Removal of Copper from Industrial Effluents Using New Biosorbents: Thermodynamic, Kinetic and Isothermal Studies and Applications

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New effective biosorbents for the removal of Cu^{2+} ions from industrial wastewater were identified. *Premna serratifolia* plant stem powder (PSSP) and its active carbon (PSSAC) were strongly observed to adsorb Cu^{2+} ions in a wide pH range 6 to 9. Extraction conditions were optimized and sorption capacities are found to be 40.1 mg/g for PSSP and 45.6 mg/g for PSSAC. The extraction of Cu^{2+} from simulated solutions of concentration 25 mg/L were 85% with PSSP and 90% with PSSAC. Common co-ions were marginally interfered. The spent sorbents can be regenerated and reused. Thermodynamic studies revealed the spontaneity and favourability of the sorption process at high temperatures. Homogeneity of sorbents surfaces and monolayer formation of Cu^{2+} ion on the surfaces, were inferred from the analysis of adsorption isotherms. Pseudo-second order kinetics explain well the sorption. The developed adsorbents were also effectively applied to treat polluted industrial effluents for the removal of Cu^{2+} ions.

Keywords: Copper removal, Biosorbents, *Premna serratifolia*, Industrial effluents treatment.

INTRODUCTION

The wealth and prosperity of countries indispensably linked with the growth of industries. But the establishment of industries with least concern of environmental safety is endangering the very existence of human beings. The disposal of untreated or improperly treated effluents from the industries containing toxic elements into the water bodies is adversely affecting the quality of surface and groundwater [1]. The contamination of water with heavy metal ions is one of major environmental problem.

Copper is a heavy metal ion and found in high concentrations in wastewater from industries based on electroplating, metal finishing, etching, paints, plastics, *etc.* [2,3]. High concentrations of copper ions are found in the mining effluents also. In fact, copper is recognized as one of the widely spread heavy metal contaminant in natural water. The presence of traces of copper ions in the disposed effluents will be an environmental threat because the copper ions are non-degradable and are accumulated with time due to a variety of environmental and bio-chemical processes [2,3].

Copper ions are toxic and cause liver, gastroenterological and neurological problems in human beings [3] and their presence in water bodies cause stress to aquatic life and disturb the ecocycles. The maximum concentration of copper ions allowed in industrial discharges is 0.25 ppm [3]. So, investigations to reduce the concentration of copper ions below this allowed limit from industrial wastewater, assumes importance [4].

Traditional methods based on membrane filtration [5], electrodialysis [6], cementation [7], electroflotation [8], reverse osmosis [1], photocatalysis [9] are reported in literature. These methods are non-economical, not applicable for treating larger quantities of effluents and need technical expertise for continuous monitoring of the purification process. In the recent years, water remediation by using adsorbents derived from biomaterials, are interesting the researchers. The merits of these biosorbents are that the methods are effective, ecofriendly and their precursors are renewable plant materials. Various active carbons pertaining to rice husk [10], *Phaseolusaureu shulls* [11], *Ceibapentandra hulls* [12], green vegetable wastes [13] and peanut hull [14], are used for water remediation for copper ions. Stem powders of *Hibiscus cannabinus* plant and barks

of *Limonia acidissima* plant [15], coffee waste [16], egg shells coated with Fe_2O_3 [17], alkali treated fly ash [18], sugar beet pulp [19], biomaterials of *Cordia dichotoma*, *Albizia thompsonii* and *Polyalthia cerasoides platnat* [20], are investigated for the removal of copper ions from contaminated water. Ascorbic acid tread red mud immobilized in Ca-alginate beads is also investigated for its effectiveness [21].

In present study, many biomaterials were investigated for their adsorptive nature for copper ions. It is identified that biomaterials of *Premna serratifolia* plant have good adsorption for Cu^{2+} ions. Hence in this study, the stem powder of *Premna serratifolia* plant and its active carbon, were investigated for their adsorption for Cu^{2+} ions. The conditions for good adsorption were optimized and the sorption mechanism was investigated. Further the bioadsorbents were employed to treat the industrial effluents at the optimum extraction conditions developed in this investigation.

