Asian Journal of Chemistry; Vol. 34, No. 1 (2022), 191-200

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23445

Simultaneous Removal of Copper and Lead Ions from Industrial and Mining Effluents Using Biosorbents Derived from *Rhododendron arboreum* Plant: Adsorptive Optimization and Mechanism Evaluation

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Received: 28 July 2021; *Accepted*: 5 October 2021; *Published online*: 16 December 2021; AJC-20635

The present investigation is focused on developing simple and effective bioadsorbents for the simultaneous removal of Cu^{2+} and Pb^{2+} ions from industrial and mining effluents. *Rhododendron arboreum* plant biomaterials are identified to have strong adsorptivity for Cu^{2+} and Pb^{2+} ions. Stem powers (RSP), their active carbon (RSAC) and the active carbon doped in Ca-alginate beads, RSAc-Ca.alg, are investigated for the simultaneous removal of Cu^{2+} and Pb^{2+} ions. Various extraction conditions were investigated and optimized for the maximum Cu^{2+} and Pb^{2+} removal. The sorption capacities were 35.0 mg/g for RSP, 38.5 mg/g for RSAC and 45.8 mg/g for RSAC-Ca.alg. Common co-ions were marginally interfered and spent sorbents can be used after regenerating with 0.1 HCl for a multiple number of cycles. Thermodynamic analysis indicated the spontaneity of adsorption process and favourability of adsorption at elevated temperatures. The high positive ΔH values indicate the endothermic nature of sorption and mechanism is ion-exchange and or a sort of complex formation between Cu^{2+}/Pb^{2+} ions and functional groups of sorbents. High positive ΔS values indicate intensive disorder at solution/solvent boundary and thereby, favouring enhanced sorption. Sorption is well explained by Langmuir isotherm model and pseudo-second order kinetics. The sorbents were applied to treat effluent samples collected from industries and mining in India and Ethiopia for the removal of Cu^{2+} and Pb^{2+}. The results show that both the metal ions can be successfully removed at the optimum extraction conditions arrived in this investigation. The merit of this investigation is that at a convent working pH 6, effective simultaneous removal of toxic Cu^{2+} and Pb^{2+} ions from industries can be achieved with simple biosorbents derived from *Rhododendron arboreum* plant.

Keywords: Copper and Lead removal, Biosorbents, *Rhododendron arboretum*, Ca-alginate beads, Industrial effluents.

INTRODUCTION

Contamination of water bodies with heavy metals is a potential threat to environment and human beings. The metal ions are non-degradable and once they enter the water bodies, they get involved in the eco-systems simulations and thereby resulting their accumulation with progress of time [1-3]. Of these heavy metal ions, lead and copper ions are carcinogenic and their presence even in traces in water are detrimental to human and microorganisms [1,2]. The ailments caused by these metal ions in human beings are neurological disorders, nephrological problems, gastroenterological disorders, sleeplessness and even cancer. Lead is classified as 'human carcinogens by USEPA [1-3]. The permissible limits as per WHO are 2.0 mg/L for copper and zero or at the maximum 0.01 mg/L for lead [3].

Copper and lead ions are present in many effluents released from the industries based on these metals. They include manufacturing of various chemicals, fertilizers, electronics, batteries, plumbing, *etc.* [4-6]. Another important source for the existence of both the metal ions is the mining effluents. Frequently sulfide minerals contain copper and lead. The effluents regenerated during the metallurgical process, contain copper and lead ions. Further, over utilization of copper sulphate in agriculture fields as fungicide is another source of contamination. The recovery of these metal ions from effluents is also important from the economic point of view. Hence, removal and recovery of these metal ions assume importance.

Traditional technologies based on precipitation, solvent extraction, ion-exchange, membrane filtration, electrowinning, electrode deposition and reverse osmosis are employed for the removal of lead or copper [7-10]. The precipitation methods suffer from the problems of disposal of sludge generated. The other methods are not economical as they involve many chemicals, complicated procedures and need expert supervisions. As an alternative, the adsorption methods are interesting for the investigators. Because of their simplicity and efficiency, they are intensively investigated. Some of the effective adsorbents reported for the removal lead are Saudi activated bentonite [11], poly ethylenimine grafted gelatin sponge [12], waste tires ash [13], bicomponent polymer brushes [14] and multiwalled carbon nanotubes with *tris*-(2-aminoethyl)amine [15] and ash of okra biowaste [16].

Employing biomaterials derived plants, is another trend in the adsorptive removal methods. As these biomaterials are derived from abundantly available renewable plant sources and possess unexplored sorption nature, they turned to be increasing source of research activity in the recent years. The biosorbents investigated for the removal of lead ions are the activated carbons of maize tassesl [17] pumpkin-seed-shell [18], tamarind wood [19], pinecone [20], caryotaurens seeds [21], coconut shell [22], exhausted coffee grounds [23], hydrazine sulphate-activated red mud [24], banana pseudo stem [25], walnut shell powder [26], apple juice residue [27], *etc.*

For copper remediation, the sorbents used are the activated carbons of *Ceiba pentandra* hulls [28], rice husk [29], peanut hull [30], green vegetable waste [31] and *Phaseolus aureus* hulls [32]. Treated fly ash with NaOH solution [33], rose waste biomass [34], iron oxide coated egg shells powder [35], peels of potato and banana [36], spirogyra (green alga) [37], sugar beet pulp [38], HCl-treated clay [39], cross-linked chitosan [40] and coffee waste [41] are also investigated for the extraction of Cu^{2+} ions.

