

ASCORBIC ACID TREATED RED MUD IMMOBILIZED IN Ca-ALGINATE BEADS AS AN EFFECTIVE ADSORBENT FOR THE REMOVAL OF COPPER IONS FROM INDUSTRIAL WASTEWATER

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ABSTRACT

Ascorbic acid treated red mud-immobilized in 'Calcium alginate'- beads (ARM-Ca-alg) is investigated as an adsorbent for removing toxic Cu^{2+} ions from water adopting batch modes of extraction methods. Treatment of red mud with a reducing agent like ascorbic acid enhances its adsorption nature towards Cu^{2+} , having easily convertible oxidation states. Extraction parameters are investigated for maximum absorptivity of Cu^{2+} ions. Adsorption capacity is found to be as high as 126.0 mg/g. Further, ARM-Ca-alg exhibits good adsorption throughout pHs: 3 to 10 and thereby, enabling the adsorbent for its applicability for samples having varying pHs. Cu^{2+} -ions can be removed entirely from Cu^{2+} solution (50 mg/l) by equilibrating the solution for 2 h with 1.25 g/l of ARM-Ca-alg, at pH: 6, rpm: 350 and temp: 303 K. Spent adsorbents can be re-generated and reutilized for 7 cycles with marginal loss of adsorption capacity. Thermodynamic parameters are evaluated. The observed -ve ΔG values emphasize the endothermic and spontaneity of the process of adsorption. High ΔH value (44.404 KJ/mole) for 'ARM-Ca-alg' reflects that adsorption is through chemisorption. The primary mechanism of adsorption may be due to ion-exchange and/or reduction of Cu^{2+} to less soluble Cu^+ depending upon the solution's pH. ΔS values (positive) implies disorder at the solid-liquid boundary. It renders the Cu^{2+} penetrate more into the layers of 'ARM-Ca-alg,' resulting in more absorptivity. Of the various adsorption isotherms applied, Langmuir isotherm explains well the sorption process, indicating the monolayer of adsorbate and homogenous distribution of adsorption sites. On analysis of the kinetics of adsorption, the pseudo-2nd-order model describes well. FESEM analysis signifies the adsorption of Cu^{2+} . ARM-Ca-alg is successfully applied to remove Cu^{2+} from industrial effluent water samples.

Keywords: Ascorbic Acid, Red Mud, Calcium-alginate; Cu^{2+} Removal, Regeneration, Applications.

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INTRODUCTION

Red mud, a waste, is generated during the extraction of Aluminium from bauxite ore.¹ It is reported that for each one ton of extraction of Aluminium, more than one ton of red mud is produced.² Due to its high alkaline content, it is posing environmental pollution problems.³ Landfilling after de-watering and drying is one of the initial methods adopted for the disposal of red mud.³ This is not a safe method because it causes environmental pollution. Hence, researchers are investigating methods for its best utility and thereby, converting a potential toxic waste to human utility and advantage. Red mud is composed of andradite, hematite, cancrinite and muscovite and it has more than 15% of Aluminium besides many valuable metals.⁴ Researchers are devolved for its various utilities.⁵⁻⁷ It is used as a composite material in the moulding of plastic materials to impart colour and tensile strength.⁵

Investigations are undertaken to use it as a source for extracting many valuable metals present in it.^{7,8} The physicochemical properties of metal oxides present in the red mud, endow good adsorption nature to the red mud. This property enables the red mud to use it as an adsorbent in water remediation for toxic ions. Treating the red mud with acids or oxidizing or reducing agents has increased the adsorption capacity many-folds. The enrichment of sorption properties is attributed to the change in chemical composition in the red mud through oxidation/reduction, complexing tendencies, etc.

Red mud or modified-red mud are used for the removal of Pb^{2+} , Zn^{2+} , Fluoride⁹, dyes^{10,11} organics¹² and phosphate¹³ from wastewater. Red mud treated with CO_2 and calcinating at 500°C , has been investigated for the removal of Zn^{2+} .¹⁴ Acid-treated red mud has shown high adsorptivity for phosphate.¹³ In some investigations, the Fe-oxide content of red mud is partially reduced to magnetite by treating with pyrite¹⁵, coal¹⁶, H_2 ¹⁷ and CH_4 ¹⁸. Thus obtained treated red mud has been employed as a sorbent in water remediation. Zr-treated Red Mud doped in 'Zn-Alginate Beads' is used for Phosphate removal.¹⁹ Indigo carmine dye is extracted with modified-red mud¹⁰. Naphthol Green B dye is removed using H_2O_2 treated-red mud.¹¹ De-fluoridation is effected with 'Zn-alginate beads' impregnated with 'H₂O₂-treated fine red'.⁹ The major drawback of adopting red mud-based materials as adsorbents, is that the separation of treated red mud particles from the water after equilibration is very difficult due to their micro-sized particles and easy gelling nature. High-speed centrifuges are needed for separating the particles from the water and even then, the filtration is a daunting task. This limits its utility as a sorbent in wastewater treatment.