EXPERIMENTAL

All chemicals and regeants employed were of analytical grade and procured from the reputed commercial sources. Simulated copper ion solutions of varying concentrations were used as per need.

Preparation of adsorbents: Various biomaterials were investigated to find their affinity for Cu^{2+} ions. *Premna serratifolia* plant stems powder (PSSP) and its active carbon (PSSAC) had shown good adsorptivity for Cu^{2+} ions. *P. serratifolia* is a small shrub (Fig. 1) and belongs to the *Lamiaceae* family of the plante kingdom. It grows in wet sandy soil, sea coasts and in mangrove habitations. The bioparts of this plant are widely used in traditional Indian medicines.

Fig. 1. *Premna serratifolia* plant having affinity for Cu^{2+} ions

Premna serratifolia **plant stems powder (PSSP):** Stems of *P. serratifolia* plant were cut to pieces, washed with distilled water and dried at at 105 ºC for 2 h in hot air oven. Thus dried material was milled and sieved to a particle size < 75 μm. It is named as PSSP as per the terms *P. serratifolia* plant stems powder and was used as adsorbent in this investigation.

P. serratifolia **plant stems activated carbon (PSSAC):** Small stem pieces of *P. serratifolia* plant were treated with conc. H_2SO_4. Sufficient amount of acid was added such that the biomaterial was completely immersed. The material in contact with conc. H_2SO_4 was allowed to be digested for overnight at room temperature. Then material was taken in a round bottom flask and subjected to heating under water-condenser set-up until the biomaterial was completely carbonized. The biochar was transferred to a beaker containing distilled water and it was separated by filtration, washed and dried at 106 ºC. Thus acid generated active carbon is named as PSSAC in lieu with the terms *P. serratifolia* plant stems activated carbon.

Method: Batch modes of extraction were applied in this work [22,23]. In brief, 100 mL of Cu^{2+} solutions of varying concentrations were taken in 250 mL iodine flasks and weighted quantities of PSSP or PSSAC were added to each flask. Initial pH of solutions were adjusted between 2 to 10. After the completion of the required time of equilibration, the solutions were filtered. The filtrates were assayed for residual Cu^{2+} ions by atomic absorption spectrophotometric method as described in literature [3]. The analysis was repeated for five time and the data was used to evaluated % removal and adsorption capacities of sorbents (q_e) as per equations:

$$\text{Adsorption capacity } (q_e) = \frac{(C_i - C_e)}{m} V \text{ and}$$

$$\text{Removal } (\%) = \frac{(C_i - C_e)}{m} \times 100$$

where C_i and C_e are initial and equilibrium Cu^{2+} ion concentrations and V = solution volume (L); m = sorbent mass (g) [24].

The variations in the percentage of extraction of Cu^{2+} was investigated with respect to various extraction conditions namely, initial pH of solution, contact time, sorbent dosage, initial Cu^{2+} concentration, presence of co-ions and temperature. In these studies, the aimed parameter was changed gradually but keeping all other conditions of extraction at optimum levels. The nature of sorption was analyzed by evaluating the various thermodynamic parameters, kinetic and adsorption isotherm models as described in the literature [24].

RESULTS AND DISCUSSION

Optimization of extraction conditions: The effect of various extraction conditions were investigated and optimized for maximum copper ions removal employing simulated copper solutions.

Effect of pH: By changing the initial pH of solution from 1 to 12, adsorptivities of PSSP and PSSAC for Cu^{2+} ions were investigated while maintaining other extraction conditions constant at optimum levels (Fig. 2), both the adsorbents had shown good adsorption in the range 6 to 9. Extraction had decreased if the pH was increased or decreased from this pH range. The pHzpc values of PSSP and PSSAC were evaluated as 6.0 and 6.5, respectively (Fig. 3).

