



Removal of Lead(II) Ions from Industrial Waste Water using Biomaterials of *Terminalia ivorensis* Plant and its Composite with Fe-Alginate Beads as Adsorbents

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Three effective adsorbents are developed for the removal of lead ions from industrial effluents based on stem powder of *Terminalia ivorensis* (TISP), its active carbon (TIAC) and a composite of Fe-alginate-beads doped with the active carbon (TIAC-beads). The beads are synthesized by crosslinking the Na-alginate with Fe^{3+} instead of conventional Ca^{2+} , with an aim to improve its adsorptivity. The conditions for obtaining the uniform beads with good morphology are established. These sorbents are investigated for their adsorptivity for Pb^{2+} ions with respect to various extractions conditions and are optimized for the maximum removal of Pb^{2+} . The sorption capacities are found to be: 34.0 mg/g for TISP, 39.0 mg/g for TIAC and 49.0 mg/g for TIAC-beads. The higher sorption of TIAC-beads may be due to the cumulative sorption nature of active carbon assisted by iron-alginate beads towards Pb^{2+} . The optimum conditions are: for TISP: pH: 5, sorbent dosage: 2.0g/and, eqi. time: 120 min; for TIAC: pH: 7, sorbent dosage: 1.5 g/L; eqi. time: 90 min; and for TIAC-beads: pH: 6, sorbent dosage: 1.0 g/L and eqi. time: 60 min. Substantial removal of Pb^{2+} is noted in a range of pHs: 4 to 9 for TIAC-beads; 4 to 8 for TISP and 6 to 8 for TIAC. This permits the applicability of the sorbents in neutral as well as less acidic and basic solutions and it is a good feature as Pb^{2+} containing industrial effluents are inconsistent in their pHs. Three fold excess of co-ions marginally interfered. Thermodynamic studies reveal that the adsorption is endothermic and spontaneous. The high ΔH values, > 30.0 KJ/mol, emphasizes the chemical nature of binding between Pb^{2+} and surface functional groups of sorbent and is increasing in the order: TISP (32.385 KJ/mol) $<$ TIAC (35.531 KJ/mol) $<$ TIAC-beads (42.480 KJ/mol). This is supported by symmetrical humps with in the curves of pH vs. % removal. Positive ΔS values reflect disorder at the solid-liquid interface-an ideal condition for Pb^{2+} ions to cross the surface barrier existing at the solid/liquid interface, resulting in good adsorptivity. Negative ΔG values indicate the spontaneity of the sorption process. Spent TISP/TIAC/TIAC-beads can be regenerated and reused for 2 cycles for TISP, 3 cycles for TIAC and 3 cycles for TIAC-beads. The sorbents are successfully applied to remove Pb^{2+} form industrial effluents.

Keywords: Lead removal, Adsorbents, *Terminalia ivorensis*, Fe-alginate beads, Applications.

INTRODUCTION

The intensive utilization of lead metal and its salts in various industries especially in automobiles, electronics, metal plating, alloying, paints, printing, glass, batteries, explosive, ceramics, plastics, etc. is attributed to its typical properties of high corrosive resistance, ductility, softness and low melting point [1-4]. The effluents from these industries contain lead salts and they have to be completely removed before the effluents are disposed off into the environment. Inadequately treated effluent disposal causes lead salts to enter into environment and thereby to water bodies [2,4]. The lead ions even in traces get accumulated in water bodies due to its non-degradable nature and get involved

in various eco-process and causes environmental threat to the living creatures due to its high toxicity [3]. Soil erosion, agricultural, mining and alkyl lead from automobiles are some other sources of lead pollution [1,4]. Lead is highly toxic and causes anaemia, neurological problems, kidney damage, brain haemorrhage, sleeplessness, neonatal deaths, etc. and USEPA classifies lead as 'human carcinogens [5-8]. WHO prefers 'zero-lead' waters and the maximum limit allowed is: 0.01 m g/L [5]. Hence, developing simple and effective methods for the removal of lead from polluted water assumes importance.

Ion-exchange, reverse osmosis, membrane filtration and electrode deposition are some of the techniques employed for the removal of lead [4,9,10]. Though these techniques produce

lead-free water, they are not adoptable in poor countries as they are not economical, needs technical expertise and fails totally when large amounts water are to be purified. Sorption methods based on adsorbents are increasingly investigated for the treatment of lead as these methods are proving to be simple and effective. Synthetic adsorbents such as poly ethylenimine grafted gelatin sponge [11], Saudi activated bentonite [12], polymers with bicomponent polymer brushes [13] and polystyrene beads with commercial *tris*-(2-aminoethyl)amine [14], waste tires ash [15] and okra wastes ash [16] are also investigated.

Increasing research interest is seen in investigating bio-materials as adsorbents in view of their abundance, cheap, renewable sources and effectiveness. Activated carbons of pumpkin seed shell [17], pine cone [18], coconut shell [19], maize tassel [20], tamarind wood [21], *Caryota urens* seeds doped in calcium-alginate beads [22] are also reported as promising adsorbents. Acid-activated clay [23], waste tire rubber ash [24], Saudi activated bentonite [25], exhausted coffee grounds [26], bentonite [27,28], Lentil husk [29], hydrazine sulphate-activated red mud [30] are also employed.