In the present investigation, neutral red mud is treated with ascorbic acid to enhance its sorption nature. Thus, modified red mud is doped in the 'Ca-alginate-beads' to make the filtration easy. Thus, synthesized beads are observed to have a strong affinity for Cu^{2+} ions. In the present work, the beads are investigated for their sorption properties for Cu^{2+} .

Removal of Cu^{2+} is a potential area of research in water-treatment methods because of toxicity to human beings.^{20,21} Its presence in drinking waters results in the liver, neurological and gastroenterological ailments. Even traces of Cu^{2+} affect aquatic life in water bodies and causes stress on eco-systems.²⁰⁻²³ As per WHO guidelines, 2.0 ppm is the maximum allowed limit in water.^{20,23} One of the main sources of Cu-contamination is the disposal of untreated / in-adequately treated effluents from Cu-based-industries namely, electroplating, plastics, metal finishing, leather, synthetic fibers, etc. into the environment. Even traces Cu ions in groundwater or surface water get accumulated with time through the 'bio-amplification' process as Cu ions are non-degradable and cross the permissible limits.

Reverse Osmosis²¹, Cementation²⁴, electro-flotation²⁵, electro-dyalisis²⁶ membrane filtration²⁷, and photocatalysis^{16,17} are investigated for removing Cu^{2+} from water. The unconventional methods based on bio-sorbents are also employed.^{23,29-38} Bio-adsorbents derived from peanut²⁹, *Phaseolusaureus*³⁰ and *Ceibapentandra hulls*³¹, vegetable waste materials,³² peels of banana³³, spent coffee³⁴, *limoniaacidissima plant barks*²³ and *hibiscus cannabinus* plant stems²³, are studied for their adsorptive nature. Fly ash³⁵, alkali-treated fly ash³⁶, slurry-waste³⁷, acid-modified clay³⁸ and eggshells-coated with Fe_2O_3 ³⁹, are also used. A review of various Cu^{2+} adsorptive methods is available in literature.²¹

In the present work 'ascorbic acid-treated red-mud-doped in the Ca-alginate beads (ARM-Ca-alg)' is investigated for its sorption nature to remove Cu^{2+} ions from water. Extraction conditions have been optimized. Adsorption nature is analyzed by thermodynamic, kinetic and adsorption isotherms and surface morphological (FESEM) studies. The method developed is applied to treat the real samples collected from industries.

EXPERIMENTAL

Chemicals

A.R. grade chemicals viz., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sodium alginate, CaCl_2 , HNO_3 , and HCl were procured through Merck & Co. Double distilled water was used for solutions preparation.

Adsorbent

Red mud procured from Vedanta Aluminium Ltd, Orissa was used. It has 15.47% Alumina, 58.78% of Fe_2O_3 , and 6.58% of SiO_2 , 4.39% TiO_2 , 3.63% Soda, 1.49% of CaO , 0.11% of V_2O_5 and 0.159% of P_2O_5 .

Treatment

Red mud was thoroughly washed to neutrality with distilled water and oven-dried at 105°C for four hours. It was cooled and grounded to a size of $< 75\mu$. 10 g of these materials were mixed with 100 ml of 1 M Ascorbic acid and heated to boiling. Then the solution was cooled to room temperature and filtered. Thus, treated red-mud was washed with distilled water to neutrality. Then the material was oven-dried at 105°C for one hour and stored in an air-tight-colored bottle.

Doping of Beads with Treated Red Mud

2.5 g of sodium alginate was added to 100 ml of distilled water. The resulting solution was heated to 60°C while continuously stirring at 1000 rpm to get a homogeneous solution. Then 0.5 g of Ascorbic acid-

modified red mud was added to this solution with stirring. The resulting solution was cooled and added dropwise with the help of a uniform-bored dropper into a supercooled (-2°C) 2.0% CaCl_2 solution. The drops of solutions got cross-linked with Calcium ions to form beads the moment they touch the cooled CaCl_2 solution as shown in Fig.-1.



Fig.-1: Various Stages of Preparation of ARM-Ca-alg Beads

Thus formed beads were digested overnight with mother-liquor. The beads were filtered, washed with distilled water and dried in a hot air oven at 80°C and stored in an airtight brown bottle. Thus obtained Ascorbic acid-modified red mud doped in the beads of Calcium-alginate is named as 'ARM-Ca-alg'.

Adsorption Experiment

Batch modes of extractions⁴⁰⁻⁴² were adopted using simulated Cu^{2+} solutions. The general procedure followed was as follows:

General Procedure

To a known volume of Cu^{2+} -solution in 250 ml iodine-flasks, requisite quantities of 'ARM-Ca-alg' were added. Initial pHs were adjusted to required values with dil. HCl/NaOH . The flasks were shaken in mechanical shakers for a definite time at 350 rpm. After equilibration, the solution was filtered. Residual Cu^{2+} in the filtrate was analysed by the Atomic adsorption spectroscopic method as described elsewhere.²⁰ Shimadzu Atomic Absorption Spectrophotometer was employed in this work.

