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## Exploitation of Beach Sand as a Low Cost Sorbent for the Removal of Pb(II) Ions from Aqueous Solutions

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**Abstract:** Beach sand is used to remove traces of Pb(II) ions from aqueous solutions. Effect of shaking speed, amount of sorbent, shaking time, nature and concentration of different electrolytes and deionized water along with buffer of pH (2–10) have been studied. Maximum sorption of Pb(II) ions (>94%) is achieved from  $10^{-4}$  M HNO<sub>3</sub>. Sorption data have been tested using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) sorption isotherms. Thermodynamic parameters such as  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  have been evaluated. Kinetics of sorption is followed by Morris-Weber, Reichenberg and Lagergren equations. Influence of diverse ions on the sorption of Pb(II) ions is also investigated.

**Keywords:** Beach sand, Pb(II) ions, sorption, sorption isotherms, kinetics, thermodynamics

### INTRODUCTION

Large scale use of metals and their compounds in households and industries makes their concentrations in the aqueous media to alarming limits. Lead,

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a widely used heavy metal in industrial products, has various toxic effects on human health (1). Lead storage batteries, lead glazed ceramics, and lead based paints are constantly used in everyday life. Lead is also used in gasoline, ammunition, metal products, pigments, glass making, and in plastics (2, 3). The industrial and domestic waste carry elevated concentration of lead (4). Higher concentrations of Pb(II) ions (0.5–0.8 mg/L) in the blood causes anemia, kidney disorder, brain damage, bone diseases, skin and lung cancer (2, 5, 6). The tolerance limits of Pb reported for air are 0.1–0.15 mg/m<sup>3</sup>, water 15 µg/dm<sup>3</sup> and for food <0.5 mg/d (7, 8). It is, therefore, necessary to remove the Pb(II) ions from the water systems. The low cost locally available materials are being extensively used for the removal/preconcentration of heavy metal ions from aqueous medium (9–11). To remove Pb(II) ions from aqueous solutions, different low cost materials including fly ash (12), clay (13), and AlPO<sub>4</sub> (14) have been used. Many workers have exploited different cheaper materials to remove toxic metal ions from aqueous solutions including zeolite (15), bentonite (16), goethite (17, 18), and glauconite (19). During this investigation beach sand collected from the Hawks Bay, Karachi, Pakistan, has been used as a sorbent for the removal of Pb(II) ions from aqueous solutions.

## EXPERIMENTAL

### Materials and Reagents

All reagents used were of analytical or equivalent grade. Doubly distilled deionized water (conductivity  $0.5 \pm 0.1 \mu\text{S}/\text{cm}$  and pH  $(6.5 \pm 0.2)$  was used throughout this investigation. The stock solution of Pb(II) ions was made in doubly distilled deionized water using analytical grade lead nitrate (Fluka).

The beach sand collected from Hawks Bay, Karachi, Pakistan, was sieved with Ro-tap type mechanical shaker; the sieve sizes obtained are listed in Table 1. The mesh size of 300 µm was selected for the sorption studies because of its larger proportion in the total sand. The BET surface area of the beach sand of 300 µm size was found to be  $\sim 1 \text{ m}^2 \text{ g}^{-1}$ . The BET surface area reported for Haro river sand, i.e.  $1.47 \text{ m}^2 \text{ g}^{-1}$  is of the same order of magnitude as reported in (20).

Characterization of the beach sand (300 µm) by X-ray diffraction technique gave calcite 70%, quartz 26% and aragonite 03% by weight. A portion of beach sand was repeatedly washed with doubly distilled deionized water until it became dust free and gave colorless supernatant. During washing the sand was occasionally stirred and left in deionized water for a few hours. To remove the moisture the treated sand was put inside an electric oven for 8 to 10 hours at 110°C. After complete removal of moisture, the sand was placed into vacuum desiccator.

**Table 1.** Percent distribution of beach sand with size

Size (μm)	Weight %
1956	5.6
975	8.4
600	17.5
300	43.4
150	25.2

### Procedure

The batch dynamic method was employed to measure the sorption of Pb(II) ions onto beach sand. A fixed volume (15 cm<sup>3</sup>) of the sorbate solution having Pb(II) ions concentration (9.65 × 10<sup>-6</sup> M) was shaken for a particular interval of time in a 50 cm<sup>3</sup> vessel using 200 mg of the sorbent. The concentration of the analyte solution was determined before ( $C_i$ ) and after shaking ( $C_e$ ) by Metrohm VA trace analyzer model 747. An aliquot (10 cm<sup>3</sup>) was taken into the vessel of the analyzer and concentration of Pb(II) ions was determined by hanging mercury drop electrode (HMDE) at a peak potential of -380 mV. The percent sorption and distribution coefficient ( $R_d$ ) were calculated using the following equations:

$$\%Sorption = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

$$R_d = \frac{C_i - C_e}{C_e} \times \frac{V}{W} \left( \text{cm}^3 \text{ g}^{-1} \right) \quad (2)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentration of Pb(II) ions in solution respectively,  $V$  is the volume of Pb(II) ions solution (15 cm<sup>3</sup>) and  $W$  is the mass of sorbent (200 mg). The results are the average of at least triplicate measurements at 30 ± 2°C unless specified otherwise. In most cases the precision is around ± 2%.