As revealed from the literature these investigations are reported to remove either Pb^{2+} or Cu^{2+} and not both the ions at a time. The investigations pertain to such simultaneous removal of Pb^{2+} and Cu^{2+} are very few [42]. The sorbents that can remove the co-existing Cu^{2+} and $Pb^{2+}$from the industrial effluents is an interesting aspect. The Cu^{2+} and Pb^{2+} ions coexist in many effluents of industries and mining. Hence, this study is aimed to investigate various biosorbents for the simultaneous removal of Pb^{2+} and Cu^{2+}. When trying different biomaterials as adsorbents towards this aim, it is observed that *Rhododendron arboreum* plant stems powder and its active carbon, have strong selective sorption for both Cu^{2+} and Pb^{2+} ions. One of the inherent demerits of employing these materials is the slow filtration [43]. To avoid it, the active carbon is impregnated in sodium alginate beads cross linked with Ca^{2+} ions. Thus, stem powers, active carbon and the Ca-beads impregnated with active carbon, are investigated for their adsorptivity for Cu^{2+} and Pb^{2+} ions with respect to the optimization of extraction conditions, assessing thermodynamic, kinetic and adsorption isotherm parameters and applications.

EXPERIMENTAL

Analytical grade chemicals were used. Simulated Cu^{2+} and Pb^{2+} solutions and their admixtures were prepared in distilled water. Sock solutions of 25.0 mg/L of Pb^{2+} and 50.0 mg/L of Cu^{2+} were prepared in distilled water and diluted depending upon the requirement.

Plant: *Rhododendron arboreum* is a small ever green tree and it belong to the family of *Ericaceae* in Plantae Kingdom (Fig. 1). It grows in the temperature range 15 to 20 ºC. This plant is found in abundance in the Great Himalayas and other parts of Asia.

Fig. 1. *Rhododendron arboreum* plant having affinity for Cu^{2+} and Pb^{2+} ions

Preparation of adsorbents

***Rhododendron arboreum* plant stems powder (RSP):** *Rhododendron arboretum* plant stems were cut, washed, dried at 105 ºC for 3 h in oven. The material was pulverized and sieved to < 75 µm size. Thus obtained material was named as RSP in accordance with Rhododendron plant stems powder and preserved in brown bottle.

Activated carbon of *Rhododendron arboretum* plant stems (RSAC): The stems of *Rhododendron arboretum* plant were used as the precursor for the activated carbon preparation. The stems of *Rhododendron arboretum* plant were cut into small pieces and half-dried under sunlight. The biomaterial was immersed in conc. H_2SO_4 in a round bottom flask and allowed to be digested overnight. The flask was heated with condenser set-up until all the biomaterial was converted to biochar. Thus obtained material was filtered, and washed until the filtrate was neutral. The material was dried in hot air oven at 105 ºC for 2 h. The material was grounded and then sieved by 75 µm ASTM and preserved in a brown bottle. The synthesized active carbon was named as RSAC (*Rhododendron arboretum* plant stems activated carbon).

Calcium alginate beads doped with RSAC (RSAC-Ca-alg): Sodium alginate solution in distilled water (2.5% w/v) was heated slowly to reach 80 ºC to obtain a homogenous gel. To this gel, 2.5 g of RSAC was added with constant stirring. The resulting solution was stirred until homogeneous solution was obtained. Then the solution was cooled to room temperature. Thus resulting solution was added dropwise into a previously cooled (10 ºC) 2.0% $CaCl_2$ solution. The moment the drops were touched to Ca^{2+} solution, excellent beads were developed. The formed beads were allowed to be in contact with the mother liquid for an overnight for the complete digestion to occur. Then beads were filtered and dried at 90 ºC for 3.0 h. The beads obtained were named as RSAC-Ca-alg.

Adsorption studies

Extraction method: Batch extractions were applied in assessing the adsorptivity of sorbents for Cu^{2+} and Pb^{2+} [43-45]. Desired amounts of sorbents were added to 100 mL of 20.0 mg/L of Cu^{2+} or 15 mg/L of Pb^{2+}solution (simulated) taken in 250 mL conical flasks. Initial pH was adjusted. The flasks were agitated for required times at 400 rpm in an orbital shaker at 30 ± 1 ºC. The sorbents were separated and the filtrate was assayed for residual Cu^{2+} or Pb^{2+} using Atomic Absorption Spectrophotometer, AA-500, PG Instruments Ltd., UK as per the standard procedures in the literature [1].

Experiments were repeated for five times for assessing the accuracy and precession of the analyses. Average values were adopted to determine accuracy and precession of analyses. Cu^{2+} or Pb^{2+} removal (%) and adsorption capacities of sorbents (q_e) were estimated as per standard equations:

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

and

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

where C_i and C_e are the initial and equilibrium Cu^{2+} or Pb^{2+} ion concentrations and V = solution volume (L); m = sorbent mass (g) [46].

The influences of pH, dosage of sorbent, contact time between sorbent and Cu^{2+} or Pb^{2+} solution, initial Cu^{2+} or Pb^{2+} concentrations, co-anions and temperature on adsorptivity of adsorbents, were assessed. In these studies, the aimed factor was gradually varied. But other factors were maintained at optimum levels. Inference of co-anions when present in two fold excess of Cu^{2+} or Pb^{2+} ions was also investigated.

RESULTS AND DISCUSSION

Optimization of extraction conditions: The affinity of the sorbents, RSP, RSAC and RSAC-Ca/alg, for Cu^{2+} and Pb^{2+} was investigated with simulated solutions containing single metal ions.