Prosopis mimosaceae sawdust [31], mucilaginous leaves of *Diceriocaryum eriocarpum* plant [32], Jackfruit leaves-treated [33], tomato waste [34], apple juice residue [34], raw sawdust and its treated biochar [35], walnut shell powder [36], Banana Pseudo stem [37], rice bran-treated [38], *Annona squamosa* shell [39], hazelnut [40] and almond shell [40], are also investigated for their sorption nature towards Pb^{2+} ions.

The present work is an investigation in this direction. Our investigations reveal that some of the species of plants have specific affinity towards heavy metal ions such as Cr(VI) and Cu(II) [41-44]. In the same lines we identified that the stem powders of *Terminalia ivorensis* plant has strong adsorptive nature towards Pb^{2+} ions. The adsorptiveness is increased with the active carbon synthesized from these stem powders by carbonizing the later with conc. H_2SO_4 . One of the disadvantages of these powder-adsorbents, is that the filtration is slow. To overcome this lapse, the active carbon is doped in iron-alginate beads synthesized by crosslinking the Na-alginate with Fe^{3+} . The beads preparation by employing Fe^{3+} for crossing linking rather than the conventional Ca^{2+} , is novel and adopted to import more sorption nature to the beads. Thus obtained beads containing the active carbon besides facilitating the easy filtration, have enhanced adsorptivity towards Pb^{2+} . This increase in adsorptive capacity may be due to the cumulative sorption nature of active carbon and iron-alginate beads towards Pb^{2+} . In the present work, three adsorbents namely: stem powder of *Terminalia ivorensis*, its H_2SO_4 -generated-active carbon and beads doped with the active carbons are investigated for their adsorptivity towards Pb^{2+} .

EXPERIMENTAL

All the procured chemicals and solvents were of A.R. grade. The reagents and simulated solutions were prepared by using double distilled water. A 50 ppm Pb^{2+} stock solution was prepared and diluted as per need.

Preparation of adsorbents: *Terminalia ivorensis* stems were cut to pieces, washed with distilled water and dried in

hot air oven at 105 °C for 3 h. After complete drying, the stems were crushed to fine powder. The material was sieved to obtain the powder having size less than 75 μ . Thus obtained *Terminalia ivorensis* stems powder is named as TISP.

Half dried pieces of stems of *Terminalia ivorensis* were digested in conc. H_2SO_4 for 2 h using condenser setup until the stems were completely carbonized. Thus obtained carbon was filtered and washed with distilled water until the washings were neutral. Then the carbon was dried at 105 °C for 1 h in hot air oven and preserved in air-tight brown bottle. Thus generated *Terminalia ivorensis* active carbon is named as TIAC.

Synthesis of beads: A new method of synthesis of beads by cross-linking sodium alginate with Fe^{3+} , Fe-alginate, was investigated and established in this work in the same lines of preparation of Ca-alginate [45] and Zn-alginate [46] beads. Conditions of the formation of 'Fe-alginate beads' were optimized. The following described procedure was found to be highly successful in the formation of uniform Fe-beads with good morphology.

Method: A solution of sodium alginate (2% w/v) in distilled water was heated to 60 °C with stirring to get a gel-like solution. TIAC (2 g) was added to it and the resulting solution was stirred for 1 h. The solution was cooled to room temperature and then added dropwise into a 2% $FeCl_3$ solution, which was previously cooled and maintained at 10 °C. Beads containing TIAC were formed and allowed to be in contact with the mother-liquor for overnight for the complete digestion process to occur, resulting uniform-sized beads. Then beads were filtered, washed with distilled water, dried in hot air oven at 102 °C for 1 h and termed as TIAC-beads.

Adsorption studies: Simulated Pb^{2+} solutions were subjected to batch methods [47-49] of extraction to establish optimum conditions of extraction for the maximum possible removal of Pb^{2+} . Lead(II) ion (15 ppm) solutions of 100 mL were taken into 250 mL iodine flasks. Then a known amounts of TISP, TIAC or TIAC-beads, were added and initial pHs of solutions were adjusted from 1 to 12 with dil. HCl/dil. NaOH. The solutions were shaken in orbital shaker for required time at 250 rpm and at 30 ± 1 °C (room temperature). The contents in the flasks were filtered. The filtrates were analyzed for residual concentration of Pb^{2+} by using atomic adsorption spectroscopic method as described earlier [1].

Adsorbed amounts of Pb^{2+} ions:

$$q_e = \frac{C_i - C_e}{m} V \text{ and}$$

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

where C_i = initial Pb^{2+} concentration; C_e = equilibrium Pb^{2+} concentration; and V = volume of solution (L); m = mass of sorbent (g).

RESULTS AND DISCUSSION

Adsorption parameters: The effect of various extractions conditions on the adsorptivities of TISP, TIAC and TIAC-beads for Pb(II) was investigated with an aim to establish optimum conditions for the maximum possible extraction of Pb^{2+} .