## RESULTS AND DISCUSSION

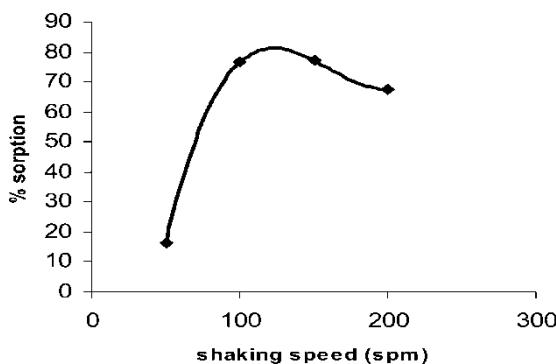
### Optimization of Pb(II) Ions Sorption

A large number of parameters such as selection of appropriate sorptive medium, amount of sorbent, concentration of sorbate, the contact time between sorbent and sorbate influence the sorption of metal ions at trace or subtrace levels (18). Therefore, the sorption of Pb(II) ions onto beach sand is optimized first keeping all the experimental conditions constant except one which is under investigation. Firstly, the shaking speed is optimized

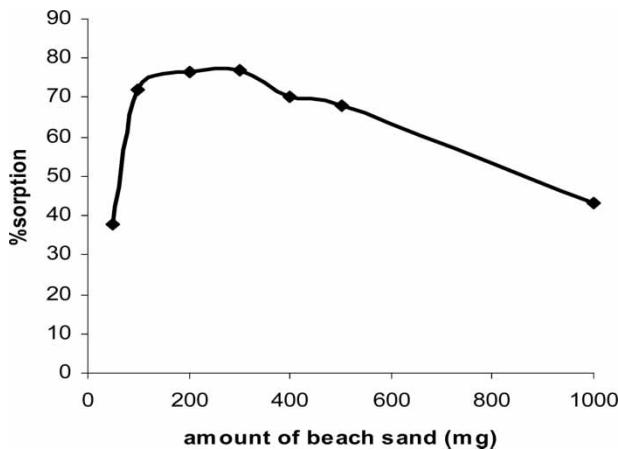
from 50–200 strokes per minutes (spm) using deionized water as sorptive medium and arbitrarily chosen Pb(II) ions concentration ( $9.65 \times 10^{-6}$  M), shaking time 10 minutes, amount of beach sand 100 mg/15 cm<sup>3</sup>. The results are given in Fig. 1. The percent sorption increases with increasing shaking speed and attains a maximum value around 100 strokes per minutes(spm) then starts decreasing with an increase in the shaking speed. For further experiments, 100 spm is chosen as optimized shaking speed. It suggests that at higher agitation speed attractive forces are predominant by repulsive forces.

The percent sorption with respect to the dosage of sorbent is another factor which needs to be optimized. Therefore, the influence of the amount of sorbent on the sorption of Pb(II) ions ( $9.65 \times 10^{-6}$  M) is examined from 100–1000 mg using 10 minutes shaking time and 100 spm shaking speed. The percent sorption increases with increasing amount of beach sand and attains a maximum value around 200 mg (~74%) then starts decreasing with a further increase in the amount of sorbent (Fig. 2). Therefore, for further investigations 200 mg sorbent is used. This behavior can also be explained on the basis of distribution ratio  $R_d$ , which also shows a reduction with the each increment of the dosage of sorbent as shown in Fig. 3. This is because of the compactness of the sorbent sites within the crystal structure and the reduction in the dispersion of the particle searching for the attractive sites. A similar trend is observed in the sorption of antimony onto the Haro river sand while changing the amount of sorbent under optimized conditions (20).