Extraction studies were made by changing the concentration of aimed parameter while keeping other parameters at constant levels. The parameters investigated were: pH of the solution, 'ARM-Ca-alg' dosage, contact time between adsorbent and Cu^{2+} solution, initial concentrations of Cu^{2+} ions and temperature. The interference of three-fold excess of co-ions on % of extraction of Cu^{2+} was assessed. Observed data were presented in Fig.-2 to 12; Tables: 1 to 4. Regeneration and re-use of spent 'ARM-Ca-alg' were also investigated. Further, the developed methodology was applied to effluent samples from Cu-based industries. Figure-13 and Table-4 depict the findings.

Percentage Cu^{2+} removal and amount of Cu-adsorbed per gram of 'ARM-Ca-alg', were evaluated using respectively the equations^{43,44}:

$$\% R = \frac{(C_i - C_e)}{C_i} 100 \text{ and } q_e = \frac{(C_i - C_e)}{m} V$$

Where, C_i = initial conc. of Cu^{2+} (mg/L), C_e = Cu^{2+} conc. at equilibrium (mg/L), V = volume of Cu^{2+} solution in litres and m = mass of ARM-Ca-alg.

RESULTS AND DISCUSSION

The influence of different extraction conditions on the absorptivity of 'ARM-Ca-alg' for Cu^{2+} was investigated using simulated samples. The salient features are presented hereunder.

pH

The initial pH of solutions profoundly affects the absorptivity of 'ARM-Ca-alg' for Cu^{2+} ions. Substantial amounts of Cu^{2+} are removed in an extensive pH range: 3 to 10. The finding is novel as the adsorbent is effective in acidic, basic and neutral pHs. Figure-2 depicts the pH effect on the absorptivity. Complete removal of Cu^{2+} from 20 mg/L Cu^{2+} is observed with 1.25 g/L of 'ARM-Ca-alg' at pH: 6 after 2.0 hours of equilibration.

pH_{ZPC} of ARM-Ca-alg is evaluated and its value is 6.0. (Fig.-3). At this pH_{ZPC} , the sorbent has balanced negative and active sites and it is neutral⁴². Above pH: 6, the surface of 'ARM-Ca-alg' acquires a negative charge and below this value, the surface is positively charged due to protination.^{44,45}

As per the speciation of Cu (II) ions in solutions, different species exist depending upon the pH of the solution.⁴⁶ Less than pH: 3, the main species is: Cu^{2+} . Between pHs 3 to 6, $Cu(OH)^+$ exists and between pHs 6 and 11, $Cu(OH)_2$ is formed. Above 11, negative species⁴⁶: $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$, are also formed. So, the adsorption in the extensive pH range: 3 to 10, maybe viewed from a different perceptive. In acidic conditions, the adsorption may be due to the exchange of protons with Cu^{2+} . Further, at these conditions, Cu^{2+} is reduced to Cu^+ by reducing agents such as Fe^{2+} generated during the ascorbic acid-treatment of red mud. The redox potentials are: for Cu^{2+}/Cu^+ : 0.153 V and for Fe^{2+}/Fe^{3+} : 0.77 V. The Cuprous salts are highly insoluble and hence, they get clogged into the matrix of the adsorbate and thus ensuing more removal. As solution pH is increased more than pH_{ZPC} , the hydroxylated species $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$ are bounded to 'ARM-Ca-alg' functional groups more probably via hydrogen bonding viz., '-O-H O - Cu^{2+} '. Moreover, at high pHs, hydroxyl species are more insoluble, forming aggregates, resulting in more absorptivity of ARM-Ca-alg for Cu^{2+} .

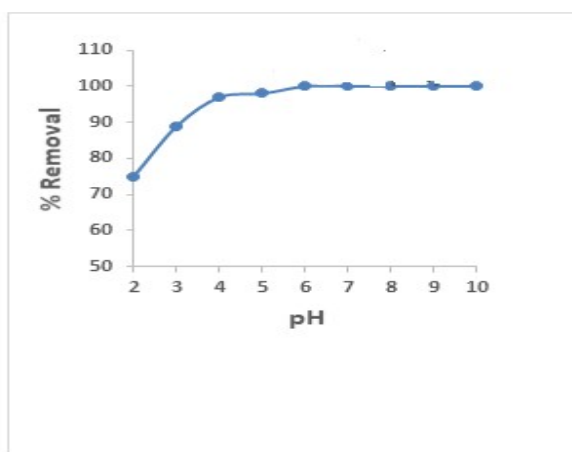


Fig.-2: Effect of pH (Conc. of Cu^{2+} : 20ppm)

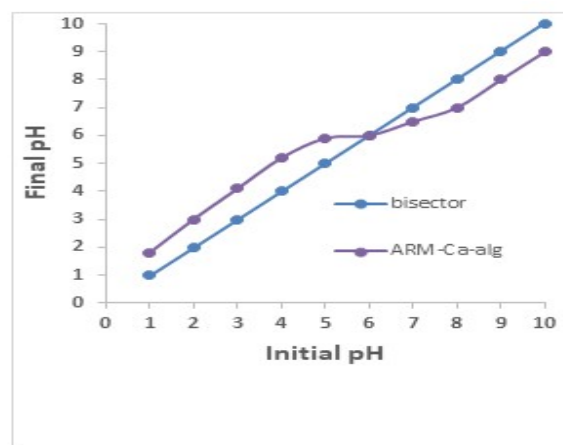


Fig.-3: pH_{ZPC} evaluation for ARM-Ca-alg.