Initial pH: To assess the effect of initial pHs of solutions on the adsorption capacities of the sorbents, extraction studies were made in the pH range of 1 to 12. The other conditions of extraction were maintained constant: for TISP: pH: 5, sorbent dosage: 2.0 g/L & time of equilibration: 120 min; for TIAC: pH: 7, sorbent dosage: 1.5 g/L, and time of equilibration: 90 min; and for TIAC-beads: pH: 7, sorbent dosage: 1.0 g/L & time of equilibration: 60 min. It is observed that as the pH is increased, the adsorptivity is also increased and it is reached to maximum at pH: 5 for TISP, pH: 6 for TIAC and pH: 7 for TIAC-beads (Fig. 1). The adsorptivity for Pb^{2+} is in the order: TIAC-beads > TIAC > TISP. A maximum of 95.0% for TIAC-beads (at pH: 6), 85.0% for TIAC (at pH: 7) and 75.0% for TISP (at pH: 5), are observed. TIAC-beads have shown substantial adsorptivity even less in acidic and less basic solution *i.e.* in the pH range: 4 to 9: 80.0% at pH: 4; 90.0% at pH: 5; 95.0 at pH: 7; 86.9% at pH: 8; 80.0% at pH: 9. After pH: 9, the % removal has sharply fallen. Similar tendency is noted for TISP also. With the maximum removal of 75.0% at pH: 5, good sorption is noticed between pH: 4 to 8.0: 68.0% at pH: 4; 75.0% at pH: 6; 76.0% at pH: 7; 65.0% at pH: 8. After pH: 8, % removal sharply falls down.

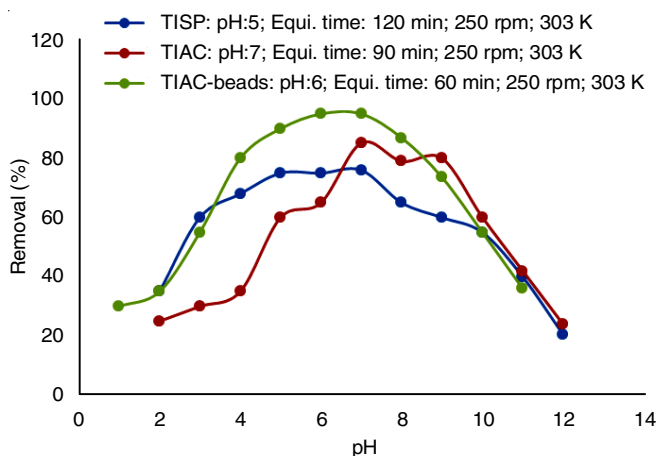


Fig. 1. pH vs. % removal of Pb^{2+} (conc. of Pb^{2+} : 15 ppm)

These observation may be interpreted from the view point of pHzpc and Pb-speciation. The pHzpc for TISP, TIAC and TIAC-beads were assessed as per standard procedures and they were found to be: 5.7 for TISP, 6.2 for TIAC and 7.1 for TIAC-beads (Fig. 2). At these pH values, the surface of the adsorbent is neutral with equal positive sites and negative sites. Above these pH values, the surface acquires negative charge due to the dissociation of functional groups namely -OH, -COOH, *etc.* Below these pHs, the dissociation is less favoured and at sufficiently low pHs, the surfaces may be protonated and thereby positive charge is acquired. Coming to the speciation of Pb(II), the nature of species depends upon the pH conditions: less than pH 4: Pb^{2+} , pH: 4-6: $Pb^{2+}/Pb(OH)_2(s)/PbOH^+$ and pH: 7-12: $Pb(OH)^3-$ and $Pb(OH)_4^{2-}$ [51]. The good adsorption in the pH range from 4 to 7 in the case of TISP and TIAC-beads, indicate a kind of surface complex formation between Pb^{2+} and the functional groups of TISP and TIAC-beads. This is supported by symmetrical humps with in the curves of pH vs.

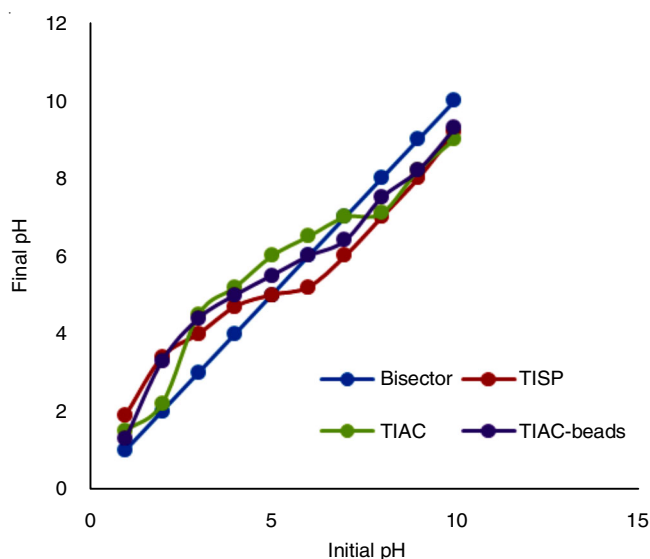


Fig. 2. Evaluation of pHzpc for TISP, TIAC and TIAC-beads

% removal (Fig. 1) in the pH range: 4 to 8. Above pH: 9, the three adsorbents have shown less adsorptivity. This is in expected lines. At high pH values, the surface of the adsorbents is negatively charged and lead exists as: $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$. As the charge on the species is negative and the surface of the adsorbents is also negative, the ions experience repulsion and hence, adsorption sharply fallen.