The sorption of Pb(II) ions ( $9.65 \times 10^{-6}$  M) is also investigated as a function of nature and concentration of electrolyte. Initially, the sorption is monitored as a function of pH of sorptive solution using buffers of pH (2–10), using 200 mg/15 cm<sup>3</sup> of beach sand, shaking speed 100 spm and shaking time 25 minutes. The results are shown in Fig. 4. The percent sorption registers a decrease with an increase in pH. The maximum sorption

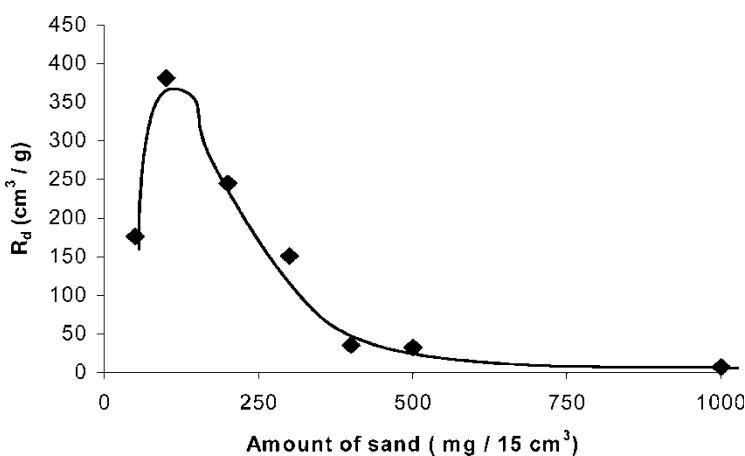


**Figure 1.** Influence of shaking speed on % sorption of Pb(II) ions onto beach sand (100 mg/15 cm<sup>3</sup>) using 10 minutes shaking time.



**Figure 2.** The effect of amount of beach sand on percent sorption of Pb(II) ions ( $9.65 \times 10^{-6}$  M) employing 100 spm shaking speed and 10 minutes shaking time.

around 90% is noticed at pH 4. The only species of Pb(II) ions at this pH will be  $\text{Pb}^{2+}$  ions (21). The decrease in sorption of Pb(II) ions with increasing pH may be due to the formation of strong hydroxyl complexes of Pb(II) ions at higher pH. To select an appropriate medium for maximum sorption, solutions of  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HClO}_4$  are studied in the concentration range of  $10^{-2}$ – $10^{-4}$  M, along with deionized water. The dilute solutions ( $10^{-4}$  M) of all three acids gave maximum sorption of 95% from  $\text{HNO}_3$ , 91% from  $\text{HCl}$  and 90% from  $\text{HClO}_4$  along with 80% from deionized water.



**Figure 3.** The effect of amount of beach sand on sorption of Pb(II) ions ( $6.5 \times 10^{-6}$  M) employing 100 spm shaking speed and 10 minutes shaking time.

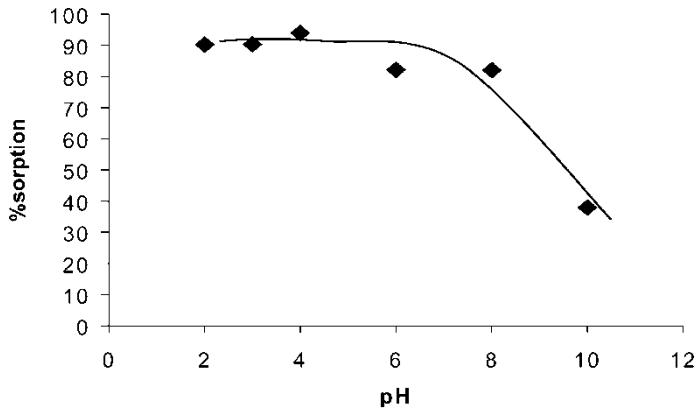


Figure 4. Variation of % sorption of Pb(II) ions onto beach sand with pH.

Dilute nitric acid solutions of  $10^{-2}$ – $10^{-4}$  M have also been explored as a function of shaking time from 5–40 minutes. The results are presented in Fig. 5. In all acid concentrations the percent sorption rises with increasing shaking time. The maximum sorption is achieved in a shorter duration for most dilute solutions ( $10^{-4}$  M) which increases with a decrease in acid concentration. For further investigations  $10^{-4}$  M nitric acid solution as sorptive medium, 25 minute shaking time and 200 mg beach sand have been selected. The pH of  $10^{-4}$  M nitric acid solution comes out to be  $4 \pm 0.1$ . The dominant species of Pb(II) upto pH 6 would be  $\text{Pb}^{2+}$ , at pH 7  $\text{Pb}^{2+}$  (~82%),  $\text{Pb}(\text{OH})^+$  (~18%), at pH 8  $\text{Pb}(\text{OH})^+$  (~58%),  $\text{Pb}^{2+}$  (~38%), and polymeric species of  $\text{Pb}_3(\text{OH})_4^{2+}$  (~3%), and  $\text{Pb}(\text{OH})_2$  (~1%).