Effect of pH: With all the sorbents, good sorption of both the metal ions were observed in pH range '4 to 7' with maximum at pH 6 (Fig. 2). Below or above this pH range, the extraction decreases. The pHzpc values for the RSP, RSAC and RSAC-Ca-alg are 6.0, 6.5 and 7.0, respectively as evaluated from Fig. 3. At these pHzpc values, the surface of the sorbent is neutral. Above these values, the surface is charged negatively due to the 'dissociation' of functional groups. Below these values, 'protonation' of functional groups occurs. Hence, the surface is positively charged. In the pH range of 4 to 7, the main species of copper ions were Cu^{2+} and $Cu(OH)^+$ and for lead ions $Pb^{2+}/Pb(OH)_2(s)/PbOH^+$ [47,48]. The good sorption in acidic side of the pH range 4-7 may be due to the exchange of the metal ion with H^+ of the functional groups of the sorbents. Further in case of Cu^{2+} ions and with RSAC as sorbent, the active carbon may cause reduction of 'cupric' to 'cuprous' and the 'cuprous' compounds being sparingly soluble, more extraction is observed. At pH 6, the extractions of Cu^{2+} ion were 80.0% with RSP; 85.0% with RSAC and 94.0% with RSAC-Ca.alg. At the same pH, Pb^{2+} extractions were 78.0% with RSP; 82.0% with RSAC and 92.0% with RSAC-Ca.alg. At high pH values, the extractions were decreased for both the metal ions. At these high values, lead and copper exist as anions and these negatively charged species are repelled by the negatively charged surface of the sorbents, resulting decrease in extraction.

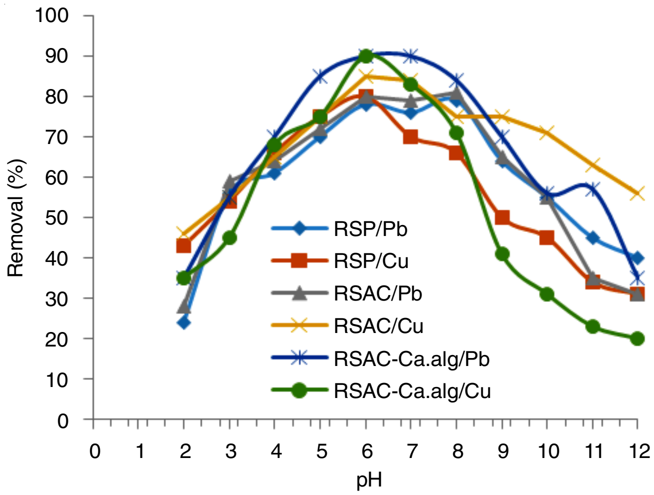

Fig. 2. pH Vs % extraction of Cu^{2+}/Pb^{2+}

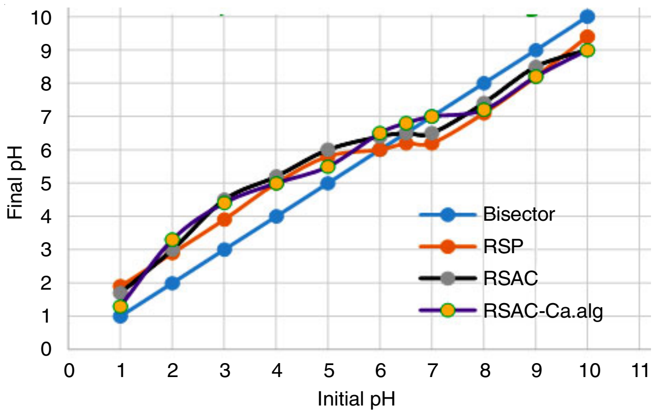

Fig. 3. Evaluation of pHZPC for RSP, RSAC and RSAC-Ca.alg

Effect of sorbents dosage: The extractions of Cu^{2+} and Pb^{2+}ions were influenced by the dosage of sorbents. At low concentrations, the extractions were almost linearly proportional to the dosage of sorbents. But the proportionality was lost as the concentrations of sorbents were further increased and it reached to a steady state after certain dosage of the sorbents (Fig. 4). For the extraction of Cu^{2+} ions, the steady state was reached at 2.5 g/L with RSP; 2.0g/L with RSAC; 1.5 g/L with RSAC-Ca.alg. In the case of Pb^{2+} extraction, the study sates were reached at 2.0 g/L with RSP; 1.5 g/L with RSAC; 1.0 g/L with RSAC-Ca.alg.

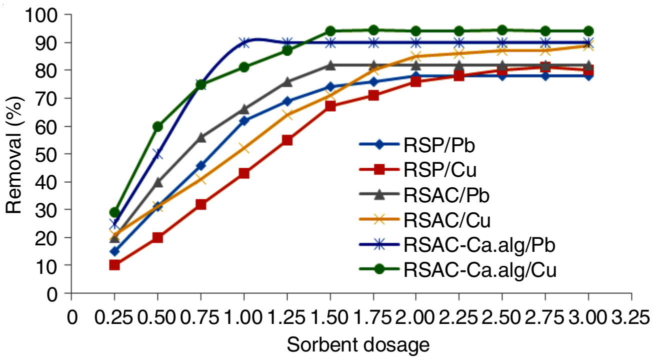

Fig. 4. Effect of sorbent dosage (initial conc. of Pb^{2+}: 15 mg/L; Cu^{2+}: 20 mg/L)

At low sorbent concentrations, as the dosage increases, active sites also increase proportionally, resulting linear relationship. The loss of proportionality at high concentrations may be due to blocking and/or obstructing the paths ways for Cu^{2+} and Pb^{2+} ions to reach to active sites of the sorbents.

