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Sorption Potential of Styrene-Divinylbenzene Copolymer Beads for the Decontamination of Lead from Aqueous Media

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Sorption Potential of Styrene-Divinylbenzene Copolymer Beads for the Decontamination of Lead from Aqueous Media

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Abstract: The decontamination of lead ions from aqueous media has been investigated using styrene-divinylbenzene copolymer beads (St-DVB) as an adsorbent. Various physico-chemical parameters such as selection of appropriate electrolyte, contact time, amount of adsorbent, concentration of adsorbate, effect of foreign ions, and temperature were optimized to simulate the best conditions which can be used to decontaminate lead from aqueous media using St-DVB beads as an adsorbent. The atomic absorption spectrometric technique was used to determine the distribution of lead. Maximum adsorption was observed at 0.001 mol L^{-1} acid solutions (HNO_3, HCl, H_2SO_4 and $HClO_4$) using 0.2 g of adsorbent for 4.83×10^{-5} mol L^{-1} lead concentration in two minutes equilibration time. The adsorption data followed the Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherms over the lead concentration range of 1.207×10^{-3} to 2.413×10^{-2} mol L^{-1}. The characteristic Freundlich constants i.e. $1/n = 0.164 \pm 0.012$ and $A = 2.345 \times 10^{-3} \pm 4.480 \times 10^{-5}$ mol g^{-1} have been computed for the sorption system. Langmuir isotherm gave a saturated capacity of 0.971 ± 0.011 mmol g^{-1}, which suggests monolayer coverage of the

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surface. The sorption mean free energy from D-R isotherm was found to be 18.26 ± 0.75 kJ mol^{-1} indicating chemisorption involving chemical bonding for the adsorption process. The uptake of lead increases with the rise in temperature. Thermodynamic parameters i.e. ΔG, ΔH, and ΔS have also been calculated for the system. The sorption process was found to be exothermic. The developed procedure was successfully applied for the removal of lead ions from real battery wastewater samples.

Keywords: Sorption, lead, removal, styrene-divinylbenzene copolymer beads

INTRODUCTION

Lead is one of the hazardous metals due to its insidious effects on human beings particularly for children having higher metabolic rates. It enters into the human body through ingestion, inhalation, or dermal absorption. The cumulative absorption of small quantities of lead into the human body through air, water, and food can pose health hazards to human life that include gastrointestinal, genitourinary, musculoskeletal, hematopoietic, and reproductive abnormalities and anemia. The impaired functioning of central nervous system leads to headache, irritability, lack of concentration, restlessness, and peripheral neuropathy (1–3). The long term high exposure to lead compounds is associated with an increased risk of lungs cancer (4).

The main sources of lead pollution include the industrial manufacturing of automotive batteries, ceramic, ink, ammunition, soldering material and paints, formation of its antimony and tin alloys used in power and telephone cables and the use of tetra alkyl lead as antiknocking gasoline additives (1, 5). Lead is also the left over of some industrial processes to produce fertilizer and pesticide (6). In all these cases lead is transmitted into the environment either by an inadequate manufacturing process or caused by accident, thus making the water toxic beyond 0.05 mg Pb L^{-1}, the permissible limit for human consumption. Keeping in view the gravity of the situation global attention has been diverted towards understanding the behavior of lead in ecosystems and metabolism for adopting measures for its efficient removal from such industrial and municipal waste effluents.

Removal/preconcentration of lead from aqueous media has been investigated by different procedures such as coprecipitation (7, 8), formation of volatile compounds (9, 10), flotation (11), solvent extraction (12, 13), ion exchangers (14, 15), ferritization (16), and adsorption. Various workers have studied the adsorption of lead on various inorganic materials and organic compounds. Among the inorganic sorbents used for lead are metal oxides (17, 18), activated carbon (19), bentonite (20), and lateritic minerals (21). The organic sorbents for lead include polycarbonate filters (22), polyacrylonitrile and acrylonitrile charcoal composite (23) and ion exchange resin (24). All these methods are effective for the removal of lead from the waste or polluted waters but are either time consuming or expensive, hence there is a need to look into other inexpensive, rapid, and effective methods for this purpose.

