AND METHODS

Preparation of Glass Beads Modified with 3-aminopropyltriethoxysilane

In the first step of the experiment, glass beads were extensively washed with distilled water, dried for 24 h at $50\,^{\circ}$C in the oven. Prior to use, boiled for 24 h with HCl (6 mol/dm^3), washed with distilled water until all chloride ions were removed, and dried in a vacuum oven at $50\,^{\circ}$C for 24h [22]. Then, a known weight of glass beads was added to 0.01M solution of the 3-aminopropyltriethoxysilane and shaken continuously for 8 h. The samples were then left in the solution overnight. After 24h, the solutions were filtered through the filter paper and modified glass beads were washed with distilled water. The mixtures were final, dried at $60\,^{\circ}$C overnight [7]. In this study, we first etched surface of the glass bead with aqueous HCl (6M) to increase the density of the silanol, and then, by using a silane coupling agent, 3-aminopropyltriethoxysilane, introduced amino groups to the beads [19]. Surface modification of glass beads nanoparticles is shown in Fig1.
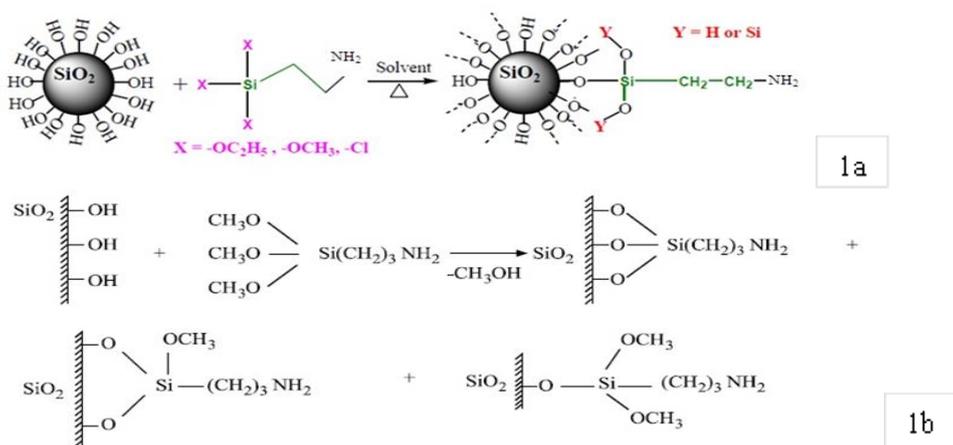

Fig.1: Structure of glass beads modified with 3- aminopropyltriethoxysilane

Batch Studies

The chemicals used for the study were analytical grades of copper nitrate (Cu (NO$_3$)$_2$.3H$_2$O) and 3-aminopropyltriethoxysilane (H$_2$N (CH$_2$)$_3$Si (OC$_2$H$_5$)$_3$) were supplied by Sigma Aldrich and Merck Co. The stock solution of Cu^{2+} was first prepared by dissolving their corresponding salt in distilled water. The pH adjustment was made by adding 0.1 M HCl or 0.1 M NaOH and controlled by HACH pH meter (HQ40d)**.** The adsorption studies were carried out in a packed bed column, and then the column was filled with a known weight of glass beads sample with 4L of metal ion solution at a particular pH for a known period. Adsorption isotherm studies were carried out using different initial metal ion concentrations (10–50 mg/L) with 500 g adsorbent at pH 7 and temperature of 25 ∘C. The heavy metal removal efficiency and amount of adsorption were Calculated by Esq. (1) and (2), respectively [23].

$$E = \frac{c_0 - c_e}{c_0} \times 100 \qquad (1)$$

$$q = (C_0 - C_e) \times \frac{V}{M} \qquad (2)$$

Where, E is the removal efficiency, C_0 (mg. L^{-1}) and C_e (mg. L^{-1}) are the initial and final metal ion concentrations in the solution, respectively, q (mg. g^{-1}) is adsorption capacity, V(L) is the solution volume and m (g) is the amount of applied adsorbent.