Contact time: The optimum time of contract between sorbents and solutions of Cu^{2+} or Pb^{2+} ions were assessed to be 1.5 h with RSP, 1.0 h with RSAC and RSAC-Ca.alg for the removal copper ions; and 2.0 h with RSP, 1.5 h with RSAC and 1.0 h with RSAC-Ca.alg for the extraction of lead ions (Fig. 5). Initially, the adsorption was more. But with the progress of time, the rate of adsoption was decreased and reached to a steady state after certain duration.

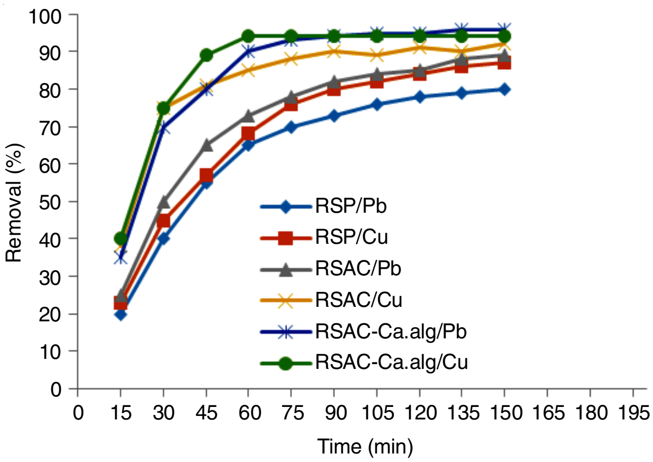

Fig. 5. Time *vs.* % removal of Pb^{2+} and Cu^{2+} (initial conc.: Pb^{2+}: 16 mg/L; Cu^{2+}: 20 mg/L)

At the beginning, the availability of adsorption sites are more for Cu^{2+} or Pb^{2+} to get adsorbed. As the time passes, the active sites are used-up progressively. After certain time, no more active sites are available, resulting a kind of steady state wherein the rates of adsorption and desorption are equal [47].

Initial concentration of Cu^{2+} and Pb^{2+}: Initial Cu^{2+}/Pb^{2+} ions concentrations have noticeble influence on the percentage of extractions (Fig. 6). With increase in initial concentration, percentage of extraction decreases. But it is interesting to note that adsorptivity (q_e) is increased (Fig. 7).

With an increase in Cu^{2+} or Pb^{2+} concentrations, the demand for active sites is more. For a fixed sorbent concentrations, only a fixed number of active sites are available. Proportional raise in demand for active sites is not met. Hence, results in the decrease in the extraction of Cu^{2+} and Pb^{2+}. Another factor to be considered is the difference in concentrations of adsorbate at the surface of the sorbents and in the bulk of solutions. With increase in the concentrations, the difference is more and more. This causes more diffusion of adsorbate ions (Cu^{2+}/Pb^{2+}) towards the surface of is sorbents. Hence, adsorptivity is increased though % removal decreased [48].

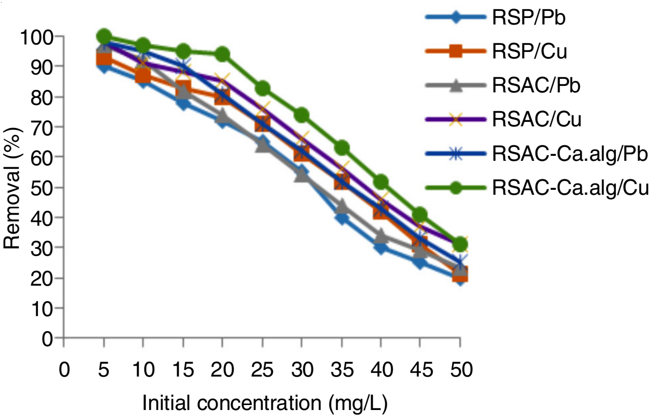

Fig. 6. Initial concentration of Pb^{2+}/Cu^{2+} *vs.* % removal

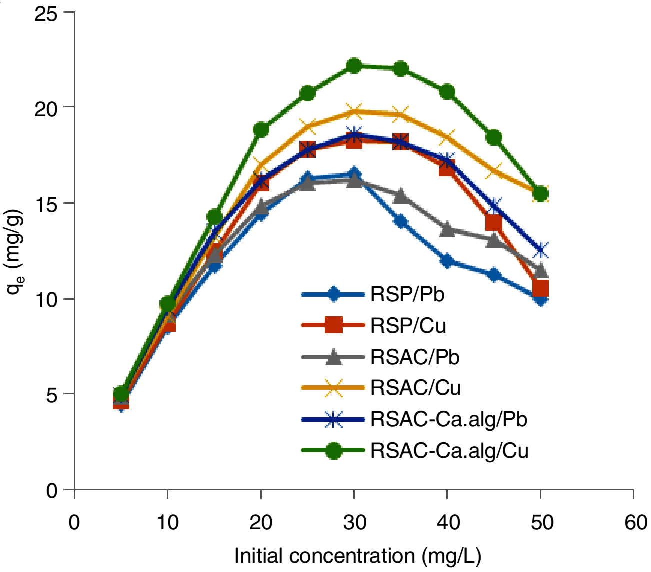

Fig. 7. Effect of initial conc. on q_e

Interference of co-ions: The effect of the presence of two fold excess of co-ions on the % of extraction was evaluated. The experiments were conducted at the optimum conditions established in this work with simulated solutions containing Cu^{2+}, Pb^{2+} and two-fold excess of foreign ions.