Contact Time

The time allowed for contact between the adsorbent, ARM-Ca-alg, and Cu^{2+} solution is an essential factor determining the extent of extraction. It was investigated and the observed results are presented in Fig.-4. It is observed from the figure that the removal is more with the progress of time, but the sorption is a slowdown and attained 'steady stage' after 120 min.

The % removal is: 27.0% / 15 min; 58.0% / 30 min; 72.0 % / 45 min; 83.5% / 60 min; 90.0% / 75 min; 94.0% / 90 min; 98.0% / 105 min and 100% / 120 min and above. So, a time of 120 min is essential for complete Cu^{2+} removal.

Many adsorption sites are initially available and so, more is % removal.⁴⁷ With the progress of time, sites are exhausted and hence, % removal is a slowdown. When all sites are occupied with Cu^{2+} ions, a 'steady-state' has resulted.

Dosage of Sorbents

By varying 'ARM-Ca-alg' dosage (0.25 g/l to 2.0 g/l) but keeping other extraction conditions at optimum levels, the absorptivity of 'ARM-Ca-alg' for Cu^{2+} was investigated. Different amounts of sorbent were added to 100 mL of 20 mg/L Cu^{2+} solutions. pH was adjusted to 6 and the resulting solution was agitated for 120 minutes at 350 rpm and 303 K. Findings were denoted in Fig.-5.

From Fig.-5, it may be inferred that the minimum dosage needed for complete Cu^{2+} removal from 20 mg/l Cu^{2+} solutions is 1.25 g/l. Sorption capacity is: 126.0 mg/g.

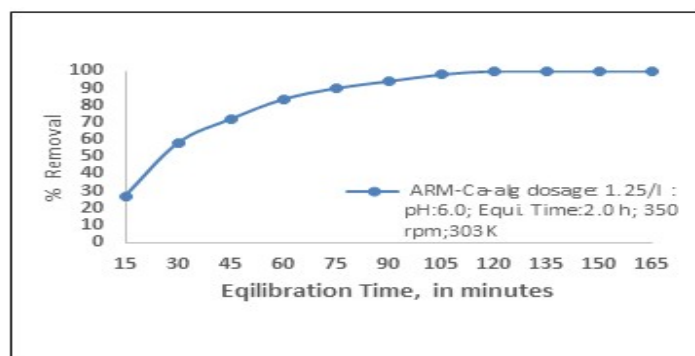


Fig.-4: Effect of Equilibration Time

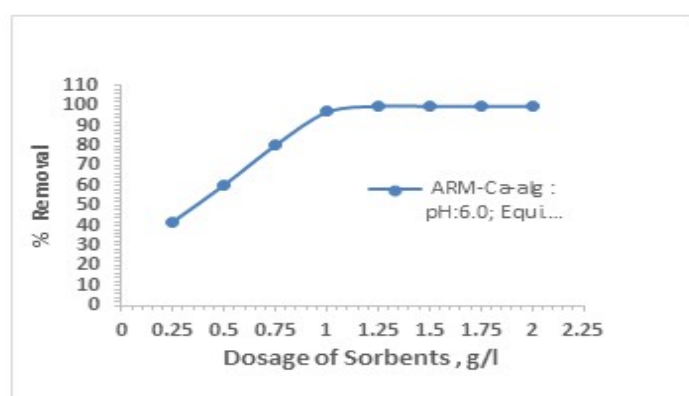
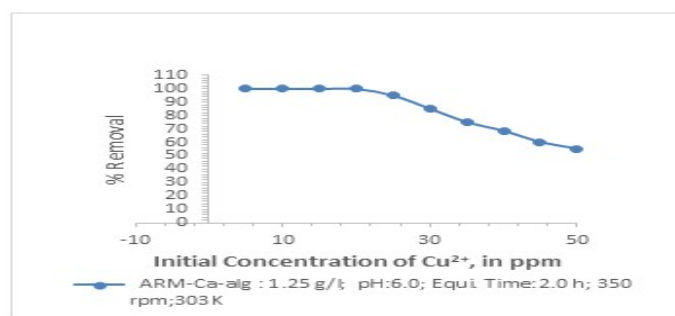


Fig.-5: Effect of Dosage of Adsorbents

Initial Concentration

Initial Cu^{2+} concentration has a profound effect on the absorptivity of 'ARM-Ca-alg' for Cu^{2+} ions. Varying concentrations of Cu^{2+} were equilibrated with 1.25 g/l of 'ARM-Ca-alg' at pH:6 for 120 minutes. The solution was then filtered and analyzed for residual Cu^{2+} . Figures-6 and 7 depict the results. As is seen from Figures, complete removal is possible from solutions of Cu^{2+} of concentrations below 20 mg/l. As the concentration of Cu^{2+} is increased by more than 20 mg/l, % removal is decreased. It is interesting to observe that the adsorption capacity of 'ARM-Ca-alg' increases with the rise in the concentration of Cu^{2+} ions, Fig.-7.