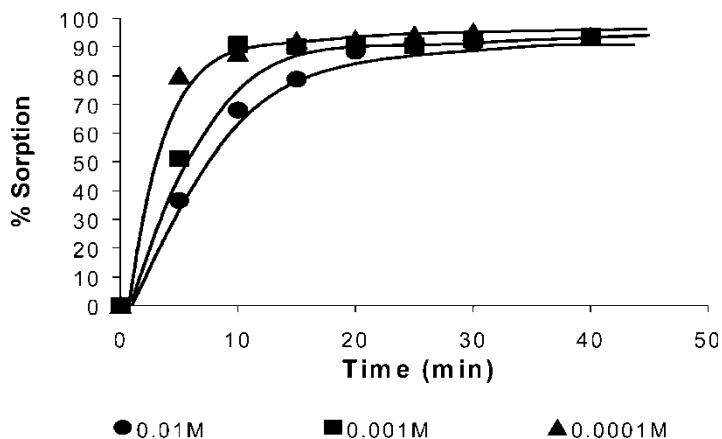


Figure 5. Sorption of Pb(II) ions in  $\text{HNO}_3$  solutions of different concentrations as a function of shaking time.

$\text{Pb}_3(\text{OH})_4^{2+}$  ( $\sim 3\%$ ) at pH 10 Pb(II) is likely to be present as  $\text{Pb}(\text{OH})_2$  ( $\sim 50\%$ ),  $\text{Pb}(\text{OH})^+$  ( $\sim 22\%$ ),  $\text{Pb}(\text{OH})_3^-$  ( $\sim 8\%$ ) and  $\text{Pb}_3(\text{OH})_4^{+2}$  ( $\sim 12\%$ ) (21). The decrease in the sorption of Pb(II) ions at higher pH is due to the presence of more hydrolyzed species in the aqueous medium.

The influence of concentration of sorbate on its sorption is also examined over a 100 fold concentration of Pb(II) ions in the range of  $10^{-6}$  to  $10^{-4}$  M using 200 mg beach sand, 25 minutes shaking time,  $10^{-4}$  M  $\text{HNO}_3$  as sorptive medium and 100 spm shaking speed. The results are shown in Fig. 6. The sorbed concentration increases with initial concentration of sorbate and attains a constant value around  $10^{-4}$  M. This suggests a saturation at the solid-solute interface at higher sorbate concentration. A similar trend has been noticed when sorption of antimony onto Haro river sand has been monitored while varying the concentration of metal ions in sorptive solution (20). Dilute aqueous solution of Pb(II) ions have been utilized as a model for low metal concentration in wastewater.

The resultant optimum conditions for the Pb(II) ions onto beach sand are at 100 spm shaking speed, 200 mg beach sand,  $10^{-4}$  M  $\text{HNO}_3$ , and 25 minutes shaking time.

### Sorption Isotherms

The sorption data were subjected to different sorption isotherms to evaluate sorption capacity of beach sand for Pb(II) ions. The sorption data at different temperatures (293, 303, 313 and 323 K) were tested with Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) sorption models. The Langmuir sorption model, a theoretical equation which described the relationship between the amount sorbed and the residual equilibrium

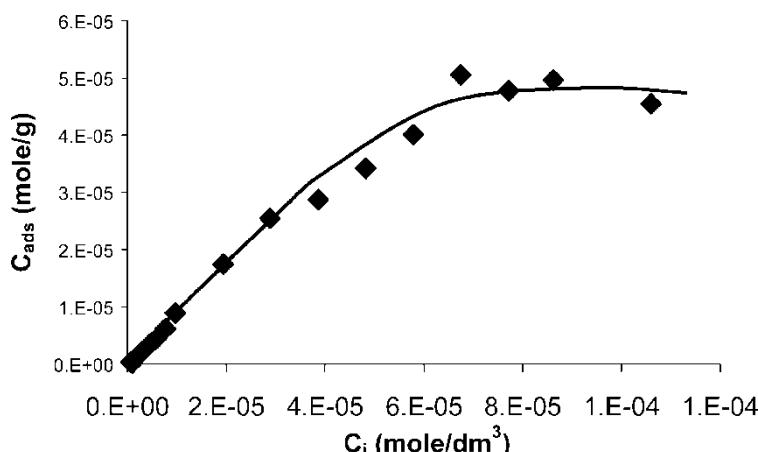


Figure 6. Influence of concentration of Pb(II) ions on its sorption onto beach sand.

concentration of sorbate in solution at constant temperature suggests monolayer formation on the sorbent surface (22) and envisages that all sites are alike and uniform energetically. There is no interaction between sorbed molecules and no steric hindrance between sorbed molecules and incoming ions. The Langmuir sorption model is tested in the following form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

where  $C_e$  is the equilibrium concentration of sorbate in solution (mole/dm<sup>3</sup>),  $C_{ads}$  is the amount sorbed (mole/g),  $Q$  is the sorption capacity and  $b$  is the enthalpy dependent sorption equilibrium constant. The  $C_e/C_{ads}$  is plotted against  $C_e$  at different temperatures and Langmuir parameters ( $Q$  and  $b$ ) using slope and intercept of the linear plots are tabulated in Table 2. The values of  $Q$  and  $b$  are in the same range within expected error over the temperatures investigated. However, the increasing value of  $Q$  with rising temperatures envisaged an endothermic sorption. The value of Langmuir constant  $b$  should increase with increasing temperature for endothermic reaction is found to be almost constant upto 313 K and a reduction in its value is observed at 323 K. This may be due to the presence of different minerals in the total beach sand, which may have expected to behave in a different manner under the same optimized conditions whereas the Langmuir model assumed a uniform energy of all the sorption sites.