Sorbents dosage: This is an important factor to be optimized to ascertain the minimum dosage needed for the maximum removal of Pb^{2+} . Keeping all other extraction conditions at constant levels, but varying the dosage from 0.5 g/L to 2.5 g/L, % removal was investigated and obtained results are depicted in Fig. 3.

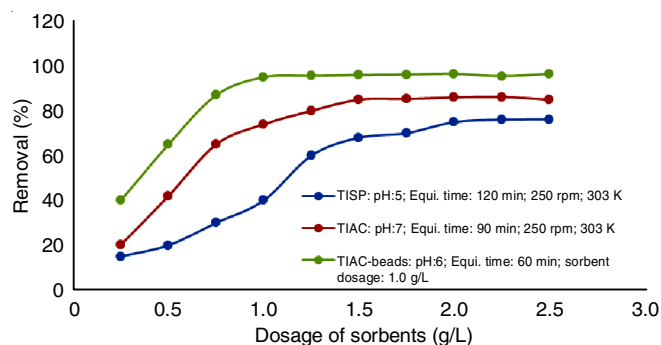


Fig. 3. Effect of dosage of adsorbents, initial concentration of Pb^{2+} : 15 ppm

With the progressive raise in dosage, the adsorptivities of TISP, TIAC and TIAC-beads towards Pb^{2+} , is also almost linearly increased initially but 'mellow down' latter and after certain dosage, the sorption, has come to a study state.

With TIAC-beads, the % removal is: 40.0% at 0.25 g/L, 65.0% at 0.50 g/L, 87.0% at 0.75 g/L and 95.0% at 1.0 g/L of sorbent dosage; above 1.0 g/L, the adsorptivity is marginally varied. Similar nature is shown in the case of TIAC and TISP. With TIAC, % removal is: 20.2% at 0.25 g/L; 42.0% at 0.50 g/L; 65.0% at 0.75 g/L; 74.0% at 1.0 g/L, 80.0% at 1.25 g/L and 85.0% at 1.5 g/L; above 1.5 g/L, adsorptivity is marginally

varied. In the case of TISP, % removal is: 15.0% at 0.25 g/L; 20.0% at 0.5 g/L; 30.0% at 0.75 g/L; 40.0% at 1.0 g/L; 60.0% at 1.25 g/L; 68.0% at 1.5 g/L; 70.0% at 1.75 g/L and 75.0% at 2.0 g/L ; above 2.0 g/L, the adsorptivity is attained steady state.

With the raise in adsorbent dosage, sorbent sites are progressively increased and hence progressive increase in % removal is expected. Initially for all the sorbents studied, the same trend is noted. But with further increase in the sorbent concentration, the proportional increase in % removal is not noted. Blocking and overlapping of sorption sites and the pathways-for the adsorbate to reach to the sorption sites, are the reasons for mellowing down of adsorptivity [50]. Further, as the adsorbate (Pb^{2+}) concentration is fixed, after certain dosage, all the Pb^{2+} ions are engaged with the available sites of adsorbents, resulting no further adsorption and hence, study state is reached [22].

Contact time: This is another factor which has profound influence on the adsorptivity of the adsorbents for the adsorbate (Pb^{2+}). By keeping all other extraction conditions at optimum levels, the adsorptivities of TISP, TIAC and TIAC-beads, were assessed by varying the duration of equilibration of solution with the said adsorbents from 15 to 180 min.

In case of TIAC-beads, almost linear raise in the % removal of Pb^{2+} is noted upto 60 min and then, a steady state is reached (Fig. 4). The % removal is observed to be: 35.0% at 15 min; 72.0% at 30 min; 85.0% at 45 min; and 95.0% at 60 min and almost remains constant after 60 min of equilibration. Similarly, for TIAC, % removal is 25.0% at 15 min; 50.0% at 30 min; 65.0% at 45 min; 74.0% at 60 min; 83.0% at 75 min; 85.0% at 90 min or above. With TISP, as is seen from the relation curve (Fig. 4), the % removal is linearly increased from 15% at 15 min to 73.0% at 105 min and the maximum of 75.0% is reached at 120 min and after which, the % removal is marginally varied.