At these values, the surfaces of the two adsorbents were neutral with equivalent positive and negative active sites. The good extractions in neutral or nearly neutral pH may be explained due to a sort of complex formation between Cu^{2+} ions and adsorbents functional groups. The same can be confirmed
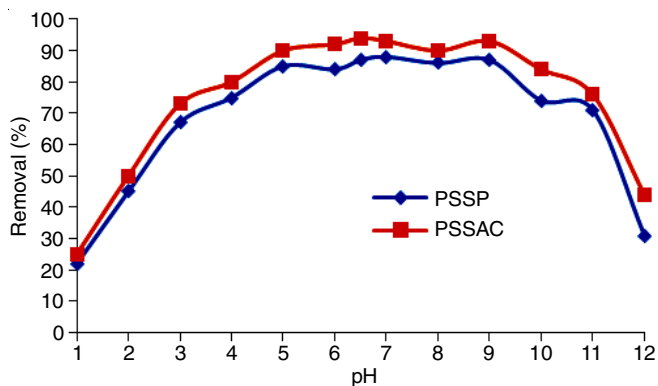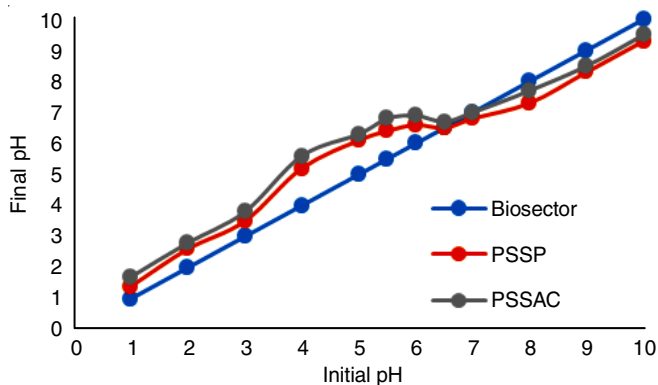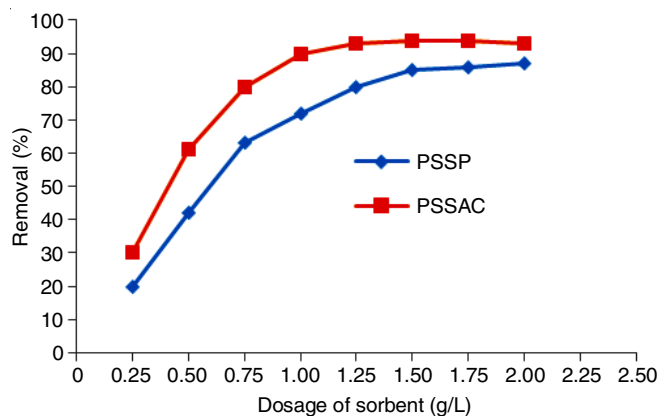
Fig. 2. Effect of pH on extractions, conc. of Cu^{2+} = 25 ppm

Fig. 3. Evaluation of pHzpc for PSSP and PSSAC

Fig. 4. Sorbent dosage *vs.* % removal of Cu^{2+} ions

by the analysis of thermodynamic date. Further, at basic pH values, the Cu^{2+} ions exist as $Cu(OH)^+$ and $Cu(OH)_2$ and hence, the insolubility of hydroxides may be also be one of the factor for good extraction. In case of PSSAC, the active carbon, reduction of Cu^{2+} to Cu^+ may be caused because of low redox Cu^{2+}/Cu^+ potential: 0.153 V [25]. The monovalent cuprous ions are less soluble in water. This results in more extractability of Cu^{2+} ions. But in high alkaline conditions, the extraction decreases. At alkaline pH of solutions, the surface of the sorbents is negatively charged due to the dissociation of functional groups of sorbents. Further, Cu^{2+} exists as anionic species namely, $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$ [25]. Hence, the species are repelled by the negatively charged adsorbents surface and thereby resulting good extractions.

Sorbent's dosages: By changing PSSP and PSSAC concentrations from 0.25 g to 2.50 g/L, % removal of Cu^{2+} was investigated (Fig. 4). The adsorpltivity of adsorbents for Cu^{2+} was influenced by sorbent dosages. At low dosages, the extractions were almost linearly proportional to the dosages. The proportional increase was not observed at high dosages of adsorbent. In fact, a study state was observed after the dosages 1.5 g/L for PSSP and 1.0 g/L for PSSAC. At low dosages, the proportional increase in extraction with increase in the dosage is due to increase in active sites with increase in the dosage. But when the dosage is high, the approaching paths for the Cu^{2+} ions to the sorbent sites was clogged or blocked. This results in a kind of study state [26].