A dimensionless constant  $R_L$  (23) is evaluated from equation (4) using Langmuir constant,  $b$ , and initial concentration of Pb(II) ions. The values of  $R_L$  at 303 K are in the range of 0.0808–0.6590. These higher values of  $R_L$  indicate reasonable sorption of Pb(II) ions onto beach sand.

$$R_L = \frac{1}{(1 + bC_i)} \quad (4)$$

The Freundlich isotherm is the most widely used mathematical description of sorption in solutions. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies (24). The Freundlich equation is

**Table 2.** Langmuir parameters for Pb(II) ions sorption onto beach sand

Temperature(K)	Q (μmole/g)	b (dm <sup>3</sup> /mole)
293	22.90 ± 0.27	(2.84 ± 0.66) × 10 <sup>4</sup>
303	21.60 ± 0.01	(2.24 ± 0.46) × 10 <sup>4</sup>
313	21.50 ± 0.20	(2.25 ± 0.33) × 10 <sup>4</sup>
323	26.80 ± 0.39	(0.91 ± 0.08) × 10 <sup>4</sup>

tested in following linearized form:

$$\log C_{ads} = \frac{1}{n} \log C_e + \log A \quad (5)$$

where  $C_{ads}$  and  $C_e$  have the same meaning as described earlier,  $1/n$  is the Freundlich characteristic constant related to energy or intensity and A is the maximum sorption capacity. The  $\log C_{ads}$  is plotted against  $\log C_e$  at different temperatures (293, 313, 303, and 323 K) and the values of  $1/n$  and A have been estimated from the slope and intercept of the linear plots using linear regression analysis. The result are listed in Table 3. The value of  $1/n < 1$  for all temperatures investigated indicates a favorable sorption of Pb(II) ions onto beach sand. The values of  $1/n$  and A are minimum at lowest temperature investigated. The increase in the value of A with temperature suggests an endothermic nature of Pb(II) ions beach sand system. Comparable values of  $A = 1.38 \text{ mmoleg}^{-1}$  and  $1/n = 0.67$  have been reported for Cd(II) ions sorption onto Haro river sand (11).

A general correlation of sorption equilibrium for microporous sorbent has been developed by Dubinin and co-workers (25), from the ideas put forward by Polanyi (26). The D-R model is tested in the following form.

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (6)$$

where  $C_{ads}$  is described earlier,  $X_m$  is the sorption capacity,  $\beta$  is a constant related to free energy and  $\varepsilon$  is the Polanyi potential, which can be calculated using equation (7).

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

where  $R$  is the gas constant in  $\text{kJmole}^{-1}\text{K}^{-1}$ ,  $T$  is the temperature in Kelvin and  $C_e$  is the equilibrium concentration of Pb(II) ions in solution. The Polanyi model postulates a fixed volume, “sorption space”, close to the sorbent surface where sorption takes place. The Polanyi defines the sorption potential ‘ $\varepsilon$ ’ for any molecule within the attractive force field of the solid surface as the work required to remove a molecule to infinity from its location in the sorption space. From the plots  $\ln C_{ads}$  vs  $\varepsilon^2$ , the values of  $\beta$  and  $X_m$  are calculated. The constant  $\beta$  gives the mean free energy of

**Table 3.** Freundlich constants of Pb(II) ions sorption onto beach sand

Temperature(K)	1/n	A (m mole/g)
293	$0.39 \pm 0.09$	$0.28 \pm 0.19$
303	$0.57 \pm 0.13$	$0.63 \pm 0.09$
313	$0.66 \pm 0.06$	$5.30 \pm 3.61$
323	$0.67 \pm 0.06$	$5.10 \pm 1.28$

sorption 'E' per molecule(particle) of the sorbate when it is transferred to the surface of the solid from infinity in the solution (27), is calculated using equation (8). Results are given in Table 4. The mean sorption energy,  $E$ , is found to vary within a narrow range of 11.03–12.16 kJ/mole which are in the range of 8–16 kJ/mole reported for ion exchange mechanism (28).