The present study deals with the sorption behavior of lead onto styrene-divinylbenzene copolymer beads (St-DVB). The beads were prepared by oil-water suspension polymerization under control conditions to obtain specific morphology of the copolymer beads specially w.r.t. porosity, surface area, mechanical strength etc. The beads so formed were dried and sulfonated to make the copolymer as cation-exchanger before it could be used as an adsorbent for lead (25).

EXPERIMENTAL PROCEDURE

Equipments

The quantification of lead was made with a Hitachi model 180/80 polarized Zeeman atomic absorption spectrophotometer coupled with a microprocessor-based data-handling facility. Both the flame and graphite furnace atomizers are equipped with a strong magnetic field to give a double-beam optical correction system based on the Zeeman effect. A water cooled, premix, fish-tail type burner, having a $10 \times 0.05\ \mathrm{cm}^2$ slot, was used for the air-acetylene flame. Hollow cathode lamp of lead from Hitachi was used as a radiation source.

Infrared spectrum of St-DVB copolymer beads was recorded on Bio-Rad Excaliber FT-IR spectrometer in the range of 4000–500 cm^{-1}, employing the KBr pellet technique.

Reagents

Stock solution of lead (1000 mg L^{-1}) was prepared by dissolving 0.1 gram of specpure metal (Johnson and Mathey) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 mL with water. Standard solutions were prepared by appropriate dilution of this stock solution. Fresh working standards were made immediately before use. Glassware was cleaned by overnight soaking in nitric acid (1:1) followed by multiple rinsing with water.

Buffer solutions of pH 1 to 12, having ionic strength of 0.1 M, were prepared by using appropriate aliquots of solutions of KCl and HCl (pH 1–3), CH_3COONa and CH_3COOH (pH 4–6), NH_4Cl and NH_4OH (pH 6–7.5) and H_3BO_3, NaCl and NaOH (pH 8–12). All pH measurements were carried out with a Metrohm 605 digital pH meter equipped with a combined glass/calomel electrode. All the reagents used were of analytical grade and were used as such. Distilled and deionized water was used throughout.

Sulfonated styrene-divinylbenzene copolymer beads (St-DVB) were produced by oil-water (o/w) suspension polymerization, the details of which have been reported elsewhere (25). The beads used for the sorption of lead had a surface area 281.1 m^2g^{-1}; pore volume 1.96 mL g^{-1}, particle size 45–100 μm, dry density 0.19 g mL^{-1} and mechanical strength of 0.16 N (25). The appearance of FT-IR absorption peaks at wave numbers 617 m [δ SO_4 bend], 677 m [aromatic ring], 776 w [ν C–C stretch], 1039s [δ S=O stretch], 1175s [β C–H inplane bend], 1491w [ν C=C aromatic ring], 1648 m [ν C=C aromatic], 2928 s [ν_{as} C–H] and 3434 [ν O–H] cm^{-1} confirm the formation of St-DVB beads (26, 27).

Sorption Measurements

A known amount of St-DVB beads was taken in a 35 mL culture tube with a screwed polyethylene cap along with 10 mL of buffer or standard acid solution. A fixed amount of stock solution was added. The contents were equilibrated for a specific time on a mechanical wrist action Griffin and George shaker. The phases were separated by centrifugation. The supernatant solution was withdrawn and the amount of lead was determined by atomic absorption spectrophotometry using the optimized instrumental parameters. A blank solution without metal was also prepared and treated similarly. All experiments were conducted at room temperature (296 ± 1 K) unless otherwise specified.

TREATMENT OF DATA

Adsorption of Metal

The percentage sorption of metal ion "M" at a given temperature was calculated by the difference in the concentration of the aliquots drawn before and after equilibration. The percentage adsorption and distribution coefficient (K_d) were calculated using the equations:

$$\%\,\text{adsorption} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

The distribution coefficient (K_d) was calculated from the equation

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \tag{2}$$

where C_i = initial concentration of the metal in the solution (mol L^{-1}), C_f = concentration of the metal in the solution after equilibrium (mol L^{-1}), V = volume of the adsorbate solution (mL), m = amount of the adsorbent (g).

Calculation of Thermodynamic Parameters

Thermodynamic parameters were calculated using the following relation:

$$K_c = \frac{C_{ads}}{C_{eq}} \tag{3}$$

where K_c = equilibrium constant, C_{ads} = equilibrium concentration of the metal adsorbed (mol L^{-1}), C_{eq} = equilibrium concentration of the metal in the solution (mol L^{-1}).