It could be inferred that many anions and cations caused marginal interference (Fig. 8a-b). Phosphate, Al^{3+}, Fe^{2+} and Zn^{2+} interfered to some extent but in any case the extraction was not come down below 72.0%.

Effect of temperature: The solution temperature effect on extractions was investigated at temperatures *viz.* 303, 313, 323 and 333 K (Fig. 9). Extraction increases with increase in temperature. With raise in solution temperature, the surface

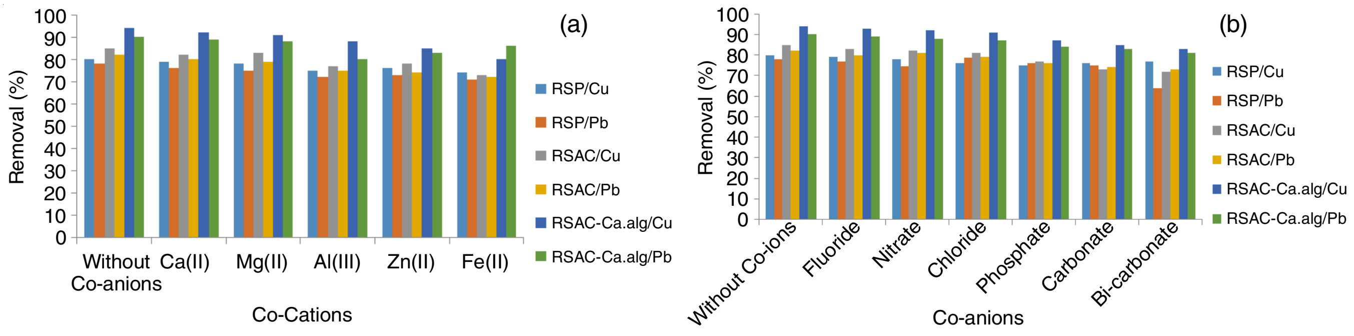

Fig. 8. Effect of (a) Co-cations and (b) Co-anions

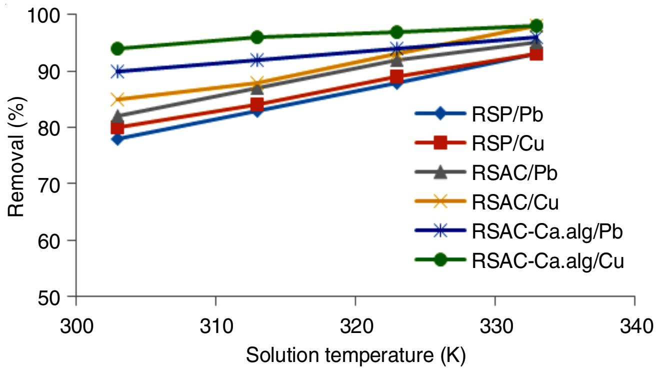

Fig. 9. Effect of tempeature on extraction of Cu^{2+} and Pb^{2+}

functional of the sorbents acquires more and more kinetic vibrational energies. This causes the decrease in the thickness of surface layers and widens the pores on the surface of the sorbents. Further, Cu^{2+} or Pb^{2+} ions acquire more kinetic energies. These aspects facilitate Cu^{2+} or Pb^{2+} ions penetrate more into the matrix of sorbents and thereby reaching underlying active sites [48]. Hence, more adsorption is observed as temperature increases.

Simultaneous removal of copper and lead ions from simulated solutions: The important finding of this investigation with single metal ion solutions is that at pH 6, both Cu^{2+} and Pb^{2+} ions can be extracted. This gives an idea that both metal ions can be extracted simultaneously. Hence, binary metal ions simulated solutions were prepared with varying compositions (Table-1). These solutions were treated with the sorbents developed in this investigation at the extraction conditions established to assess whether the same conditions 'hold good or not'. Slight variations of sorbent dosage and time of equilibration are needed to achieve good extractions as presented in Table-1.

Thermodynamic analysis: The "sign" and "magnitude" of thermodynamic properties namely, ΔG, ΔS and ΔH, provide insight into the "strength and type" of bonding between adsorbate and sorbents. These parameters were evaluated as described in the literature using equations: $\Delta G^o = -RT \ln K_d$; $\ln K_d = \Delta S^o/R - \Delta H^o/RT$; $K_d = q_e/C$; and $\Delta G^o = \Delta H^o - T\Delta S^o$, where K_d = distribution coefficient; q_e = amount of Cu^{2+} or Pb^{2+} adsorbed, C_e = equilibrium Cu^{2+} or Pb^{2+} concentrations; T = temperature (K), R = gas constant. The evaluated parameters are presented in Table-2.

From Table-2, the spontaneity of adsorption process is confirmed from the negative ΔG values. The values increase with increase in temperature, indicating the 'favourability' of adsorption process at high temperatures. The positive ΔH values indicate the endothermic nature of sorption process. The high magnitudes of the values indicate mechanism of sorption is ion-exchange and/or a sort of complex formation between Cu^{2+}/Pb^{2+} ions and adsorbent functional groups. The positive ΔS values and its high magnitude, indicate more disorder at the boundary of adsorbent and solution. This results in more chances