Optimization of Adsorption Process using RSM approach

Response surface methodology (RSM) consists of a group of mathematical and statistical techniques devoted to the evaluation of relationships existing between a cluster of controlled experimental factors and measured responses according to one or more selected criteria [24-27]. In the present study, to collect the maximum information from the fewer number of experiments a Box-Behnken design

combining with RSM for four major variables (pH (X_1), flow rate (X_3), particle size (X_4) and metal concentration (X_2)), each with three levels (the minimum, medium and the maximum), was applied as an experimental design model. The number of experiments (N) required for the development of this design is defined as N=2k + 2, where (k) is the replicate at the middle point [28-31]. The range of independent variables and their levels are investigated in the work are given in Table 1.

Adsorption percent of heavy metals estimated as percent removal of heavy metals from the solution was taken response of the system (Y). Table 2

showed the experimental conditions and the results of modified glass beads according to the factorial design.

Table 1: Independent variables and their levels used in the response surface design

Factors	Symbol	Coded level		
		-1	**0**	**1**
pH	X_1	3	6	9
metal concentrations (mg/l)	X_2	10	30	50
flow rate(ml/min)	X_3	30	45	60
particle size (µ)	X4	50	150	250

Table 2: Response surface Box–Behnken design and results

Run	X_1: pH	X_2= metal concentration(mg/l)	X_3= flow rate(ml/min)	X_4: particle size(µ)	X_5: Modification	Cu removal (%)
1	6	30	45	150	Modification by acid	87
2	6	10	60	150	Modification by ligand	86.57
3	9	50	45	150	Modification by acid	89.30
4	3	50	45	150	Modification by ligand	28.34
5	6	30	30	50	Modification by acid	94.76
6	6	30	45	150	Modification by ligand	82.20
7	6	30	30	250	Modification by ligand	76.43
8	6	50	60	150	Modification by ligand	72.88
9	6	30	45	150	Modification by acid	87
10	9	30	45	250	Modification by acid	82.90
11	3	30	45	50	Modification by ligand	29
12	6	10	45	250	Modification by acid	89.10
13	6	50	60	150	Modification by acid	80.31
14	3	30	60	150	Modification by acid	32.20
15	6	10	60	150	Modification by acid	91.50
16	6	30	45	150	Modification by acid	87
17	6	50	45	250	Modification by acid	84.70
18	6	30	45	150	Modification by acid	87
19	6	50	45	250	Modification by ligand	78.90
20	6	30	45	150	Modification by acid	87
21	6	30	45	150	Modification by ligand	82.20
22	6	30	45	150	Modification by ligand	82.20
23	3	10	45	150	Modification by ligand	31.28
24	6	50	45	50	Modification by ligand	83.46
25	3	30	45	50	Modification by acid	33.23
26	6	30	45	150	Modification by ligand	82.20
27	3	30	30	150	Modification by acid	35.94
28	9	30	45	50	Modification by ligand	89.80
29	9	30	45	50	Modification by acid	94.30
30	6	50	45	50	Modification by ligand	83.46
31	3	30	45	250	Modification by ligand	33.27
32	3	10	45	150	Modification by ligand	32.28
33	6	10	30	150	Modification by ligand	91.84
34	6	10	45	250	Modification by ligand	89.98
35	6	30	45	150	Modification by ligand	82.20
36	6	10	45	50	Modification by acid	96.87
37	3	30	45	250	Modification by acid	26.82
38	9	50	45	150	Modification by ligand	82.46
39	6	30	60	250	Modification by ligand	72.64
40	6	50	30	150	Modification by ligand	79.33
41	9	30	30	150	Modification by ligand	90.90
42	3	30	30	150	Modification by acid	37.94
43	6	30	30	250	Modification by acid	80.30
44	3	50	45	150	Modification by acid	30.47
45	6	30	60	250	Modification by acid	77.90
46	6	10	30	150	Modification by ligand	90.84
47	3	30	60	150	Modification by ligand	31.97
48	6	30	30	50	Modification by acid	94.76
49	6	30	60	50	Modification by acid	85.60
50	9	30	30	150	Modification by acid	93.98
51	9	10	45	150	Modification by acid	93.10
52	6	30	60	50	Modification by ligand	81.52
53	6	50	30	150	Modification by acid	89
54	9	30	60	150	Modification by acid	92.29
55	9	30	45	250	Modification by acid	89.74
56	6	10	45	50	Modification by acid	94.87
57	9	10	45	150	Modification by ligand	94.50
58	9	30	60	150	Modification by ligand	86.10