Contact time: The effect of time of contract between sorbent and solution of Cu^{2+} on the percentage of extraction

was studied (Fig. 5). Initially, the rate of Cu^{2+} sorption was more but as time passes, the rate of sorption decreased. In fact, a study state was resulted after 1.5 h with PSSP and 1.0 h with PSSAC. Initially, the needed active sites were available but with progress of time, they were gradually consumed and thereby resulting a steady state [27].
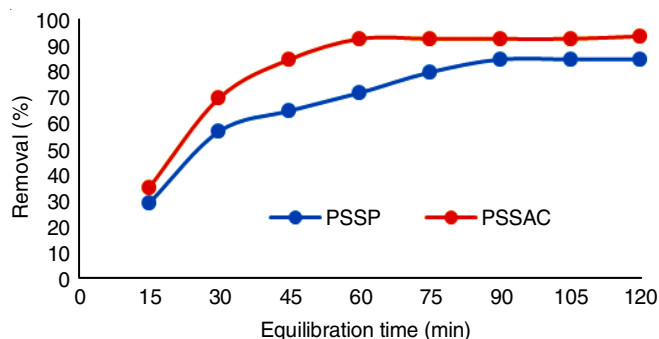
Fig. 5. Effect of time of contact on % removal (initial concentration of Cu^{2+}: 25 ppm)

Initial Cu^{2+} concentration: The adsoprtivties of PSSP and PSSAC were markedly affected by the initial Cu^{2+} ions concentrations. With the increase in initial Cu^{2+} concentration, % of extraction was decreased (Fig. 6) but adsorption capacity of the adsorbents was increased (Fig. 7). This is an interesting observation. As the Cu^{2+} concentration was increased, the active sites needed for the process of adsorption were more. But for fixed PSSP/PSSAC dosages, only a limited active sites were accessible. The required active sites were not available. Hence, % of extraction of Cu^{2+} was decreased as the initial Cu^{2+} ions concentration was increased. The other factor that influences the extraction is the difference in Cu^{2+} concentrations at the surface of PSSP/ PSSAC and in bulk of solutions. As the initial concentration increases, the difference in concentrations is progressively increased. This exerts more pressure on Cu^{2+} ions to diffuse more towards the sorbents surface and thereby, resulting more adsorptivity with increase in initial Cu^{2+} ions concentration [28].

Effect of co-ions: The effect of the presence of co-ions naturally present in water on the percentage of extraction was investigated. The simulated solutions of Cu^{2+} ions containing two-fold excess of the co-ions ions were prepared and subjected
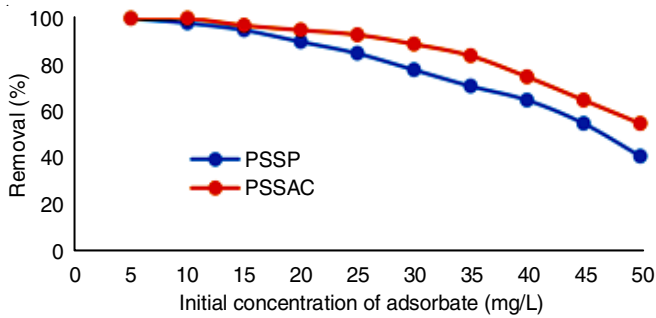
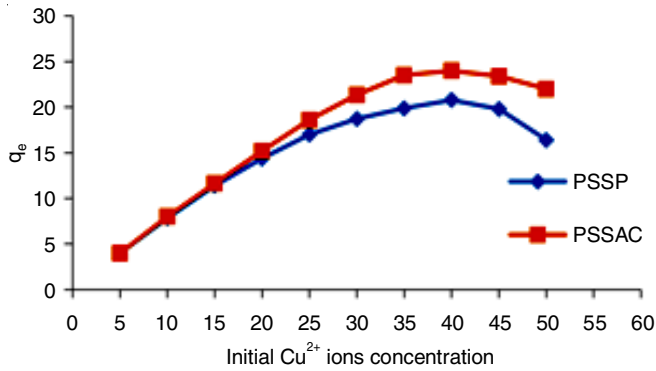Fig. 6. Effect of Initial concentration of Cu^{2+} ions on % of extraction