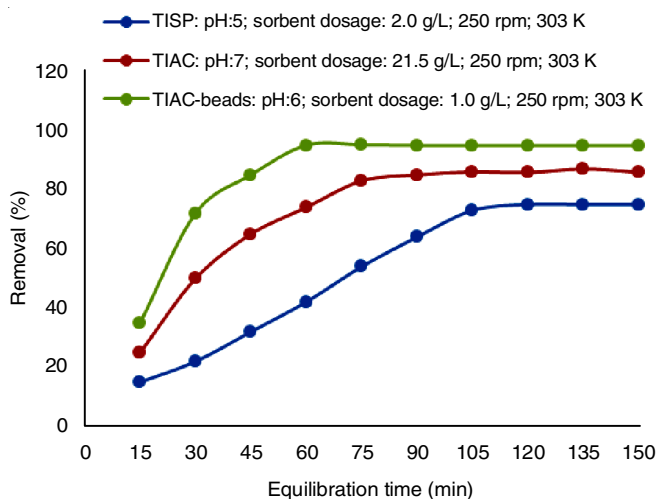


Fig. 4. Effect of equilibration time on % removal of Pb^{2+} , initial concentration of Pb^{2+} : 15 ppm

As the amount of adsorbent is fixed, 1.0 g/L for TIAC-beads; 1.5 g/L for TIAC and 2.0 g/L for TISP, the active sites are also limited. As these sites are used up with time, a steady state is reached after certain time of equilibration, at which rate

of adsorption of adsorbate is equivalent to rate of desorption [41].

Initial concentration of adsorbate: Keeping all other extraction parameters at optimum levels, the initial concentration of Pb^{2+} varied from 5.0 ppm to 50 ppm and the % of the removal was investigated. It is seen from the curves that with the raise in initial concentration, % removal decrease (Fig. 5) while the adsorption capacities, q_e increases (Fig. 6). With TISP, the % removal is maximum nearly 75% up to 15 ppm of Pb^{2+} and then onwards, it decreases. Similarly, with TIAC, % removal is around 85% up to 15 ppm of Pb^{2+} and then onwards, it decreases gradually. With TIAC-beads, % removal is maintained nearly 95% upto 15 ppm Pb^{2+} solution and after which, % removal decreased.

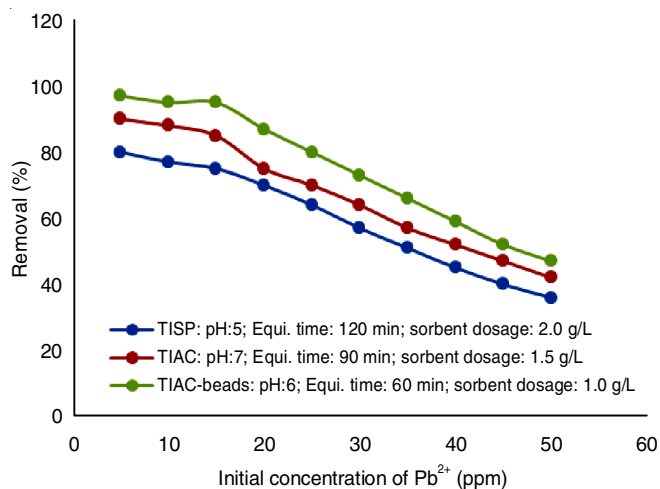


Fig. 5. Initial conc. Pb^{2+} vs. Pb^{2+} removal

At the same time, it is interesting to note that the dependency of the adsorption capacity (q_e) on the initial concentration of Pb^{2+} (Fig. 6). With TISP as adsorbent, q_e is increased from 4.1 mg/g to 17.1 mg/g as the initial concentration of Pb^{2+} is increased from 5 ppm to 30 ppm and after that, q_e is marginally increased with further increase in Pb^{2+} concentration from 30 ppm to 50 ppm (Fig. 6). The same trend is noted with other two sorbents, TIAC and TIAC-beads. In case of TIAC, q_e value is increased from 4.5 mg/g to 19.95 mg/g with the increase in the initial concentration of Pb^{2+} from 5 ppm to 35 ppm and after that, there is only marginal increase in q_e value even the initial concentration is increased more than 35 ppm. With TIAC-beads, the q_e value is increased from 4.85 mg/g to 21.9 mg/g as the initial concentration of Pb^{2+} is increased from 5 ppm to 35 ppm and that, there is no marked enhancement in the q_e value even when the initial Pb^{2+} concentration enhanced upto 50 ppm.

The reason can be explained as the Pb^{2+} concentration increased, more Pb^{2+} are driven towards the surface of the adsorbents due to concentration difference between the surface layers of the adsorbent and bulk of the solution with respect to Pb^{2+} . Hence, adsorptivity is increased. All these experiments were done with fixed amount of the adsorbent *i.e.* 2.0 g/L for TISP, 1.5 g/L for TIAC and 1.0 g/L for TIAC-beads. As the amount of adsorbents is fixed, there are only fixed number active sites. When all the sites are exhausted, further adsorption is not possi-