A second order polynomial model where interaction terms have been fitted to the experimental data obtained from the Box–Behnken design can be stated in the form of the following equation (3) [18,25,27,32,33]:

$$Y = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \quad (3)$$

Where Y is the process response or percentage of metals adsorbed (dependent variable), i and j are the index numbers for a pattern, a_o offset term called intercept term, x_1, x_2 … x_k are the coded independent variables. a_i is the first-order (linear) main effect, a_{ii} second-order main effect and a_{ij} is the interaction effect. The data were subjected to analysis of variance and the coefficient of regression (R^2) was calculated to find out the goodness of fit of the model.

RESULTS AND DISCUSSION

Effect of pH and Flow Rate on Removal of Cu^{2+} Ion

Adsorption experiments were carried out as per the selected model with a selected range of pH (3, 6 and 9) and flow rate (30 ml min^{-1} to 50 ml min^{-1}), and the other parameters were kept constant. Acidity and flow rate were the most significant parameters for assessing the effectiveness of the removal capacity of an adsorbent. There was a rapid rise in efficiency removal with increase in pH; however, the removal efficiency declined as the flow rate was slightly raised. The maximum adsorption of Cu^{2+} ion was ☐90% which occurred at pH 7 and the flow rate of 30 mL min^{-1} (Figs.2). From Fig. 2 it was shown that glass beads modified with 3- aminopropyltriethoxysilane have little impact to improve the removal of Cu^2 rather than glass beads modified with hydrochloric acid. These results are also in agreement with the study of removal Cu^{2+} in water using manganese activated saturated and unsaturated sand filters by Chedly Tizaoui [3].
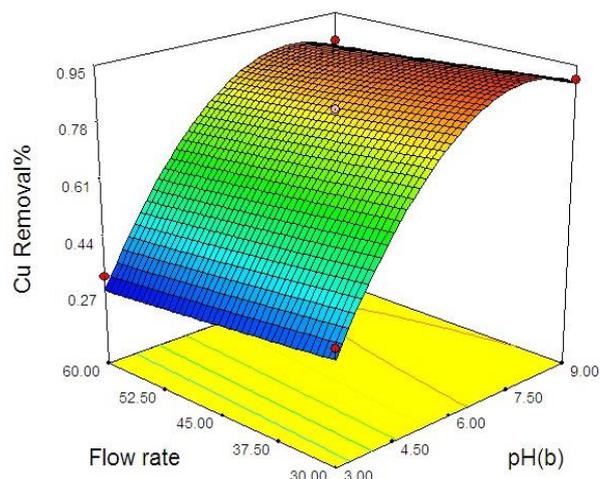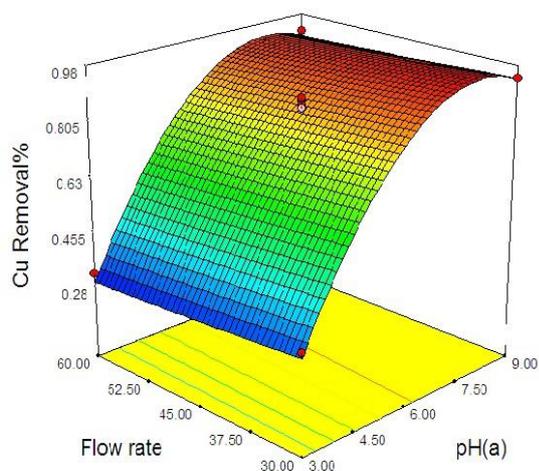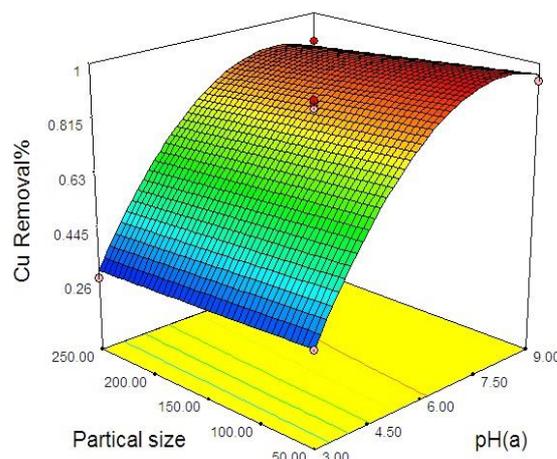