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

The experimental equilibrium data are obeyed by all three sorption isotherms tested. The variation in the sorption capacities in three sorption isotherms may be attributed to the assumptions taken into account while deriving these sorption models. In general, the sorption capacities appear to increase with temperature. This behavior of the sorption process can be explained by the fact that at a higher temperature numbers of activated sites have increased, hence providing space for Pb(II) ions to occupy on the sorbent surface. Also at high temperature the surfaces in the micropores of the sorbent structure gets sufficient amount of activation energy.

### Kinetics of Sorption

The mass transfer processes can be better visualized by their kinetic and thermodynamic investigations. Therefore, kinetic data are subjected to different equations. To study the change in the concentration of sorbate onto sorbent with shaking time, the Morris–Weber equation (29) was tested in the following form:

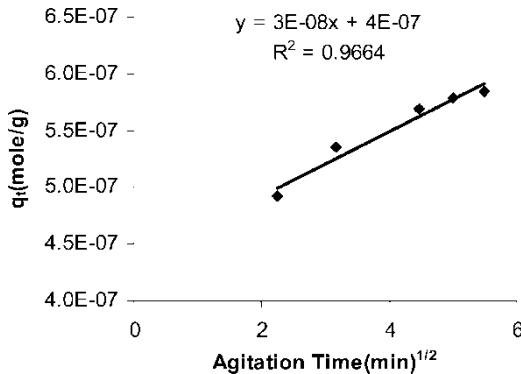
$$q_t = R_{id}\sqrt{t} \quad (9)$$

where  $q_t$  is the sorbed concentration at time 't',  $R_{id}$  is the rate constant of intraparticle transport. The plot of  $q_t$  vs  $t^{1/2}$  is given in Fig. 7. This is a linear plot with a correlation factor of 0.9664. The value of  $R_{id}$  calculated from the slope comes out to be  $30 \pm 3.3 \text{ nmole g}^{-1} \text{ min}^{-1/2}$ .

Another relationship dealing with the kinetics of Pb(II) ions sorption. i.e Reichenberg equation (30) is subjected to sorption data pertaining to a change

**Table 4.** D-R sorption characteristic constants for Pb(II) ions onto beach sand

Temperature (K)	$\beta$ (kJ <sup>2</sup> mole <sup>-2</sup> )	E (kJ/mole)	$X_m$ ( $\mu$ mole/g)
293	$-0.00347 \pm 0.000656$	$12.16 \pm 0.70$	$41.3 \pm 21.9$
303	$-0.00384 \pm 0.000543$	$11.50 \pm 0.81$	$57.8 \pm 27.32$
313	$-0.00413 \pm 0.000349$	$11.03 \pm 0.46$	$86.20 \pm 28.7$
323	$-0.00385 \pm 0.000324$	$11.44 \pm 0.50$	$64.1 \pm 22.02$



**Figure 7.** Validation of Morris-Weber equation of Pb(II) ions sorption onto beach sand.

in the sorption of Pb(II) ions onto beach sand with shaking time.

$$F = (1 - 6/\pi^2) e^{-Bt} \quad (10)$$

$Bt$  can be calculated for each value of  $F$  by the relationship

$$Bt = -0.4977 - \ln(1 - F)$$

$$\text{where } F = q_t/q_e$$

$q_e$  is the sorbed concentration at equilibrium and  $q_t$  is the sorbed concentration at time ' $t$ '. The plot of  $Bt$  against ' $t$ ' is given in Fig. 8, which gives a straight line with a correlation factor of 0.9746 but does not pass through the origin which indicates that the sorption of Pb(II) ions onto beach sand is a film diffusion process.

The validity of Lagergren first order equation (31) is also tested using the kinetic data.

$$\log(q_e - q_t) = \log q_e - kt/2.303 \quad (11)$$

where ' $k$ ' is the first order rate constant. The equation is tested by plotting  $\log(q_e - q_t)$  against time ' $t$ ' in Fig. 9 yielding a straight line with a correlation factor of 0.9861. The rate constant  $k = 0.13 \pm 0.01 \text{ min}^{-1}$  is computed from the slope of the linear plot. This is of same order of magnitude of  $0.12 \text{ min}^{-1}$  estimated for Zn(II) ions sorption onto Haro river sand (32).

### Thermodynamic Studies

The variation in temperature also affects the sorption of trace metals ions onto solid surfaces. The sorption of Pb(II) ions onto beach sand is monitored over a temperature range of 293–323 K under optimized conditions already chosen.

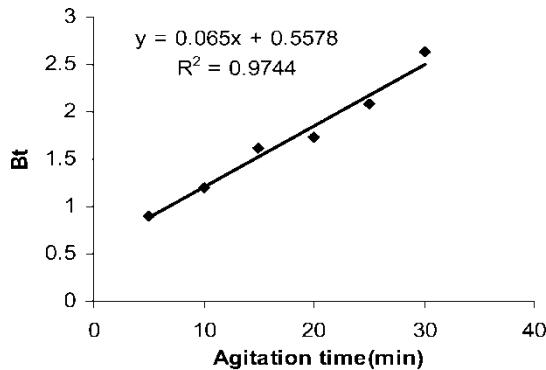


Figure 8. Reichenberg plot of Pb(II) ions sorption onto beach sand.