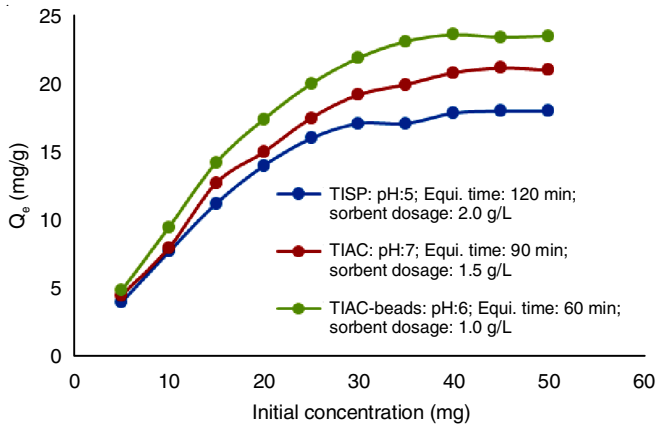


Fig. 6. Initial concentration vs. sorption capacity (q_e)

ble and the saturation resulted. Hence, only marginal enhancement in q_e values is observed after certain initial concentration of Pb^{2+} ions [42].

The same logic holds good to explain the decrease of % removal with increase in initial concentration of Pb^{2+} ion. At low concentrations, more sites are available for the adsorbate, Pb^{2+} and hence good % removal at low concentrations of Pb^{2+} . With the fixed amounts of sorbents, needed proportion of sites are not available with the increase in initial concentration of Pb^{2+} . This results in decrease of % removal of Pb^{2+} with further increase in Pb^{2+} concentration [42].

Effect of interfering ions: The interference caused by co-ions on the adsorptivity of Pb^{2+} was assessed by using simulated solutions having three-fold excess of common co-ions than that of the Pb^{2+} concentration. The solutions were subjected to the extraction of Pb^{2+} by TISP, TIAC and TIAC-beads at the optimum conditions.

It may be inferred from Figs. 7 and 8 that anions (fluoride, nitrate, chloride, phosphate, carbonate and bicarbonate) and cations (Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} and Fe^{2+}) show a marginal interference on the adsorptivities of TISP, TIAC and TIAC-beads for Pb^{2+} ions from water, at the optimum conditions developed in this investigation.

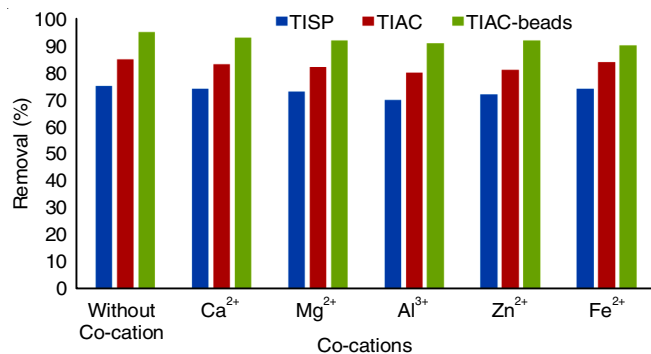


Fig. 7. Interference of co-cations on the % removal of Pb^{2+}

Thermodynamic studies: The variation of adsorptivity of TISP, TIAC and TIAC-beads towards Pb^{2+} with respect to temperature is shown in Figs. 9 and 10. With the rise in temperature, adsorptivity of the sorbents also increases. Increase in temperature, enhances the vibrational motions of surface

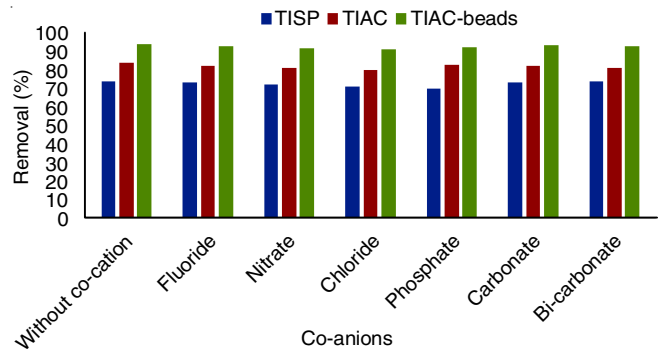


Fig. 8. Interference of Co-anions

functional groups and as a consequence of this, the more channels are opened for an adsorbate to penetrate more into the surface layers of sorbents. Further, the kinetic energy of diffusing Pb^{2+} ions is also increased. The cumulative effect is Pb^{2+} crosses the surface energy barrier at the interface of liquid and solid and hence enhanced adsorption.

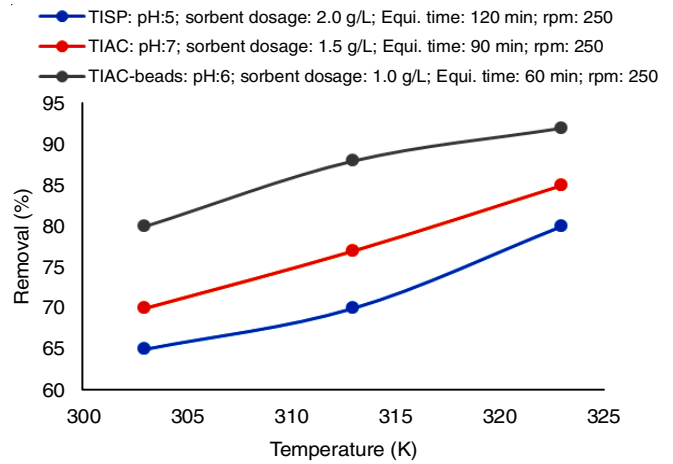


Fig. 9. Effect of temperature on the adsorptivity of sorbents, initial concentration of Pb^{2+} : 25 ppm