Fig.2: 3-D plot showing effect of pH and flow rate on the percentage removal of copper ion (b: glass beads modified with 3- aminopropyltriethoxysilane, a; glass beads modified with hydrochloric acid)

Effect of Particle Size on Removal of Cu^{2+} Ion

To investigate the influence of glass bead size on the adsorption of metals different sizes of glass beads were chosen (50, 150 and 250 µm), while the other reaction conditions were kept constant. The combined effect of pH and particle size has been presented in Fig. 3. It can be observed that the removal efficiency showed a slight upward trend with an increase in particle size. We conclude that the external surface of glass beads has an insignificant role in the heavy metals retention and that the internal sites are responsible for the cation exchange [34]. A similar trend has been observed in the removal of lead and cadmium ions from aqueous solution with adsorption onto micro-particles of dry plants **by** H. Benhima *et al*. [35]. These results are also in agreement with the study of Surface modification of glass beads with glutaraldehyde by Mustafa Ozmena [20].
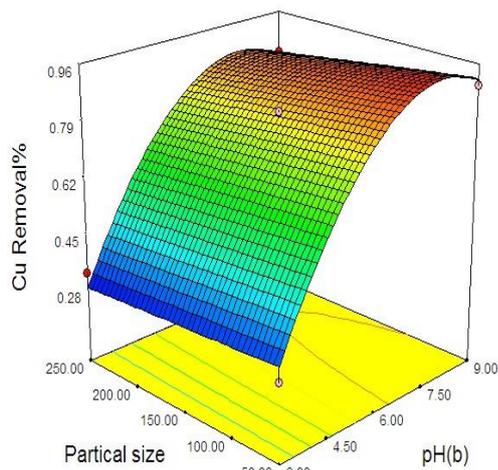
Fig.3: 3-D plot showing effect of pH and particle size on the percentage removal of copper ion (b: glass beads modified with 3- aminopropyltriethoxysilane, a; glass beads modified with hydrochloric acid)

Effect of Metal Concentration Size on Removal of Cu^{2+} Ion

The effect of Cu^{2+} initial concentration on the adsorption was investigated in various the range of 10–50 mg l^{-1}. At higher concentrations, a number of metal ions outnumber the adsorption sites, so the removal becomes independent of the initial concentration [36]. Hence, the removal efficiency of heavy metals depended on the concentration and it was observed to decrease with an increase in initial metal concentration (Fig. 4). In a further related study, Katsou et al reported that metal reduction could be achieved using a sorbent-assisted ultrafiltration system. They showed that increasing nickel and zinc initial concentrations reduced their respective removal efficiencies due to the availability of more metals, while the mineral dosage remained unchanged [37]. Consequence it was shown that pH was the major factor amongst four variables playing significant roles in removal efficiency [25]. These results are also in agreement with the study of the removal of Ni (II), Cd (II), and Pb (II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica by Heidari *et al.* [38] Liu et al in a study on the adsorption of metal ions by glass beads modified with Chitosan showed that heavy metals such as Cd^{2+}, Pb^{2+}, Cu^{2+} and Ag^+ were more 90% entrapped on a column of beads [19].

Statistical Analysis and The Model Fitting

The Box–Behnken model was used to evaluate the interactive effects of parameters for optimizing the removal of Cu^{2+} ion using the modified glass beads. There were a total of 58 runs for optimizing the variables in the Box–Behnken statistical design. Design expert was used for ANOVA software analysis of the experimental data obtained.