The values of  $\Delta H$  and  $\Delta S$  are calculated from the slope and intercept of the plot of  $\log K_c$  vs. temperature in Kelvin (Fig. 10).

$$K_c = \frac{F_e}{1 - F_e} \quad (12)$$

$$\log K_c = \frac{-\Delta H}{2.303 RT} + \frac{\Delta S}{2.303 R} \quad (13)$$

where  $K_c$  is the equilibrium constant and  $F_e$  is the fraction sorbed at equilibrium. The values of  $\Delta G$  are calculated using the equation (14) at 293, 303, 313 and 323 K. The results are listed

$$\Delta G = -RT \ln K_c \quad (14)$$

in Table 5. The positive values of  $\Delta H$  indicate that process is endothermic in nature and negative  $\Delta G$  suggests the spontaneity of the sorption of Pb(II) ions

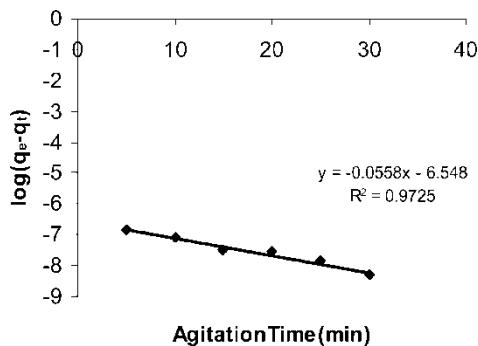
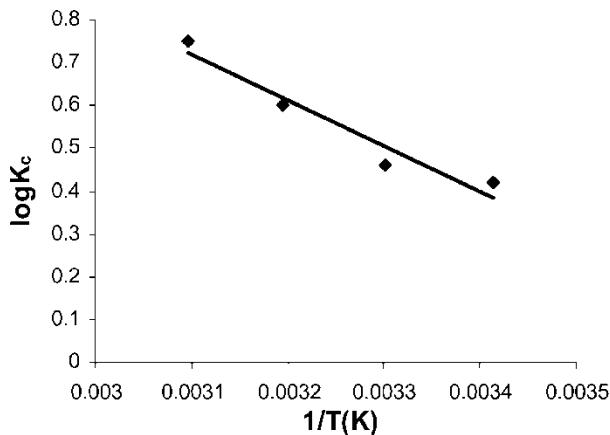


Figure 9. Lagergren plot of Pb(II) ions sorption onto beach sand.



**Figure 10.** Variation of sorption of Pb(II) ions with temperature.

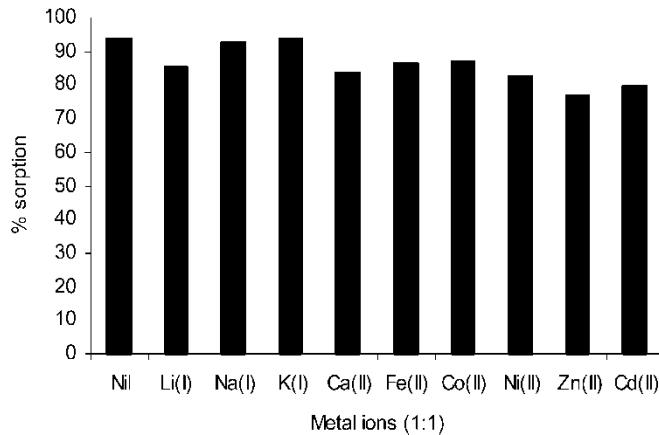
onto beach sand. The positive value of entropy change indicates enhanced disorder at the solid-liquid interface during the sorption.

### Influence of Diverse Anions and Cations

To check the selectivity of the sorbent the influence of different anions and cations on the sorption of Pb(II) ions is monitored under the optimized conditions selected for sorption. This is important because in the environmental samples the ions other than the target ion sometimes greatly affect the sorption of the required ion in the aqueous medium. Sorption of Pb(II) ions is studied in the presence of different anions and cations. The anions were added as their sodium or potassium salts, whereas cations were included as their nitrates or chlorides. The results are shown as histograms in Figs. 11 and 12. The nil result refers to the sorption of Pb(II) ions from sorptive medium without any additional diverse anion or cation. Zn(II) and Cd(II) ions reduce the sorption of Pb(II) ions from 94% to 76 and 79% respectively. This may be due to the strong affinity of these cations toward the sorbent surface. Thiosulphate, biphosphate, and EDTA ions cause