Fig. 7. Initial concentration of Cu^{2+} vs. q_e

Fig. 9. Co-anions interference

to the extraction with the PSSP and PSSAC adsorbents, at the optimum conditions established in this investigation. The results are presented in Figs. 8 and 9. It can be inferred from the data that the co-ions caused only a marginal interference.
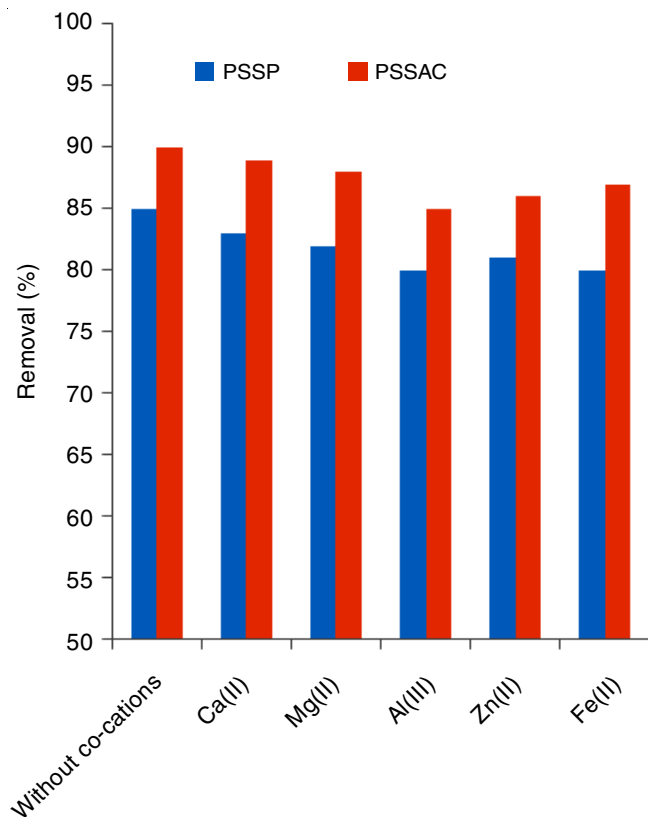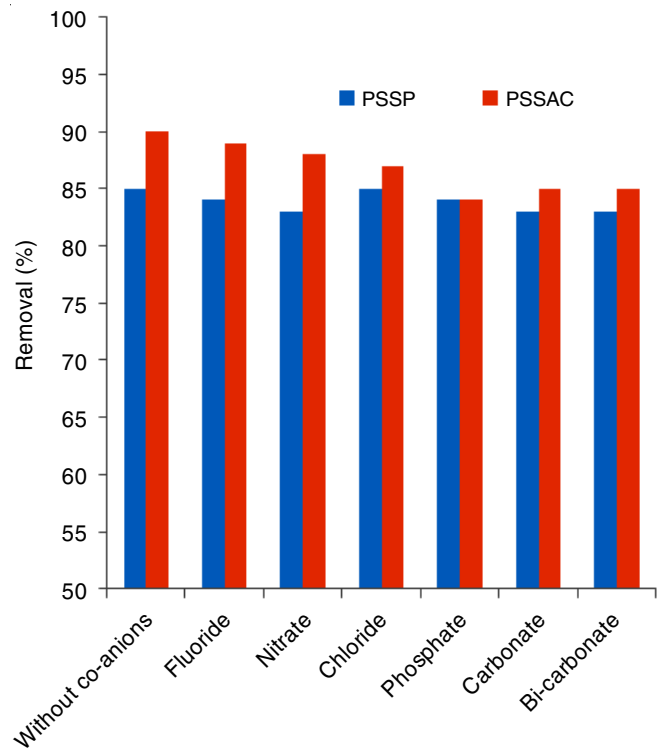