If F_e is the fractional attainment of adsorption at equilibrium, then

$$C_{eq} = C_i(1 - F_e) \tag{4}$$

and

$$C_{ads} = C_i\ F_e \tag{5}$$

where C_i = initial concentration of the metal in the solution, F_e = fractional attainment of the metal concentration at equilibrium.
By substituting the values of C_{eq} and C_{ads} from Equations (4) and (5) into Equation (3), K_c becomes:

$$K_c = \frac{F_e}{(1 - F_e)} \tag{6}$$

which shows that the equilibrium constant is independent of the amount of adsorbent and of the volume of the solution.

The values of ΔH and ΔS were calculated from the slope and intercept of the linear van't Hoff plot, respectively, using the relation:

$$\mathrm{In}K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

where ΔS = entropy change for the process, ΔH = enthalpy change for the process, R = gas constant, T = absolute temperature.
The changes in free energy (ΔG) and entropy (ΔS) for the specific adsorption have also been calculated using the equations:

$$\Delta G = -RT\ln K_c \tag{8}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{9}$$

where the symbols have their usual significance.

RESULTS AND DISCUSSION

The adsorption of lead ions from aqueous solutions on St-DVB beads was examined by optimizing various physicochemical parameters such as variable concentrations of mineral acids, pH, equilibration time, amount of adsorbent and concentration of adsorbate, using the batch method and employing the atomic absorption spectrometric technique. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. The effect of temperature on the adsorption of lead was also checked. All the reported results are the average of at least triplicate independent measurements. The expected error is within $\pm 3.5\%$ unless otherwise specified.

Effect of Acid Concentration

Interaction of various chemical compounds and electrolytes may alter the surface properties of the adsorbent, therefore, the adsorption behavior of 4.83×10^{-5} mol L^{-1} of lead solution was checked in mineral acid solutions (HNO_3, HCl, H_2SO_4 and $HClO_4$) having a concentration range from 0.001 to 2.0 mol L^{-1} using 0.2 g of St-DVB beads. The shaking time of 5 minutes was selected arbitrarily. The results presented in Fig. 1a and Fig. 1b show that the maximum adsorption ($>99\%$) of lead ions was observed at 0.001 to 0.25 mol L^{-1} acid concentration which then decreased with further increase in acid concentration from 0.25 to 2.0 mol L^{-1}. Similar trends have been reported for the uptake of lead on lateritic minerals (21). The decrease in adsorption of lead at higher acid concentrations may be attributed to the competition between the excess of H^+ ions in the medium and positively charged hydrolyzed species present in the solution. Also, a higher acid concentration appears to suppress hydrolysis of the element in hydrolyzed species, resulting in lower adsorption. It was also observed that maximum adsorption of lead occurred in 0.001 M acid concentration of all the acids, therefore, this concentration of HNO_3 was used for all the subsequent experiments regarding the optimization of adsorption conditions of lead ions on St-DVB beads.

The adsorption of metal ions on the surface of St-DVB beads can probably be explained on the basis of the surface complex formation model which is facilitated by the dissociation of acid group present in St-DVB beads. The cation exchange reaction can occur in aqueous solutions as follows:

$$\mathrm{m\,[St - DVB - SO_3H] \rightleftharpoons m\,[St - DVB - SO_3^-] + mH^+} \tag{10}$$

$$\mathrm{M^{n+} + m\,[St - DVB - SO_3 -]^- \rightleftharpoons M\,[St - DVB - SO_3 -]_m^{-(n-m})} \tag{11}$$