TABLE-1
SIMULTANEOUS REMOVAL Cu^{2+} AND Pb^{2+} FROM SIMULATED MIXTURES

Samples	Compositions (mg/L); C_i		After treatment with C_e (mg/L)					
			RSP		RSAC		RSAC-Ca.alg	
			Conditions: pH:6; Dosage: 3.0 g/L; 2.0 h		Conditions: pH:6; Dosage: 2.0 g/L; 1.5 h		Conditions: pH:6; Dosage: 1.5 g/L; 1.5 h	
	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
1	10.0	5.0	0	0	0	0	0	0
2	10.0	10.0	0.1	0.3	0.4	0.4	0	0.1
3	15.0	5.0	0.5	0.6	1.4	0.8	0.4	0.5
4	15.0	10.0	1.0	0.8	2.7	1.2	0.8	0.5
5	15.0	15.0	1.2	1.5	3.0	1.7	1.0	1.2
6	20.0	5.0	2.0	0	3.7	0	1.6	0
7	20.0	10.0	2.0	0.2	4.0	0.6	1.8	0.2
8	20.0	15.0	1.9	1.0	4.6	2.5	2.0	0.9
9	30.0	20.0	2.5	2.0	4.9	3.0	2.2	2.1
10	30.0	30.0	3.5	3.0	4.3	3.2	3.0	3.1

*The values are average of five estimations; S.D.: ± 0.12

TABLE-2
THERMODYNAMIC PARAMETERS OF SORBENTS FOR THEIR ADSORPTIVITY FOR Cu^{2+} AND Pb^{2+} IONS

Sorbent	ΔH (KJ/mol)	ΔS (J/mol)	ΔG (KJ/mol)				R^2
			303 K	313 K	323 K	333 K	
RSP/Pb	36.49	295.3	52.30	55.93	58,89	61.85	0.971
RSP/Cu	33.70	286.0	52.96	55.82	58.68	61.54	0.976
RSAC/Pb	40.39	303.3	51.50	54.54	57.58	60.60	0.991
RSAC/Cu	28.17	270.8	53.80	56.59	59.30	62.0	0.978
RSAC-Ca.Alg/Pb	27.16	271.3	55.10	57.8	60.40	63.20	0.976
RSAC-Ca.Alg/Cu	31.29	289.5	-56.40	59.3	65.11	62.45	0.995

that Cu^{2+} or Pb^{2+} ions crossing the boundary, resulting more adsoprtivity.

Adsorption nature: Adsorption mechanism was analyzed by different isotherm models. The Freundlich [52], Langmuir [53], Temkin [54] and Dubinin & Radushkevich [55] isothermal models were employed as described in the literature [56]. The isothermal parameters values are given in Table-3 (Figures not shown).

The R^2 values for Langmuir model are comparatively high for all the sorbents investigated for the extraction of Cu^{2+} and Pb^{2+}. Further, R_L values signify the favourability of adsorption as per Hall [50,51].

Adsorption kinetic analysis: Pseudo-first order [57], pseudo-second-order [58], Bangham's pore diffusion model [59] and Elovich model [60] were employed in analyzing the kinetics of adsorption. The pertaining equations were employed as per literature [57-60]. From Table-4, it may be inferred that the regression coefficient (R^2) falls in the order:

(i) Pseudo-second order > Elovich > pseudo-first order > Bangham diffusion-for RSP/Pb^{2+} removal/RSAC/Cu^{2+} removal/ RSAC-Ca.alg/Pb^{2+} removal.

(ii) Pseudo-second order > Elovich > pseudo-first order > Bangham diffusion – for RSP/Cu^{2+} removal/RSAC/Pb^{2+} removal/RSAC-Ca.alg/Cu^{2+} removal.

Recycling of sorbents: Spent RSP, RSAC and RSAC-Ca-alg were investigated for their regeneration and again use as adsorbents with various eluting agents comprising of bases, acids and salt solutions at different concentrations at various experimental conditions. The digestion of the RSP, RSAC and RSAC-Ca-alg with 0.1 N HCl solutions for overnight was effective. Thus treated spent adsorbents were filtered and washed. Dried at 105 ºC and again reused as adsorbent. This cycle of regeneration and reuse was continued for 8 times. With each regeneration of spent sorbent, there was decrease in sorption capacity. The decrease was marginal up to 2 cycles in the case of RSP, 3 cycles with RSAC and 4 cycles with RSAC-Ca.alg (Fig. 10). After these cycles of regenerations, there was marked decrease in their efficiencies.

Applications: The adsorbents developed were employed to treat samples of water collected from the effluents of various industries. The samples were collected from battery and electroplating industries in Hyderabad and Chennai, India and from

TABLE-3
EVALUATED ADSORPTION ISOTHERMS PARAMETERS

Adsorbate	Parameter	Freundlich isotherm	Langmuir isotherm	Temkin isotherm	Dubinin-Radushkevich isotherm
RSP/Pb^{2+} removal	Slope	0.171	0.094	1.403	-1.4
	Intercept	2.062	0.147	8.964	2.5
	R^2	0.342	0.967	0.219	0.771
		1/n = 0.171	R_L = 0.07	B = 1.403	E = 1.1 kJ/mol
RSP/Cu^{2+} removal	Slope	0.202	0.084	1.947	-1.1
	Intercept	2.164	0.153	10.02	2.7
	R^2	0.434	0.925	0.338	0.743
		1/n = 0.202	R_L = 0.08	B = 1.947	E = 0.8 kJ/mol
RSAC/Pb^{2+} removal	Slope	0.162	0.081	1.49	-4.1
	Intercept	2.186	0.093	9.90	2.6
	R^2	0.602	0.976	0.525	0.842
		1/n = 0.162	R_L = 0.05	B = 1.49	E = 2.8 kJ/mol
RSAC/Cu^{2+} removal	Slope	0.211	0.061	2.267	-3.4
	Intercept	2.318	0.029	11.66	2.8
	R^2	0.734	0.985	0.678	0.769
		1/n = 0.211	R_L = 0.07	B = 2.267	E = 2.4 kJ/mol
RSAC-Ca.alg/Pb^{2+} removal	Slope	0.172	0.073	1.752	-3.3
	Intercept	2.323	0.092	11.49	2.75
	R^2	0.614	0.962	0.553	0.848
		1/n = 0.172	R_L = 0.06	B = 1.752	E = 2.3 kJ/mol
RSAC-Ca.alg/Cu^{2+} removal	Slope	0.101	0.0596	1.49	-5.3
	Intercept	2.70	0.053	15.65	2.98
	R^2	0.321	0.972	0.275	0.783
		1/n = 0.101	R_L = 0.04	B = 1.49	E = 3.7 kJ/mol