Fig. 8. Co-cations interference

Effect of temperature: Solution temperature was observed to have profound influence on the Cu^{2+} extraction as was evident from Fig. 10. Percentage removal of copper ions was increased with increase in solution temperature. At the elevated temperatures, surface of sorbents was less denser and was open due to enhanced vibrational motions of functional groups on the surface. Further, Cu^{2+} ions get diffused more towards the surface of adsorbent due to the decrease in viscosity of the solution. These two factors enable the Cu^{2+} ions to move deeper into the sorbent matrix and thereby resulting more adsorption [29].
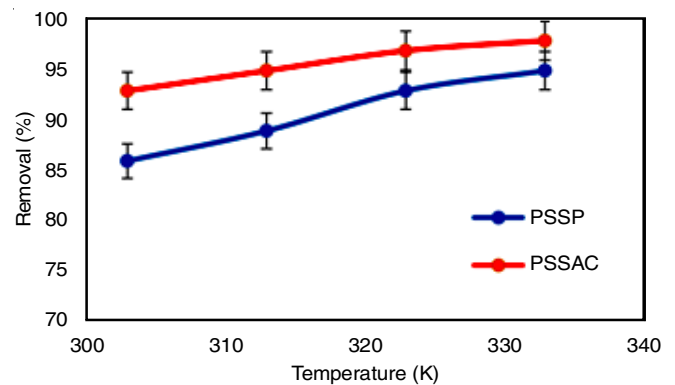
Fig. 10. Temperature vs. % removal of Cu^{2+} ions

Thermodynamic studies: Various thermodynamic parameters were assessed by using equations: $\Delta G^\circ = -RT \ln K_d$; $\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT$; $K_d = q_e/C$; and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where K_d = distribution coefficient; q_e = amount of Cu^{2+} sorbed, C_e = equilibrium Cu^{2+} concentration; T = temperature (K); R = gas constant [30]. The van't Hoff plots are presented in Fig. 11 and the evaluated data is shown in Table-1.

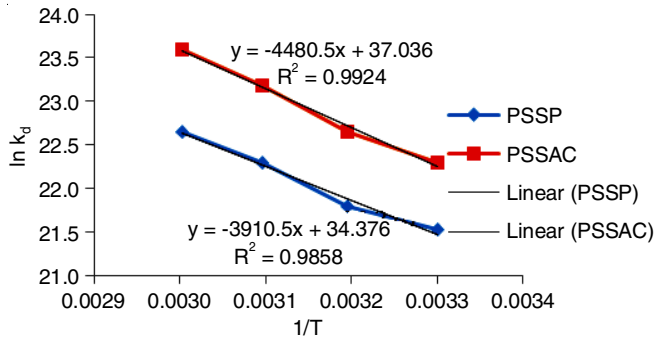| Sorbent	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (KJ/mol)				R^2
			303 K	313 K	323 K	333 K	
PSSP	32,59	285.76	54.00	57.40	59.70	62.60	0.985
PSSAC	37.25	303.88	54.83	58.08	60.90	63.94	0.992

TABLE-1
THERMODYNAMIC PARAMETERS

Fig. 11. Van't Hoff plot

The negative ΔG values confirmed the spontaneity of adsorption. The increase in values with the increase in solution temperature, signifies the 'favourability' of adsorption at elevated temperatures. Positive ΔH values confirmed the endothermic character for adsorption.

The high values of the order of 32.59 kJ/mol for PSSP and 37.25 kJ/mol for PSSAC confirmed the ion-exchange and or a sort of complex formation between Cu^{2+} and functional groups of PSSP and PSSAC. The ΔS values of the order 285.76 J/mol for PSSP and 303.88 J/mol for PSSAC, signify more disorder at the sorbent/solution boundary. This situation causes more chances for Cu^{2+} ions to cross-over boundary and hence more adsorption [30].

Adsorption nature: The nature of sorption was analyzed by applying linear models of Freundlich, Langmuir, Temkin and Dubinin and Radushkevich isotherms [31].