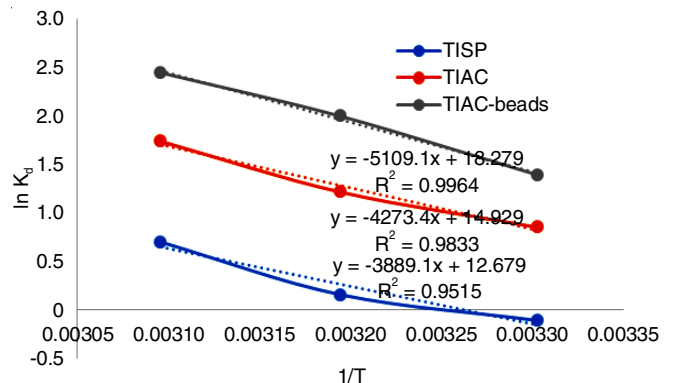


Fig. 10. $1/T$ vs. $\ln K_d$

Thermodynamic parameters, change in free energy: ΔG° (kJ/mol), enthalpy: ΔH° (kJ/mol) and entropy: ΔS° (J/K mol) were evaluated by using the following equations:

$$\Delta G^\circ = -RT \ln K_d$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$K_d = \frac{q_e}{C_e}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where K_d = distribution coefficient; q_e = amount of Pb^{2+} sorbed; C_e = equilibrium Pb^{2+} concentration; T = temperature (Kelvin), R = gas constant.

It is observed from Table-1, as the ΔH values are positive, the nature of adsorption is endothermic for TISP, TIAC and TIAC-beads. Further, as the values are more than 30.0 KJ/mol, the nature of binding of Pb^{2+} to the surface of the adsorbent is chemical in nature and it is presumed to be a kind of surface complexation between the functional groups of adsorbents surface and Pb^{2+} ions. Further, ΔH values found to be increased in the order TISP < TIAC < TIAC-beads, which emphasizes the increasing tendency of the chemical nature of binding between Pb^{2+} and functional groups on the adsorbents.

The positive ΔS values for TISP, TIAC and TIAC-beads, reflect disorder at the solid-liquid interface [45,48]. This is an ideal condition for the movement of Pb^{2+} ions through the surface layers of sorbent which results in enhancing the adsorptivity. Moreover, ΔG values for all sorbents (except for TISP at 303 K) are negative, which indicates the spontaneity of the sorption process and also emphasizes the strength of attracting forces are good enough to cross the potential barrier prevailing between at the solid and liquid interface [46,48].

Spent TISP, TIAC and TIAC-beads regeneration: In this aspect, TISP, TIAC and TIAC-beads were investigated with various eluents to know the loss of adsorption capacity with each cycle of generation-cum-reuse. The spent TISP, TIAC and TIAC-beads were investigated for their regeneration and reuse.

A 0.05 N HCl solution was found to be effective. The spent TISP, TIAC and TIAC-beads were soaked in 0.05 HCl and digested for over-night, filtered, washed with distilled water, dried and reused. From Fig. 11, it may inferred that up to 2 cycles

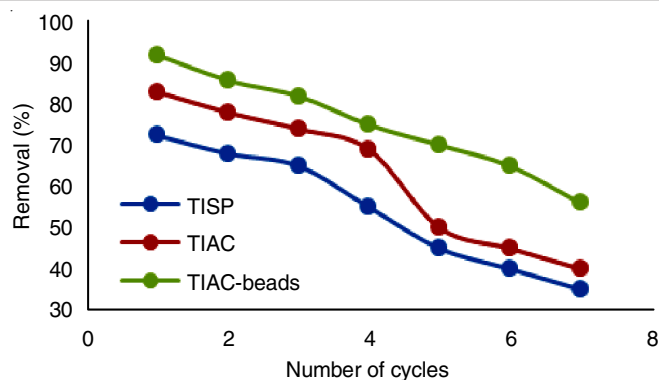


Fig. 11. Spent TISP, TIAC and TIAC-beads: regeneration and reuse

for TISP, 3 cycles for TIAC and 4 cycles for TIAC-beads, the loss in adsorptivity of the prepared sorbents are not significant.

Applications: The effectiveness of TISP, TIAC and TIAC-beads as sorbents was assessed by applying the developed procedures to real effluent samples collected from battery and lead plating industries. The samples were treated with TISP (pH: 5; sorbent dosage: 2.0 g/L; equilibrium time: 120 min), TIAC (pH: 7; sorbent dosage: 1.5 g/L; equilibrium time: 90 min) and TIAC-beads (pH: 6; sorbent dosage: 1.0 g/L; equilibrium time: 60 min) at room temperature, 303 K. It may be inferred from the Table-2 that the effectiveness of sorbents for removing Pb^{2+} from industrial effluents is in the order: TISP (77.7 to 80.6%) < TIAC (83.1 to 87.1%) < TIAC-beads (97.0 to 98.8%).