Fig.-6: Effect of Initial Concentration of Cu^{2+} Removal

With the increase in Cu^{2+} ion concentration, q_e is almost linearly (nearly) increased up to 25 mg/l. After that, the intake ability of ARM-Ca-alg remains almost constant i.e, a study state results. As Cu^{2+} conc. is increased, a concentration gradient exists between the conc. of Cu^{2+} ion in the bulk of the solution to the surface also increases. This results in driving more Cu^{2+} ions towards the surface of the sorbents, resulting in more adsorption.⁴⁸ But the quantity of ARM-Ca-alg (1.25 g/l) is fixed and so, sites for sorption are limited. When all the sites are occupied with Cu^{2+} , further 'sorption' is not possible, resulting in a steady state.⁴⁹

Co-ions Interference

Effect co-ions (four-fold excess) on % removal of Cu^{2+} was studied. Findings are noted in Fig.-8a and b. It is inferred from Figs that the co-ions have marginally affected the % removal.

Thermodynamic Studies

The influence of solution temperature on the absorptivity of 'ARM-Ca-alg' for Cu^{2+} was studied. Figures-9 and 10 depict results. Absorptivity is increased with an increase in temperature. With temperature rise, the functional groups of 'ARM-Ca-alg' are subjected to an increase in vibrations. As a consequence, the thickness of surface layers decreases. Moreover, Cu^{2+} acquires more kinetic movement. The cumulative effect is the infiltration of Cu^{2+} into the matrix of ARM-Ca-alg and hence, more adsorptivity.^{48,49}