The equations (linear forms) employed were:
Freundlich model:

$$\log(q_e) = \log k_f + \left(\frac{1}{n}\right)\log C_e$$

where C_e = sorption capacity (mg/g) and n = empirical parameter.
Langmuir equation:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{a_L}{k_L}\right)C_e + \frac{1}{k_L}$$

where q_e = sorbed amount of Cu^{2+} ions, k_L and a_L = Langmuir constants; Dimensionless separation factor, $R_L = 1/(1 + a_L C_i)$.

Temkin equation:

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

where RT/b = B, B = Temkin constant pertains to heat of sorption (J/mol), A = Temkin isotherm constant (L/g), b = Temkin isotherm constant.

Dubinin-Radushkevich equation:

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

where $\varepsilon = RT \ln (1 + 1/C_e)$.

Of the various models, the R^2 values were high for Langmuir model: 0.980 for PSSP and 0.996 for PSSAC. Hence, this model explains well the sorption and thereby, indicates monolayer adsorption of Cu^{2+} ion on homogenous sorbent surfaces. R_L values also indicate the favourability of Cu^{2+} sorption [31]. 'E' and 'B' values were calculated from Temkin and Dubinin-Radushkevich equations (Table-2).

Adsorption kinetic analysis: The kinetics of adsorption of Cu^{2+} ions on PSSP and PSSAC were analyzed by adopting various well known models namely, pseudo-first/second order [32,33], Bangham's pore diffusion and Elovich models [34,35].

The linearized forms of equations used were:
Pseudo-first order:

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log(q_e)$$

Pseudo second order:

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

Elovich model:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

Bangham's equation:

$$\log.\log\left(\frac{C_i}{C_i - q_t m}\right) = \log\left(\frac{k_o}{2.303V}\right) + \alpha\log(t)$$

Adsorbate	Characters	Freundlich	Langmuir	Temkin	Dubinin-Radushkevich
PSSP	Slope	0.176	0.068	1.975	-1.1
	Intercept	2.303	-0.016	10.61	2.7
	R^2	0.794	0.980	0.771	0.752
		1/n = 0.176	R_L = 0.01	B = 1.975	E = 0.8 kJ/mol
PSSAC	Slope	0.166	0.053	2.443	-8.2
	Intercept	2.559	0.0065	13.32	2.9
	R^2	0.756	0.996	0.776	0.898
		1/n = 0.166	R_L = 0.006	B = 2.443	E = 5.7 kJ/mol

TABLE-2
EVALUATED ADSORPTION ISOTHERMS PARAMETERS

It may be inferred from data (Table-3) that the correlation coefficient, R^2 values falls in the decreasing order: (a) Pseudo 2nd order (0.979) > Elovich (0.961) > Pseudo 1st order (0.954) > Bangham diffusion (0.892) for PSSP. (b) Pseudo 2nd order (0.963) > Pseudo 1st order (0.892) > Elovich (0.828) > Bangham diffusion (0.765) for PSSAC. Hence, the kinetics of Cu^{2+} adsorption onto the surface of PSSP and PSSAC can be well explained by pseudo 2nd order model.

Spent PSSP and PSSAC recycling: Spent PSSP and PSSAC were studied for their regeneration and reuse to have cost effectiveness of the process. Many eluents at different experimental conditions were tried. 0.1 N HCl solution was effectively regenerated the spent PSSP and PSSAC. The spent PSSP and PSSAC were digested with 0.1 N HCl for overnight at room temperature, filtered, well washed, dried in oven at 105 ºC and reused. Seven cycles were investigated. It was evident from Fig. 12 that PSSP and PSSAC retained their adsorption capacities up to 3 and 4 cycles, respectively.

Applications: With simulated copper solution of concentration: 25 mg/L, the maximum removal was observed to be 85% with PSSP at the optimum pH: 6.5 and at equilibration time: 1.5 h. while with PSSAC, the maximum removal was 90.0% at pH: 6.5 and at equilibration time:1.0 h.