TABLE-4
EVALUATED KINETICS PARAMETERS

Adsorbate		Pseudo-first order model	Pseudo-second-order	Elovich model	Bangham's pore diffusion
RSP/Pb^{2+} removal	Slope	-0.018	0.073	3.138	0.561
	Intercept	0.986	2.793	-4.268	-1.65
	R^2	0.863	0.992	0.972	0.961
RSP/Cu^{2+} removal	Slope	-0.027	0.0680	3.328	0.555
	Intercept	1.232	2.552	-4.712	-1.596
	R^2	0.807	0.993	0.975	0.968
RSAC/Pb^{2+} removal	Slope	-0.052	0.070	3.124	0.506
	Intercept	1.810	2.059	-3.428	-1.475
	R^2	0.741	0.997	0.979	0.886
RSAC/Cu^{2+} removal	Slope	-0.032	0.077	1.873	0.272
	Intercept	1.047	0.706	-3.326	-0.951
	R^2	0.999	0.999	0.907	0.903
RSAC-Ca.alg/Pb^{2+} removal	Slope	-0.025	0.0706	2.548	0.372
	Intercept	1.052	0.957	-0.736	-1.12
	R^2	0.983	0.997	0.918	0.907
RSAC-Ca.alg/Cu^{2+} removal	Slope	-0.022	0.0752	1.90	0.272
	Intercept	0.905	0.527	-3.741	-0.915
	R^2	0.621	0.997	0.792	0.786

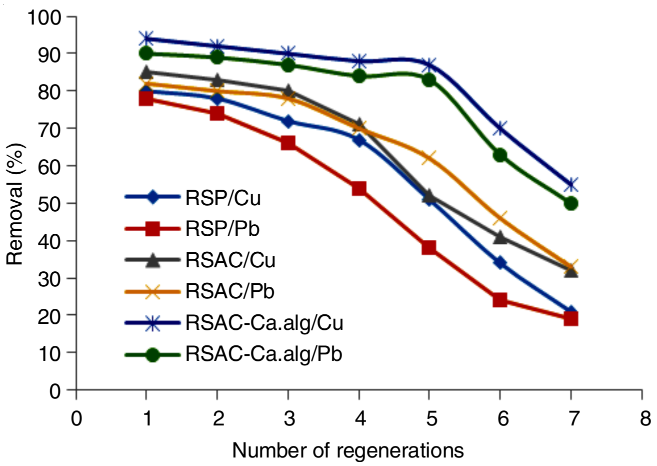

Fig. 10. Regeneration *vs.* % removal

mining industries in Ethiopia. The samples were analyzed for the content of Cu and Pb ions using AAS methods and the results are presented in Table-5. Then the samples were subjected to treatment with RSP, RSAC and RSAC-Ca.Alg at the optimum extraction conditions as presented in Table-5. The residual contents of Cu and Pb ions were also assayed by AAS methods (Table-5).

It may be concluded from the results that the RSP, RSAC and RSAC-Ca.alg successfully lowered the content of Cu and Pb ions. Among all the three adsorbents, RSAC-Ca.alg is highly effective, followed by RSAC and RSP.

Comparison with previous works: The sorbents developed in this investigation for removal of Cu^{2+} and Pb^{2+}. The adsorbents RSP, RSAC, RSAC-Ca.alg, were compared with the hither to reported sorbents with respect to their working pH and sorption capacity in Table-6. Most of the previous work are devoted to remove eithr Cu^{2+} or Pb^{2+} and not their simultaneous removal. The present work find an effective solution in this aspect. Further, the pH 6 is a convenient working pH. From the comparison data, it may be inferred that the present developed sorbents have adsorption capacities more than many sorbents developed for individual Cu^{2+} and Pb^{2+} ions. The efficiency fall in the order: RSP < RSAC < RSAC-Ca.alg.