**Table 5.** Thermodynamic parameters for Pb(II) ions sorption onto beach sand

$\Delta G$ kJ/mole				$\Delta H$ kJ/mole	$\Delta S$ J/moleK
293K	303K	313K	323K		
$-2.23 \pm 0.56$	$-4.48 \pm 0.64$	$-3.59 \pm 0.78$	$-4.72 \pm 0.18$	$20.27 \pm 3.45$	$76.58 \pm 12.01$

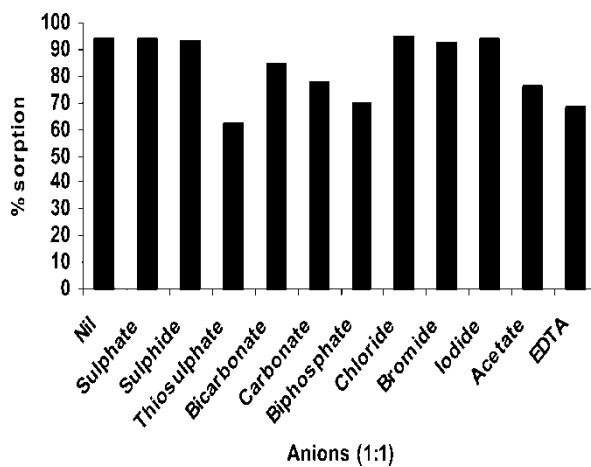


**Figure 11.** Effect of common cations on the sorption of Pb(II) ions onto beach sand.

substantial decrease in the sorption of Pb(II) ions onto beach sand in and around 60%. Higher affinity of anionic complexes of Pb(II) ions with thiosulphate, biphosphate, and EDTA as compared to Pb(II) ions themselves may be attributed to the reduction in its sorption onto beach sand. Strong complexes of Pb(II) ions with thiosulphate, biphosphate and EDTA have been reported in the literature (33–35).

### Reaction Mechanism

The beach sand is comprised of three major components i.e., calcite, quartz, and aragonite. Calcite is rhombohedral in shape in which carbonate ions are



**Figure 12.** Influence of diverse anions on the sorption of Pb(II) ions onto beach sand.

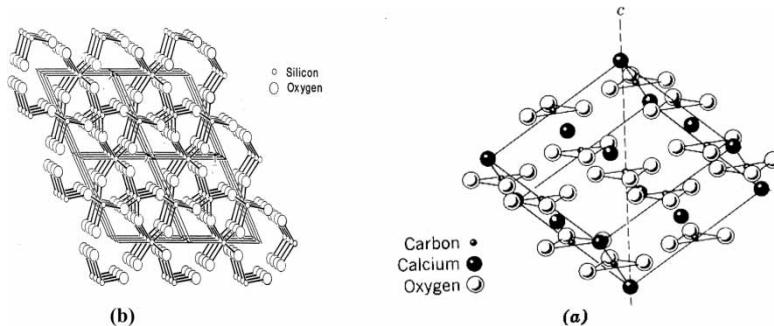


Figure 13. Crystal structures of quartz(a) and calcium carbonate(b).

arranged in a triangular manner, the oxygen of each of carbonate ions occupied three corners of the triangle, whereas calcium remained there in the center of the two planes of the triangles. The triangular carbonate groups are the basic building units of all carbonate minerals and are largely responsible for the properties peculiar to the group. The quartz has a tetrahedral structure with oxygen atoms occupying the four corners of a tetrahedron. The shape of the crystal structures of the quartz and the carbonate is shown in Fig. 13. The aragonite is also calcium carbonate with a orthorombic shape, the properties of this mineral also depend upon the carbonate (36). A possible sorption mechanism is proposed for Pb(II) ions onto beach sand, the presence of negative sites in the structure of the calcite, quartz and aragonite in the form of carbonates and oxides provides affinity for the positively charged Pb(II) ions in aqueous solutions as shown below.



## CONCLUSIONS

The beach sand can be used as a potential sorbent to remove Pb(II) ions from aqueous solutions. The process of sorption is quite selective because Pb(II) ions can easily be removed in the presence of common diverse ions from aqueous solutions. Very few of these ions tested have an effect on the sorption process. The sorption data of Pb(II) ions followed all three sorption isotherms investigated. Sorption capacity generally increased with an increase in temperature indicating the endothermic nature of sorption. Kinetics studies also suggested a favorable sorption process. Thermodynamic results also suggest that the process is endothermic and spontaneous in nature. The cost effective beach sand may be used to remove traces of Pb(II) ions present in aqueous solutions and to preconcentrate its very minute amount from the aqueous media. This sorbent appears to have a potential for the

treatment of industrial effluents containing Pb(II) ions or to clean large volume of solutions contaminated with traces of Pb(II) ions.

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