To validate the methodologies developed, the real wastewater samples collected from industries were subjected to the treatment with PSSP and ASSAC as adsorbents at the optimum conditions established with the simulated samples. In the first instance, the effluent samples collected from the industries were analyzed for Cu content (C_i) with AAS method. Then these samples were treated with PSSP and PSSAC. The unextracted Cu^{2+} was estimated (C_e). It can be seen from the Table-4 that
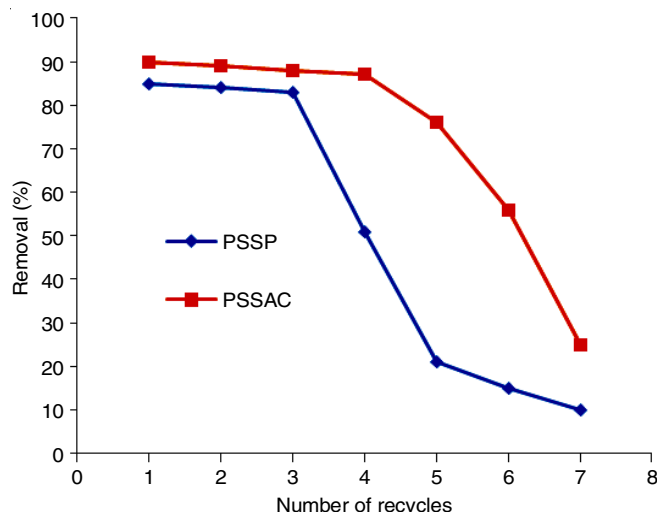

Fig. 12. Regenerations *vs.* % Cu removal

the PSSP and PSSAC are very effective in purifying water with respect to Cu^{2+} ions.

Conclusion

The present investigation was focused on finding simple biosorbents for extracting Cu^{2+} ions from industrial effluents. Stem powder of *Premna serratifolia* plant (PSSP) and its active carbon (PSSAC) were identified to have good adsoptivity for Cu^{2+} ions in a wide pH range of 6 to 9. The extraction conditions were optimized for the effective removal of Cu^{2+} ions. High sorption capacities were 40.1 mg/g for PSSP and 45.6 mg/g for PSSAC. Copper ions removal was 85% with PSSP and 90% with PSSAC from Cu^{2+} solution of concentration 25 mg/L

TABLE-3
EVALUATED KINETIC PARAMETERS

Adsorbate	Parameter	Pseudo-first order	Pseudo-second order	Elovich model	Bangham's pore diffusion
PSSP	Slope	-0.016	0.065	3.629	0.508
	Intercept	1.121	2.338	-5.339	-2.41
	R^2	0.954	0.979	0.961	0.892
PSSAC	Slope	-0.0399	0.064	3.618	0.448
	Intercept	1.39	1.437	-3.663	-2.233
	R^2	0.892	0.963	0.828	0.765

TABLE-4
APPLICATIONS

Samples	Cu concentration in effluents (analyzed by AAS method), C_i (mg/L*)	After treatment with PSSP*		After treatment with PSSAC*	
		C_e (mg/L)	Extraction (%)	C_e (mg/L)	Extraction (%)
Battery effluents					
1	8.4	Zero	100	Zero	100
2	10.1	Zero	100	Zero	100
3	12.2	Zero	100	Zero	100
4	14.2	Zero	100	Zero	100
5	17.1	0.4	97.6	0.2	98.8
Mining effluents					
1	14.0	Zero	100	Zero	100
2	17.4	0.7	95.9	Zero	100
3	20.1	3.4	83.0	3.0	85.1
4	22.3	4,2	81.2	3.6	83.5
5	23.4	4.8	79.4	4.1	82.5

*Mean of four determinations; SD: ± 0.209

at pH: 6.5 with sorbent concentrations: 1.5 g/L for PSSP and 1.0 g/L for PSSAC after an agitation time of 1.5 h for PSSP and 1.0 h for PSSAC. Common co-ions were less interfered and the spent PSSP and PSSAC could be regenerated and reused. The adsorption mechanism was assessed by evaluating thermodynamic parameters. The adsorption nature was analyzed by adopting various adsorption isotherms and kinetic models. The developed adsorbents were successfully applied to treat the industrial effluents.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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