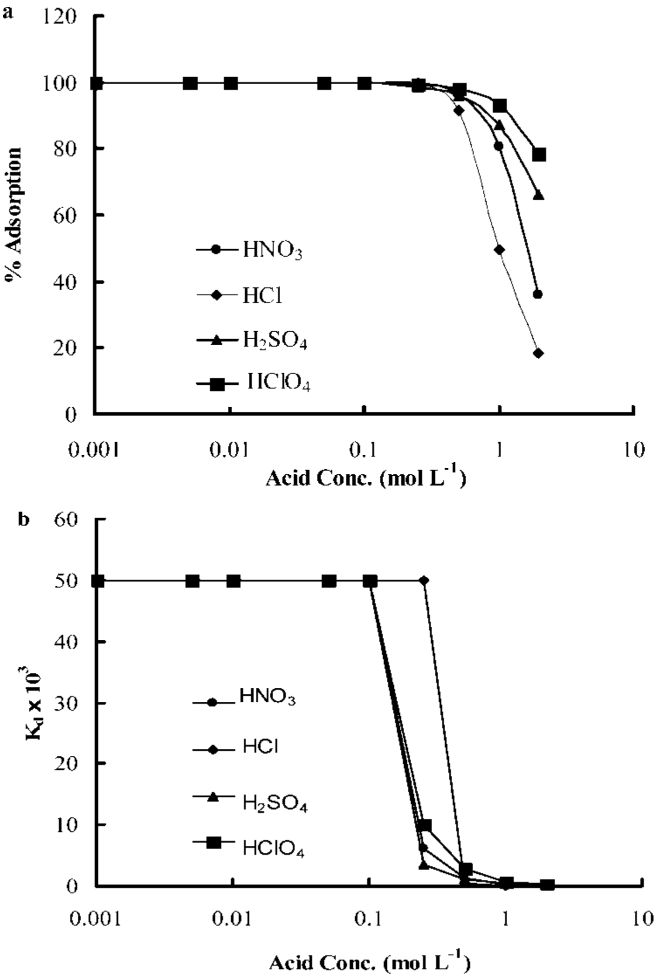

Figure 1. (a) Effect of percent adsorption of lead ions on St-DVB beads as a function of acid concentration. (b) Effect of K_d for the adsorption of lead ions on St-DVB beads as a function of acid concentration.

The overall reaction can be represented as:

$$M^{n+} + m\,[St - DVB - SO_3H] \rightleftharpoons M\,[St - DVB - SO_3-]_m^{-(n-m)} + mH^+ \tag{12}$$

where M^{n+} = metal ion with n^+ charge, $-SO_3H$ = acidic part of St − DVB surface, mH^+ = number of protons released.

The reaction equation (12) is reversible in acid solution. Similar mechanism has been reported for the adsorption of lead ions on activated bentonite (20), and titanosilicate molecular sieves (28). In the present study the decrease in the adsorption of lead at higher acid concentration can be explained on the basis of competitive reaction of the protons in the medium and positively charged lead ions.

Effect of pH

The removal of an adsorbate from aqueous solutions by adsorption is highly dependent on the pH of the medium, which affects the surface charge of the adsorbent, degree of ionization, and speciation of the adsorbate species. Such study helps in indicating the appropriate pH of the effluent/wastewater for achieving maximum efficiency in the removal of metal ions by an adsorbent. The pH dependence study of lead adsorption on St-DVB beads was, therefore, carried out from aqueous solutions of different pH covering a range of 1 to 12, using 0.15 g of adsorbent and fixed amount of lead (4.83 x 10^{-5} mol L^{-1}). The results obtained are shown in Fig. 2. The percent adsorption increases with an increase in pH of the solution, and was maximum at pH 6 and remained constant upto pH 8.0. Above this pH the lead solution was turbid, therefore, the results have not been reported beyond pH 8.0. The optimum pH values of 3–6 and 5.5 for maximum uptake of lead ions have been reported for Chelex-100 resin (14) and poly(methyl methacrylate) microspheres (29). Relatively lower adsorption of lead ions at low pH could probably be due to the competition between H^+ ions and lead ions for a fixed number of adsorption sites. The enhanced

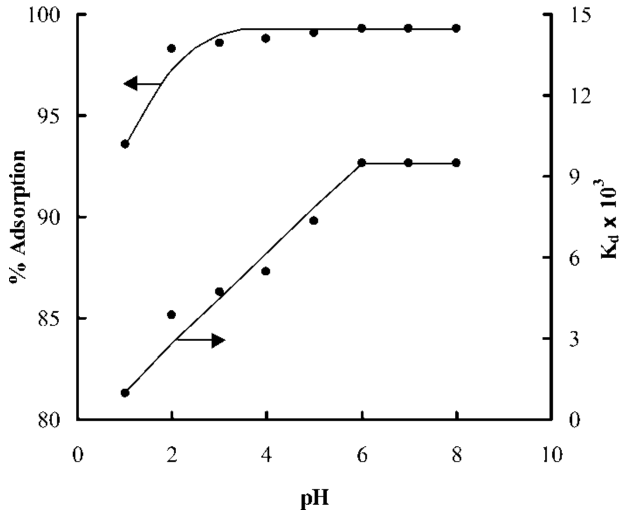

Figure 2. Effect of pH on the adsorption of lead ions on St-DVB beads.

adsorption of lead ions at higher pH values could probably be due to the condensation reaction between the hydrolysis product of the sorbate ions and the sorbent carrying $-SO_3H$ groups. It can, therefore, be concluded that the overall adsorption of lead ions on the surface of St-DVB beads used is mainly due to the surface complexation phenomena.