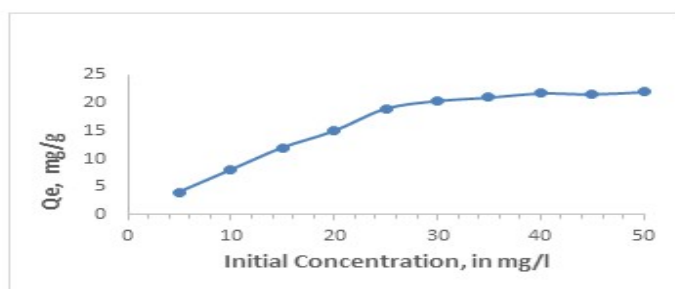


Fig.-7: Initial Cu^{2+} Concentration Vs q_e

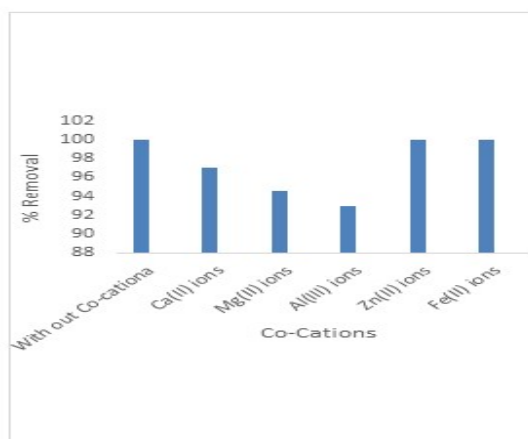


Fig.-8a: Co-cations Interference

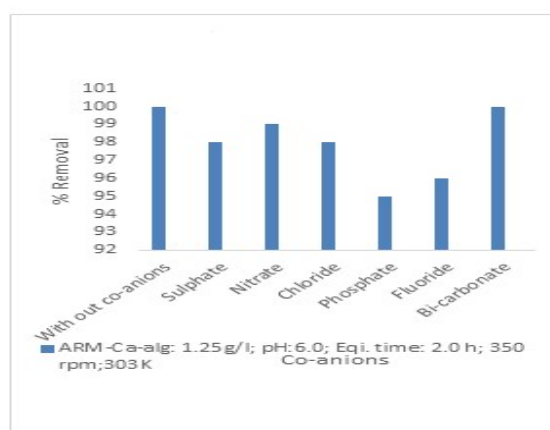


Fig.-8b: Co-anions Interference

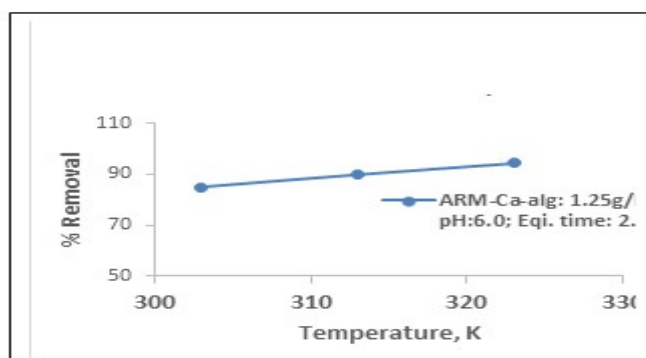
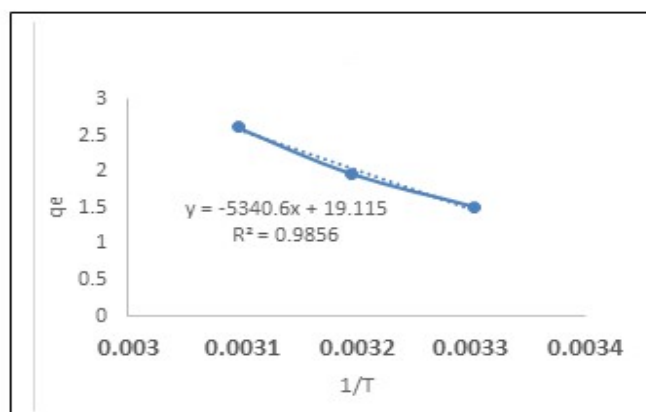


Fig.-9: Effect of Temperature on % Removal (Cu^{2+} Conc.: 30 mg/l)

Thermodynamic parameters were evaluated as per the equations: $\Delta G^0 = -RT \ln K_d$; $\ln K_d = \Delta S^0/R - \Delta H^0/RT$; $K_d = q_e/C_e$; and $\Delta G^0 = \Delta H^0 - T \Delta S^0$. Figure-10 and Table-1, depict the findings.

Fig.-10: 1/T Vs $\ln q_e$ Table-1: Thermodynamic Parameters - Absorptivity of ARM-Ca-alg for Cu^{2+}

T(K)	ΔH (kJ/mole)	ΔS (J/mole)	R^2	ΔG (kJ/mole)
303	44.404	158.932	0.9856	-3.75
313				-5.34
323				-6.95

Negative ΔG values indicate the spontaneity and endothermic nature of adsorption. Further, it emphasizes that Cu^{2+} ions acquire a sufficient proportional increase in energy with an increase in solution temperature to traverse the potential barrier existing between the interface of solid and liquid.⁴⁸ Change in enthalpy (ΔH) value is as high as +44.404 kJ/mole. The positive sign signals the endothermic nature of adsorption. The magnitude of the value indicates that the adsorption is not due to mere physisorption but involves either ion-exchange or chemisorption or both.⁴⁷ It is presumed that the adsorption mechanism is physisorption. If ΔH is: 2.1 to 20.9 kJ/mole; Ion-exchange or chemisorption if the value is: 20.9 to 418.4 kJ/mol.

The adsorptive mechanism is ion-exchange and/or reduction of $\text{Cu}^{2+}/\text{Cu}^+$ ions and subsequent agglomeration depending upon the solution pH. Positive ΔS value and its magnitude is the testimony of disorder at the solid/liquid interface.⁴⁷ More disorder causes more Cu ions to cross over the interface, resulting in more absorptivity.

Adsorption Isotherms

Adsorption phenomenon was analyzed by applying Langmuir, Freundlich, Dubinin-Radushkevich isotherm, and Temkin models.^{47,48,50} The equations used were:

$$\text{Langmuir : } (C_e/q_e) = (a_L/k_L)C_e + 1/k_L$$

$$\text{Freundlich (linear form) : } \log(q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e$$

Where, k_L and a_L is the Langmuir constants and other symbols are as mentioned earlier. Dimensionless separation factor, R_L is evaluated with equation:

$$R_L = 1/(1 + a_L C_i)$$

Temkin equations are :

$$q_e = B \ln C_e + B \ln A$$

and $B = RT/b$

Where A = Temkin isotherm constant (L/g), B = heat of sorption (J/mol), b = Temkin isotherm constant, T = Temperature (K) and R = Gas constant.

Dubinin-Radushkevich equation is:

$$\ln q_e = -\beta \varepsilon^2 + \ln q_m$$

Where, $\varepsilon = RT \ln(1 + 1/C_e)$, β = energy constant and q_m = Dubinin-Radushkevich monolayer adsorption capacity (mol/g). Using the formula $E = 1/\sqrt{2\beta}$ and by the slope of the Temkin isotherm constants, the heat of sorption (B) and mean free energy (E) are evaluated. The findings are presented in Table-2.

Table-2: Adsorption parameters

S.No.	Isotherms		Slope	Intercept	R ²
1.	Langmuir Isotherm	R _L =0.0133	0.0166	0.1034	0.9890
2.	Freundlich Isotherm		0.0824	2.1451	0.9456
3	Dubinin-Radushkevich Isotherm	E=0.708	-3E-05	5.467	0.8723
4.	Temkin Isotherm	B=14.203	11.676	121.24	0.9245

As the R_L value is between 0 and 1, adsorption is favorable. R² values fall in the order: Langmuir Isotherm > Freundlich Isotherm > Temkin Isotherm > Dubinin-Radushkevich Isotherm.