Conclusion

This work is focused on the simultaneous removal of Cu^{2+} and Pb^{2+} ions using biosorbents. Stem powder and its active carbon of *Rhododendron arboreum* plant were identified to have selective affinity for Cu^{2+} as well as Pb^{2+} ions. Hence, stem powers, RSP, their active carbon, RSAC and the active carbon doped in Ca-alginate beads, RSAc-Ca.alg, were investigated for the simultaneous removal of Cu^{2+} and Pb^{2+} ions. Various extraction conditions *viz.*, pH, sorbent dosage, contact time, initial concentration, temperature, *etc.* have been optimized for the maximum Cu^{2+} and Pb^{2+} removal. The sorption capacities are as high as 35.0 mg/g for RSP, 38.5 mg/g for RSAC and 45.8 mg/g for RSAC-Ca.alg for the removal of both ions. The merit of this investigation is that good sorption capacities for both the ions are shown at a convenient working pH: 6. Common co-ions even in two-fold excess have marginal interference. The sorbents can be regenerated and reused. Thermodynamic analysis indicate the spontaneity of adsorption process. The increase in negative ΔG values with increase in temperature indicates the favourability of adsorption process at high temperatures. The positive ΔH values indicate endothermic nature of sorption process. The high magnitudes of the values indicate mechanism of sorption is "ion-exchange and or a sort of complex formation" between Cu^{2+}/Pb^{2+} ions and adsorbent functional groups. Positive high ΔS values indicate more 'disorder' at the boundary of adsorbent and solution. This condition favours more adsorptivity for both Cu^{2+} and Pb^{2+} ions. Of the various kinetic models analyzed for understanding the kinetics of adsorption, Pseudo-second order effectively describes the sorption. The nature of sorption is well explained by Langmuir model. The developed adsorbents were applied to treat effluent samples from industries and mining. The results showed that effective removal of Cu^{2+} and Pb^{2+} can be achieved

TABLE-5
APPLICATIONS

Samples	Cu and Pb content in industrial/mining effluents (analyzed by AAS method)		After treatment with C_e (mg/L)					
			RSP		RSAC		RSAC-Ca.alg	
			Conditions: pH:6; Dosage: 3.0 g/L; 2.0 h		Conditions: pH:6; Dosage: 2.0 g/L; 1.5 h		Conditions: pH:6; Dosage: 1.5 g/L; 1.5 h	
	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
A: Effluents samples collected at battery industries								
1	2.5	1.5	0	0	0	0	0	0
2	3.9	2.9	0	0	0	0	0	0
3	4.8	6.9	0.1	1.0	0.3	0.8	0	0.2
4	5.1	10.0	1.0	2.0	0.5	2.5	1	0.8
5	6.0	15.0	2.0	3.7	1.5	3.0	1.5	1.6
B: Effluents samples collected at electro plating Industries- effluents								
1	1.0	2.5	0	0	0	0	0	0
2	1.5	2.0	0	0	0	0	0	0
3	1.9	3.4	0	0.4	0	0.1	0	0
4	2.5	4.1	0	0.9	0	0.6	0	0
5	3.1	1.0	0.6	0	0.3	0	0	0
C: Mining effluents								
1	5.0	6.4	0.3	0.3	0.2	0.1	0	0
2	9.5	2.8	0.8	0.1	0.4	0	0	0
3	15.3	2.0	3.3	0	1.4	0	0	0
4	20.0	5.2	4.0	0.9	2.1	0.5	0	0
5	24.9	7.2	5.2	1.1	5.6	0.7	0	0

*C_i = initial Pb^{2+}/Cd^{2+} concentration; C_e = equilibrium Pb^{2+}/Cd^{2+} concentration; *Mean of four determinations; SD: ± 0.170

TABLE-6
COMPARISON WITH LITERATURE WORKS

Sorbent	Pollutant	pH	Adsorbent capacity (mg/g)	Ref.
Saudi activated bentonite	Pb^{2+}	6.0	47.7	[11]
Waste tire rubber ash	Pb^{2+}	6.0	22.35	[13]
Maize Tassel based activated carbon	Pb^{2+}	5.4	37.31	[17]
Pumpkin seed shell-active carbon	Pb^{2+}	7.0	14.286	[18]
Tamarind wood ($ZnCl_2$ treated)	Pb^{2+}	6.5	43.85	[19]
Coconut shell carbon	Pb^{2+}	–	30.0	[22]
Activated red mud immobilized in calcium alginate beads	Pb^{2+}	6.0	13.8	[24]
Ceiba pentandra hulls active carbon	Cu^{2+}	7.0	21.0	[29]
Phaseolus aureus hulls activated carbon	Cu^{2+}	7.0	20.0	[32]
NaOH treated fly ash	Cu^{2+}	6.2	64.00	[33]
Rose waste biomass	Cu^{2+}	5.0	56.00	[34]
Egg shells coated Iron oxide	Cu^{2+}	6.0	44.00	[35]
Spirogyra (green alga)	Cu^{2+}	5.0	133.00	[37]
Clay treated with HCl	Cu^{2+}	5.0	83.30	[39]
Chitosan	Cu^{2+}	4.5	88.43	[40]
Stems of *Hibiscus cannabinus* plant	Cu^{2+}	4.0	15.0	[61]
Limoniaacidissima plant barks	Cu^{2+}	4.0	13.5	[61]
Modified fly ash	Cu^{2+}	7.0	21.50	[62]
Granular activated carbon	Pb^{2+}	5.3	2.89	[63]
Biochars	Pb^{2+}	6.8	1.7	[64]
Activated polyacrylonitrile	Pb^{2+}	5.0	12.7	[65]
Indian curry leaf powder	Pb^{2+}	4.5	13.62	[66]
RSP	$Cu^{2+} + Pb^{2+}$	6.0	35.6	Present work
RSAC	$Cu^{2+} + Pb^{2+}$	6.0	38.5	Present work
RSAC-Ca.alg.	$Cu^{2+} + Pb^{2+}$	6.0	45.8	Present work

at the optimum conditions of extraction. The merit of this investigation is that at a convent working pH 6, effective simultaneous removal of toxic Cu^{2+} and Pb^{2+} ions from industries can be achieved with simple biosorbents derived from *Rhododendron arboreum* plant.

ACKNOWLEDGEMENTS

The authors thank the authorities of K L University for providing the necessary. facilities for this research work.

CONFLICT OF INTEREST

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

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