Influence of Equilibration Time

The effect of variation of shaking time on the adsorption of lead ions on St-DVB beads was checked by shaking 10 mL of 4.83×10^{-5} mol L^{-1} of lead solution in 0.001 mol L^{-1} of HNO_3 with 0.2 g of adsorbent. The equilibration time was varied from 0.5–10 minutes and the results have been shown in Fig. 3. It is seen that the percentage adsorption remains constant and quantitative during the selected periods. Therefore, 2 minutes of equilibration time was considered to be sufficient for the adsorption of lead ions on St-DVB beads and was employed for all the subsequent experiments. The short equilibration time suggests that the adsorption process is a surface phenomenon proceeding between the metal ions and sorbent carrying $-SO_3H$ groups.

Variation of Amount of Adsorbent

The influence of the amount of adsorbent on the adsorption efficiency was also studied by shaking 10 mL of 4.83×10^{-5} mol L^{-1} of lead ions solution using the optimized parameters. The amount of St-DVB beads was varied from 25 to

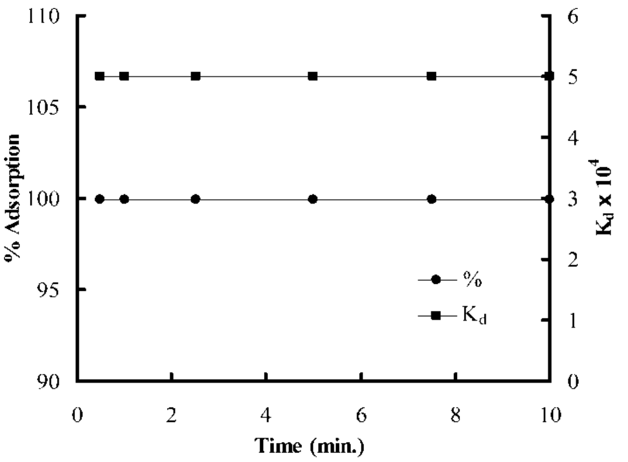

Figure 3. Influence of equilibration time on the adsorption of lead ions on St-DVB beads.

750 mg and the results have been reproduced in Fig. 4, which shows that 150 mg of St-DVB beads are sufficient for the quantitative removal of lead ions from the aqueous solution used. With further increase in the weight of St-DVB beads, the sorption remained constant upto 750 mg. Therefore, 200 mg of St-DVB beads was considered sufficient for the quantitative removal of lead ions from aqueous solutions and was used for further investigation.

Effect of Adsorbate Concentration

The adsorption lead ions on St-DVB beads was studied as a function of its own concentration under the optimized conditions of acid concentration, equilibration time, and the amount of the adsorbent. The initial sorptive concentration of lead ions was varied from 250 to 5000 mg L^{-1}. The results were reproduced in Fig. 5, which indicates that the percentage adsorption of lead was decreased with the increase in initial concentration. The decrease in the sorption of lead ions with the increase in its concentration on St-DVB beads may be attributed to the saturation of the available active sites in a fixed amount of adsorbent.

The data for the adsorption of lead ions on St-DVB beads has been analyzed in terms of the Freundlich mode of adsorption. It was found that the Freundlich adsorption isotherm was capable of describing the data in the entire concentration range of lead ions studied. The Freundlich isotherm

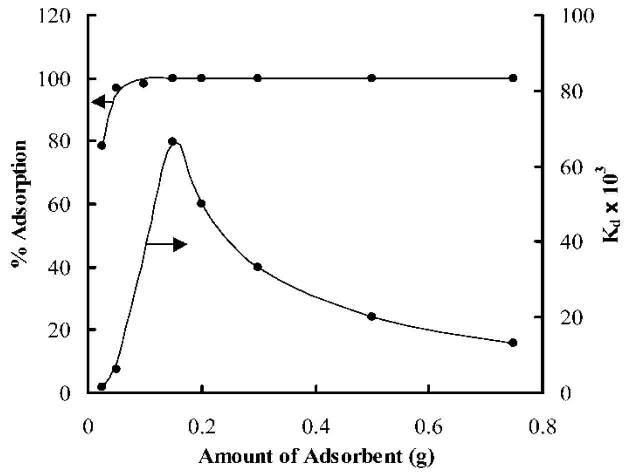

Figure 4. Variation of amount of adsorbent on the adsorption of lead ions on St-DVB beads.