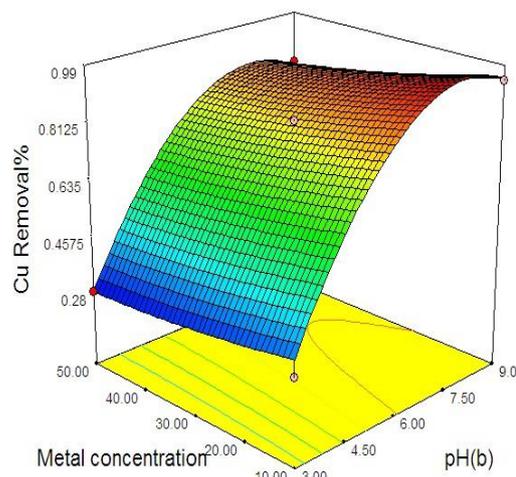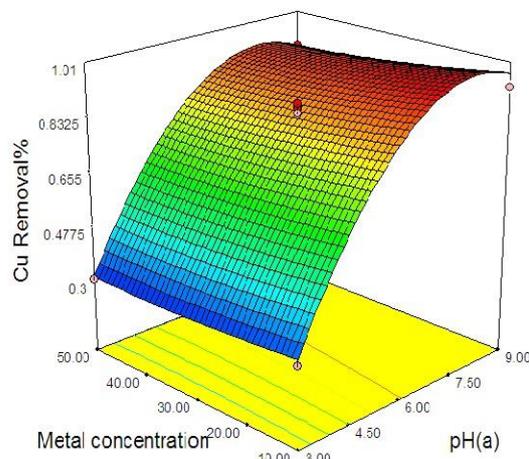Analysis of variance (ANOVA), goodness-of-fit and the adequacy of the models were presented in Table 3

Fig.4: 3-D plot showing effect of pH and particle size on the percentage removal of copper ion (b: glass beads modified with 3- aminopropyltriethoxysilane, a; glass beads modified with hydrochloric acid)

Table 3: Fit statistics for Y (average removal).

	Master model	Predictive model
Mean	0.75	0.75
R-square	98.79%	98.90%
Adjusted R-square	0.9819	0.9819
Coefficient of variation	4.11	4.11

The high value of R^2 (0.9879) indicating that only 1.21% of the total variance was not explained by the model. A very low value 4.11 of the coefficient of the variation (C.V.) clearly indicated a very high degree of precision and a good deal of reliability of

the experimental values. The model was found to be adequate for prediction within the range of experimental variables. The significance of each coefficient and the interaction strength between each independent factor was determined using *a p - value*. If *p*-value is the smaller, it is the bigger the

significance of the corresponding coefficient [39,40]. The model expressed by Eq. (3), where the variables take their coded values, represents removal efficiency of selected heavy metals (Y) as a function of pH (x_1), metal concentration (x_2), flow rate (x_3) and particle size (x_4).

$$Y = 0.84 + 0.29X_1 - 0.041X_2 - 0.027X_3 - 0.033X_4 - 0.014X_1X_2 + 4.025X_1X_3 - 0.014X_1X_4 - 0.24X_1^2 - 0.014X_2^2 + 2.358X_3^2 - 2.35X_4^2 \quad (4)$$

The statistical significance of the factors and their interactions at various levels of probability are shown in Table 4. As shown in Table 4, the linear coefficients (X_1, X_2, X_3, and

X_4), a quadratic term coefficient (X_1^2) and cross product coefficients ($X_3 \times X_4$) were important variables in the adsorption process, with very small P values (P ≤ 0.05).