Comparison: The present developed sorbents TISP, TIAC and TIAC-beads are compared with the sorbents available in literature with respect to pH conditions and sorption capacities. From the comparison data (Table-3), it may inferred that the present developed sorbents have good sorption capacity than many reported in literature. The TIAC-beads have substantial sorption capacity of the order of 49.0 mg/g and its working

TABLE-1
THERMODYNAMIC PARAMETERS OF SORBENTS FOR THEIR ADSORPTIVITY FOR Pb^{2+} IONS

Sorbent	ΔH (KJ/mol)	ΔS (J/mol)	ΔG (KJ/mol)			R^2
			303K	313K	323K	
TISP	32.335	105.42	0.395	-0.665	-1.7157	0.9515
TIAC	35.531	124.127	-2.079	-3.320	-4.560	0.9833
TIAC-beads	42.48	151.98	-3.57	-5.09	-6.61	0.9964

TABLE-2
APPLICATIONS

Samples	C_i^*	Adsorbents					
		TISP		TIAC		TIAC-beads	
		C_e^*	Removal (%)	C_e^*	Removal (%)	C_e^*	Removal (%)
Lead-Battery Industry effluents							
1	4.5	1.0	77.7	0.6	86.6	0.1	97.7
2	3.1	0.6	80.6	0.4	87.1	0.05	98.4
3	5.0	1.1	78.0	0.8	84.0	0.15	97.0
Lead-Plating Industry effluents							
1	2.5	0.55	78.0	0.4	84.0	0.03	98.8
2	6.2	1.2	80.6	0.9	85.5	0.19	96.9
3	7.1	1.5	78.9	1.2	83.1	0.23	96.8

* C_i = initial Pb^{2+} concentration; C_e = Pb^{2+} concentration at equilibrium, *Average of five determinations; SD: ± 0.51

TABLE-3
COMPARISON OF PRESENT WORK WITH REPORTED WORKS

Adsorbent	pH	Sorption capacity	Ref.
Fluted pumpkin seed shell active carbon	7.0	14.286	[17]
Acid activated clay	6.0	9.08	[23]
Pine cone activated carbon	6.7	27.53	[18]
Waste tire rubber ash	6.0	22.35	[24]
Coconut shell carbon	–	30.0	[19]
Saudi activated bentonite	6.0	47.70	[25]
Maize Tassel based Activated carbon	5.4	37.31	[20]
Zinc chloride activated tamarind wood	6.5	43.85	[21]
Multi walled carbon nano tubes	3.0	43.00	[26]
Caryota urens seeds active carbon	7.0	42.90	[22]
Ca-alginate doped with Caryota urens seeds active carbon	7.0	89.60	[22]
Bentonite	5.5	73.00	[28]
Calcium alginate beads doped with hydrazine sulphate-activated red mud	6.0	13.80	[30]
Lentil husk	5.0	81.43	[29]
TISP	5 (substantial removal in pH range: 4 to 8)	34.00	Present work
TIAC	7 (substantial removal in pH range: 6 to 8)	39.00	Present work
TIAC-beads	6 (substantial removal in pH range: 4 to 9)	49.00	Present work

pH is: 4 to 9 with maxima at 6. This wide pH range allows the application in neutral as well as slightly acidic and basic conditions. Even in the case TISP, there is good adsorptivity in a wide range of pH from : 4 to 8 with maximum at 7. In the case of TIAC, the effective pH range is 6 to 8 with maximum at 5.

Conclusion

In the present investigation, three adsorbents namely stem powder of *Terminalia ivorensis* (TISP), its H₂SO₄-generated active carbon (TIAC) and Fe-alginate beads doped with the active carbon (TIAC-beads) are investigated for their sorption efficiency towards Pb²⁺. Iron-alginate beads doped with the active carbon, TIAC-beads, were synthesized by crosslinking the Na-alginate with Fe³⁺ instead of conventional Ca²⁺, with an aim to import more sorption capacity to the beads besides facilitating easy filtration. The developed sorbents: TISP, TIAC and TIAC-beads sorption capacities were found to be: 34.0 mg/g for TISP, 39.0 mg/g for TIAC and 49.0 mg/g for TIAC-beads. The good sorption of TIAC-beads may be due to the cumulative sorption nature of active carbon assisted by iron-alginate beads towards Pb²⁺. Three fold excess of co-ions (anions and cations), normally found in effluents, have little effect on the adsorptivity of TISP, TIAC and TIAC-beads towards Pb²⁺. Moreover, spent TISP/TIAC/TIAC-beads can be regenerate and reused for 2 cycles for TISP, 3 cycles for TIAC and 3 cycles for TIAC-beads. The sorbents were also successfully applied to remove Pb²⁺ from industrial effluents.

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CONFLICT OF INTEREST

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

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