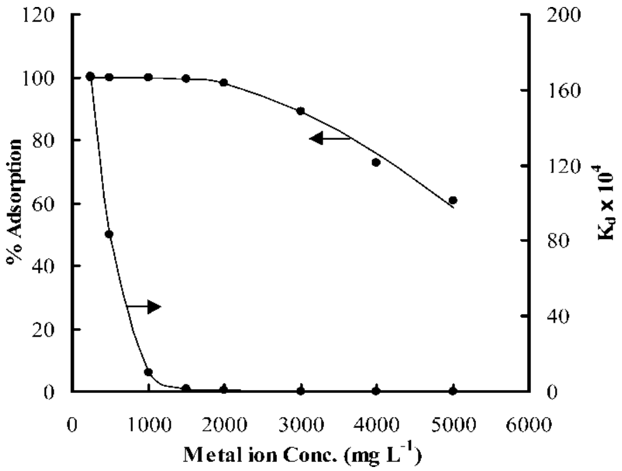

Figure 5. Effect of adsorbate concentration on its adsorption on St-DVB beads.

was tested in the following linearized form:

$$\log C_{ad} = \log K + 1/n \log C_e \quad (13)$$

where C_{ad} = amount of lead adsorbed on St-DVB at equilibrium (mol g^{-1}), C_e = equilibrium concentration of lead in solution (mol L^{-1}), K and 1/n = Freundlich constants.

A plot of log C_{ad} versus log C_e yields a straight line (Fig. 6). This linear plot supports the applicability of the Freundlich isotherm model in the present study. The values of Freundlich constants 1/n and K give a measure of the adsorption intensity and capacity of the adsorbent, respectively. These constants were evaluated from the slope and the intercept of the straight line (Fig. 6) using a least square fit program and were found to be 0.164 ± 0.012 and $2.345 \times 10^{-3} \pm 4.480 \times 10^{-5}$ mol g^{-1}, respectively. The fractional value of 1/n ($0 < 1/n < 1$) signifies the heterogeneity of the surface of St-DVB beads (30). The applicability of the Freundlich isotherm in the present study is in accordance with the adsorption studies of lead ions on mesoporous titanosilicate molecular sieves (28).

The sorption data was subjected to Langmuir adsorption isotherm. The Langmuir adsorption isotherm is generally recognized for monolayer capacity and the strength of the intermolecular attractive forces is believed to fall off rapidly with distance. The linearized form of the Langmuir model is:

$$C_e/C_{ad} = C_e/C_m + 1/bC_m \quad (14)$$

where C_e = equilibrium concentration of metal ions in solution (mol L^{-1}), C_{ad} = amount of metal ions adsorbed per gram of adsorbent (mol g^{-1}), C_m =

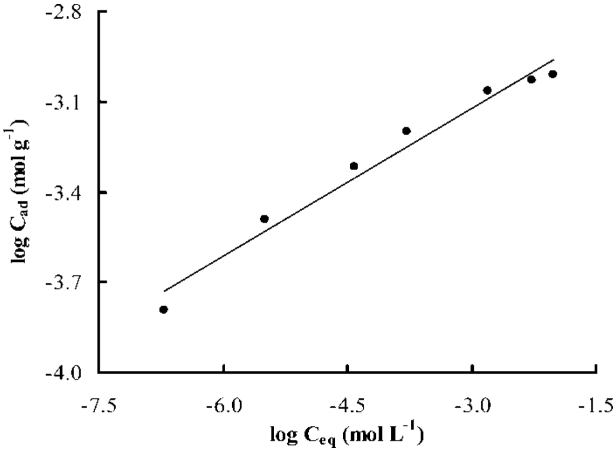

Figure 6. Freundlich adsorption isotherm of lead ions on St-DVB beads.

constant related to maximum amount of solute adsorbed, b = constant related to the binding energy of the solute.