So, the Langmuir Isotherm model better explains the adsorption process than the rest of the models. Hence, this model reflects the monolayer of adsorption and uniform distribution of active sites.

Adsorption Kinetics

Pseudo-1st and 2nd orders, Bangam's pore diffusion and Elovich model equations were employed in analyzing the kinetics of adsorption.^{47,48,50} Equations are:

$$\text{Pseudo-1st order: } \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

$$\text{Pseudo-2nd order: } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

$$\text{Bangam's pore diffusion: } \log \left[\log \left(\frac{C_i}{C_i - q_t m} \right) \right] = \log \left(\frac{K_o}{2.303 V} \right) + \alpha \log(t)$$

$$\text{Elovich equation: } q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$$

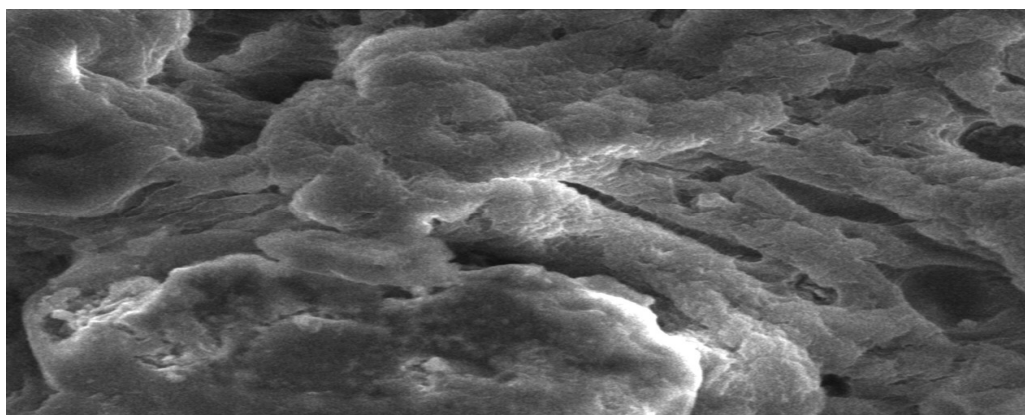
Table-3: Kinetic Parameters

S. No.	Models	Slope	Intercept	R ²
1.	Pseudo- first-order	-0.0101	1.9834	0.8456
2.	Pseudo-Second-order	0.0173	0.3456	0.9890
3.	Elovich Model	27.456	-11.49	0.9456
4.	Bangham's pore-diffusion	0.2467	-1.8795	0.9670

In Table-3 the results are presented. R² values fall in the order: pseudo-2nd order > Bangham's pore diffusion > Elovich > pseudo 1st order. So, the pseudo 2nd order model describes well the sorption process.

FESEM Analysis of Adsorption Phenomenon

To characterize the adsorption of Cu²⁺ onto 'ARM-Ca-alg' surface, FESEM images taken before and after Cu²⁺ adsorption was recorded. HITACHI S-3700N SEM instrument at the magnification of 10,000X was employed. The images were depicted in Fig.-11 and 12.

Fig.-11: FESEM Image of 'ARM-Ca-alg'-Before Cu²⁺ Adsorption

Drastic contrast can be visualized between the images taken before and after adsorption. Pores, cavities, corners and edges are observed in the image-before adsorption. They almost disappeared in the image-

after adsorption. Moreover, some shiny spots have appeared. These features bear the testimony of Cu^{2+} is 'onto' the surface of ARM-Ca-alg.