Table 4: Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squre	df	Mean Squre	F Value	P-Value
Model	2.96	19	0.16	163.29	□0.0001
A-pH	2.02	1	2.02	2122.66	□0.0001
B- Metal concentration	0.041	1	0.041	43.21	□0.0001
C- Flow rate	0.017	1	0.017	17.82	0.0001
D- Metal cocentration	0.026	1	0.026	27.06	□0.0001
E- Modification	0.0112	1	0.0112	12.86	0.0009
AB	1.5374E-003	1	1.5374E-003	1.61	0.2118
AC	1.296E-004	1	1.296E-004	0.14	0.7144
AE	1.150E-004	1	1.150E-004	1.21	0.2791
AD	2.957E-003	1	2.957E-003	3.10	0.0863
BC	1.210E-004	1	1.210E-004	1.27	0.2669
BD	1.090E-003	1	1.090E-003	1.14	0.2916
BE	4.243E-003	1	4.243E-003	4.54	0.0415
CD	3.285E-003	1	3.285E-003	3.45	0.0712
CE	9.614E-003	1	9.614E-003	1.01	0. 3216
DE	4.704E-007	1	4.704E-007	0.049	0.8254
A^2	0.74	1	0.74	778.01	□0.0001
B^2	2.367E-003	1	2.367E-003	2.48	0.1234
C^2	7.215E-003	1	7.215E-003	0.076	0.7847
D^2	7.190E-004	1	7.190E-004	7.542E-004	0.9782
Residual	0.036	38	0.036		
Lack of Fit	0.036	30	0.036	18.31	0.0001
Pure Error	5.200E-004	8	5.200E-004		

Isotherm Models

The Langmuir and Freundlich isotherms were the most common types of models describing correlate the equilibrium data [41,42]. The resulting isotherms provided the value of the maximum metal loaded of 1.494 mg g^{-1} for Cu (II). The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and Freundlich isotherm supposes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed [41]. The linear form of the Langmuir equation after rearrangement is [42]:

$$\frac{c_e}{q_e} = \frac{1}{b\,v_m} + \frac{c_e}{v_m} \quad (5)$$

Where C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}), q_e is the equilibrium metal adsorption capacity of the

adsorbent (mg g^{-1}), V_m is the amount of adsorbate at complete monolayer coverage (mg g^{-1}), and b (Lmg^{-1}) is a constant that relates to the heat of adsorption.

Freundlich isotherm has the following form [42].

$$q_e = k_f c_e^{\frac{1}{n}} \quad (6)$$

K_f and n are Freundlich constants indicating adsorption capacity and intensity, respectively. K_f and n were determined from linear plot of log qe against log Ce. Shahbazi *et al.* found the maximum sorption value to be about 1.7, 1.2 and 0.9 mmol g^{-1} for Cu (II), Pb (II) and Cd (II) respectively onto Functionalised SBA-15 Mesoporous Silica [43] The Langmuir isotherm plot was given in Fig. 5.
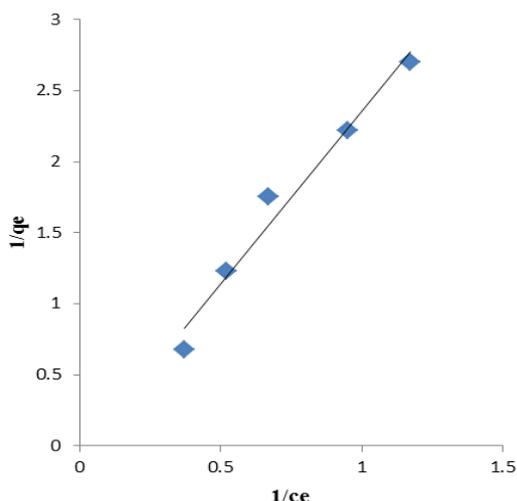
Fig.5: Langmuir isotherm plot for adsorption of copper ion (cu (II) onto modified glass beads

It was found that the adsorption of copper ion onto glass beads fits better with the Langmuir model (R^2_{Cu} = 0.9973) as compared to the Freundlich model (R^2_{Cu} = 0.8826) under the concentration range studied. Adsorption parameters of the Langmuir and Freundlich isotherm for the adsorption of Cu^{2+} ion onto glass beads showed in Table5. Shahbazi studied the functionalized SBA-15 mesoporous silica by melamine-based dendrimer amines for adsorptive characteristics of Pb (II), Cu (II) and Cd (II). They showed that adsorption isotherms was fitted better by the Langmuir (R^2 = 0.98–0.99) than the Freundlich model (R^2 = 0.93–0.97) [44].

Table 5: Adsorption parameters of the Langmuir and Freundlich isotherm for the adsorption of Cu^{2+} onto glass beads.

metal	Freundlich isotherm			Langmuir isotherm		
	R^2	n	K_n	R^2	b	a
cu	0.8826	2.58	0.114	0.9973	0.34	0.58

Kinetic Modeling

The effect of contact time on copper ion adsorption was studied in different time intervals ranging from 0min to 100 min. Fig.6 demonstrates the efficiency removal of copper ion versus time (min).