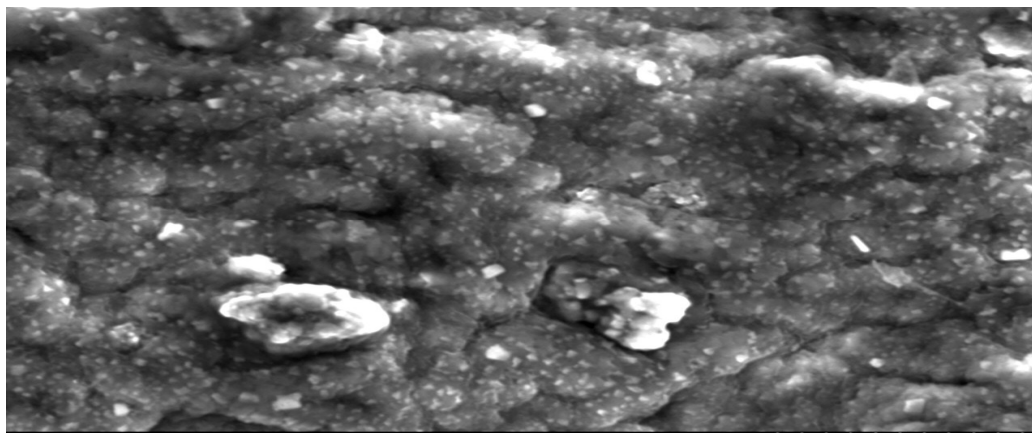


Fig.-12: FESEM Image of 'ARM-Ca-alg'-After Cu^{2+} Adsorption

Regeneration and Reuse

Re-cycling of spent adsorbents after generating them to their initial adsorption capacity is one of the main features of this aspect of research. This enables the assessment of the cost-effectiveness of the developed adsorbent. For this, many eluents were tried to re-generate the spent adsorbent and of which, 0.1 N HCl is found to be effective. Acid-generation signifies the mechanism of adsorption is ion-exchange. Figure-13 represents the variation of adsorption capacity with the number of recycles of a generation of the adsorbent. It may be inferred from the Fig.-13 that 'ARM-Ca-alg' remains as an effective adsorbent until Seven regenerations. This is a remarkable finding.

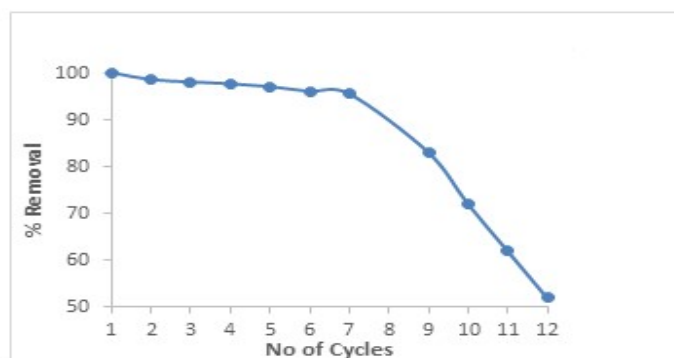


Fig.-13: No. of Cycles Vs % Removal

Applications

The adsorbent developed in this work, ARM-Ca-alg, was applied to real samples collected at Cu-based industries. Samples were assayed for their Cu-concentrations by Atomic Absorption Spectrophotometric method. Then a definite quantity of the samples was equilibrated with 1.25 g/l of 'ARM-Ca-alg' at pH:6 for 2.0 hours. Then the water was filtered and the filtrate was analyzed for the residual Cu-content. Table-4 depicts the results. It is inferred that 'ARM-Ca-alg' completely removes Cu^{2+} ions from wastewater.

Table-4: Applications: Cu^{2+} conc. before and after adsorption of samples
(Samples procured from Copper-based industries).

Samples	Cu^{2+} Concentration		% Removal
	Initial Cu^{2+} Concentration C_i (mg/lit)*	Final Cu^{2+} Concentration, C_f (mg/lit)*	
1	3.89	Zero	100%
2	4.34	Zero	100%
3	5.01	Zero	100%
4	6.22	Zero	100%

*Average of five estimations; S.D.:0.34

CONCLUSION

Ascorbic acid-modified red mud impregnated in Calcium alginate beads (ARM-Ca-alg) is synthesized and investigated as a sorbent for its sorption for toxic Cu^{2+} . Batch methods are adopted. Treatment of red mud with a reducing agent, ascorbic acid, enhances its adsorption nature towards Cu^{2+} which is having easily convertible oxidation states Cu^+ and Cu^{2+} . Physicochemical conditions of extraction are optimized for maximum Cu^{2+} adsorptivity. Cu^{2+} can be removed entirely from 50 mg/L Cu^{2+} solutions by equilibrating 2 h with 1.25 g/L of ARM-Ca-alg, at pH: 6, rpm: 350 and temp: 303 K. Adsorption capacity is found to 126.0 mg/g. It is more than many adsorbents reported in the literature.

ARM-Ca-alg has shown good adsorptivity for Cu^{2+} in an extensive pH range: 3 to 10. This aspect enables its applicability for samples having varying pHs, especially for industrial effluent samples. Spent ARM-Ca-alg can be re-generated and reused for 7 cycles with almost no reduction in adsorption capacity.

Thermodynamic parameters are evaluated. '-ve' ΔG values reflect the spontaneity and endothermic nature of sorption. High ΔH value (44.404 KJ/mole) for 'ARM-Ca-alg' denotes the adsorption mechanism is through 'chemisorption'. The main mechanism of adsorption may be through ion-exchange and/or reduction of Cu^{2+} to less soluble Cu^+ depending upon the solution's pH. The ΔS values indicate a disorder, a favorable condition for good adsorption. This allows Cu^{2+} to penetrate more into the layers of 'ARM-Ca-alg', resulting in more adsorptivity.

Of the Various adsorption isotherm models analyzed, the better fit model falls in the order: Langmuir Isotherm > Freundlich Isotherm > Temkin Isotherm > Dubinin-Radushkevich Isotherm. The Langmuir model indicates the monolayer of adsorbate and equal distribution of active sites. Kinetics of sorption are analyzed and observed that the Pseudo-2nd order model explains well. FESEM analysis reveals that Cu^{2+} is 'onto' the surface of the adsorbent. The developed methodology using ARM-Ca-alg as an adsorbent is successfully applied to remove Cu^{2+} from industrial water samples.

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