The complete removal of Cu^{2+} took place after 40, 50 and 60 min, respectively. So adsorption equilibrium was established in about 60 min. After this period, the amount of adsorbed copper ion did not change significantly with time. In order to determine the rate constants, pseudo-first order and pseudo second order were employed to model the adsorption data during 60 min. The experimental data fitted to pseudo-second-order kinetic. The pseudo-second order equation assumes that the adsorption process involves chemisorption's mechanism and the rate of site occupation is proportion to the square of the number of unoccupied sites [45]. The linear form of pseudo-first-order is represented by [46,47]:
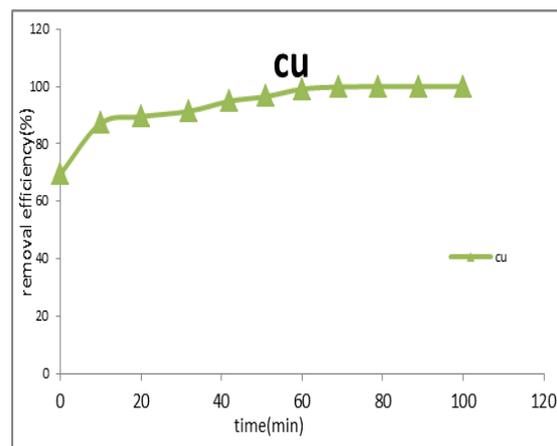

Fig.6: Biosorption kinetics of the copper ion removal on modified glass beads (flow rate= 30mlmin-1, glass beads size= 38-63μ, pH=7)

$$\ln(q_{eq} - q) = \ln q_{eq} - \frac{K_1 t}{2.303} \qquad (7)$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption, q_e and q_t (mg g^{-1}) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. The value of $k_1$was calculated from the slope of the linear plot of log (q_e-q_t) verses t. The linear form of pseudo-second-order equation can be written as (Eq. 8) [48,49]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

Where K_2 is pseudo-second order constant (g mg^{-1} min^{-1}), t is contact time (min), q_e is the equilibrium metal adsorption capacity of the adsorbent (mg g^{-1}), q_t is the amount of pollutant adsorbed at t (mg g^{-1}). If the pseudo-second order equation fit the adsorption data, there should be good linearity between $\frac{t}{q_t}$ and t [48]. The results demonstrate that the pseudo- second order equation was ideally applicable to copper ion. Adsorption parameters of the pseudo first order and pseudo- second order kinetics are given in table 6. These results are also in agreement with the study of Selective adsorption of Pb (II), Cd (II), and Ni (II) ions from aqueous solution using Chitosan–MAA nanoparticles by Aghdas Heidari [50].

Table 6: Adsorption parameters of the Pseudo first order and pseudo- second order kinetics for the adsorption of Cu^{2+} ion onto glass beads

metal	pseudo-first order			pseudo-second-order		
	R^2	q_e	K_1	R^2	q_e	K_2
Cu	0.974	0.026	0.009	0.9978	0.048	7.04

CONCLUSION

This study was aimed at investigating the efficiency of modified glass beads for the removal

of Cu^{2+} from aqueous solution in a fixed-bed column. The experimental data demonstrated that the modified glass beads have got the potential for highly efficient removal of the Cu^{2+} from aqueous solution. The BBD was found out to be a valuable tool in establishing optimal conditions through a response surface study. Four variables, namely ''flow rate, pH, initial concentration of the selected metals and glass bead size'' were regarded as factors in the optimization study. The maximum removal efficiency of the selected metals (estimated to be □90%) was determined at the following conditions: pH≥6, 30 mL min⁻¹ flow rate with a glass bead size of 38-63 µm. The equilibrium data for Cu^{2+} adsorption fitted better to the Langmuir model, which suggests heterogeneity in the sorption sites. Finally, it can be concluded that the modified glass beads with 3-aminopropyltriethoxysilane is a new sorbent for effective removal of Cu^{2+} from aqueous solution.

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