The graphic presentation of C_e/C_{ad} vs. C_e gives a straight line for lead ions as shown in Fig. 7, confirming that this expression is indeed a reasonable representation of the chemisorption isotherm. Similar results have been reported for the adsorption of lead ions on poly(methyl methacrylate) microspheres (29). The numerical values of constants C_m and b evaluated from the slope and intercept were found to be 0.971 ± 0.011 m mol g^{-1} and 13.043 ± 0.891 L mol^{-1}, respectively. The value of saturation capacity C_m corresponds to the monolayer coverage and defines the total capacity of the

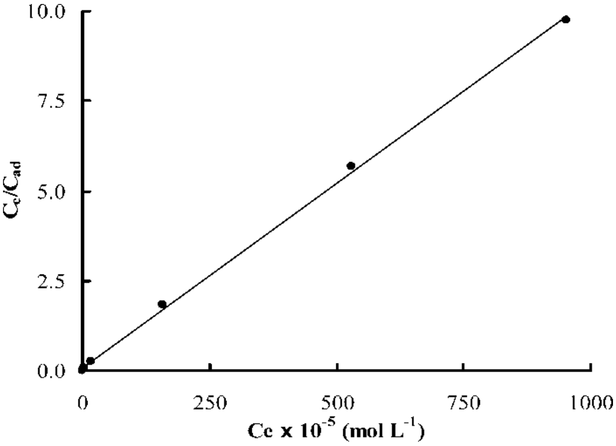

Figure 7. Langmuir isotherm of lead ions adsorption on St-DVB beads.

adsorbent for a specific adsorbate and should, therefore, be substantially independent of temperature.

In order to study the nature of the adsorption phenomenon, either physical or chemical adsorption, the data were applied to Dubinin-Radushkevich (D-R) isotherm model. The D-R equation is:

$$C_{ad} = C_m \exp(-\beta \varepsilon^2) \tag{15}$$

where C_{ad} is the amount of lead adsorbed on St-DVB beads (mol g^{-1}), C_m is the maximum amount of lead ions that can be adsorbed on sorbent under the optimized experimental conditions (mol g^{-1}), β is a constant related to sorption energy (kJ^2 $mole^{-2}$) and ε is Polanyi potential which is mathematically represented as:

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{16}$$

where R is the gas constant in kJ mol^{-1} K^{-1}, T is the absolute temperature in Kelvin and C_e is the equilibrium concentration of lead ions in solution (mol g^{-1}). The linearized form of the D-R isotherm is:

$$\ln C_{ad} = \ln C_m - \beta \varepsilon^2 \tag{17}$$

when ln C_{ad} was plotted against ε^2, a straight line was observed (Fig. 8). The computed values of β and C_m from the slope and intercept of this straight line were $-1.50 \times 10^{-3} \pm 6.14 \times 10^{-5}$ kJ^2 mol^{-2} and 1.241 ± 0.01 mmol g^{-1} respectively. The value of sorption energy "E" can be correlated to β by

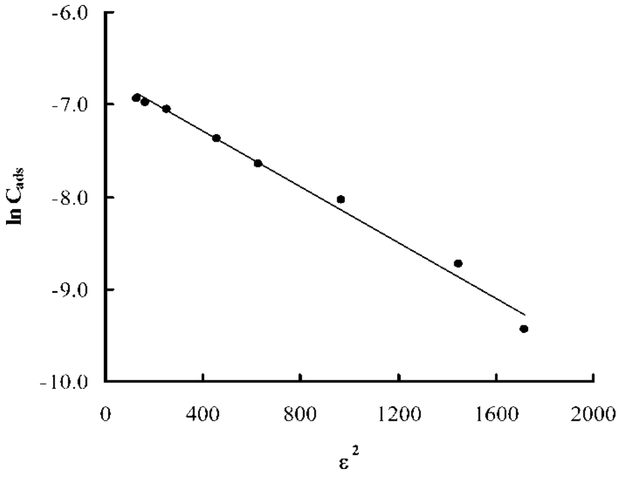

Figure 8. Dubinin-Radushkevich plot for adsorption of lead ions on St-DVB beads.

using the following relationship (31).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{18}$$

which is the free energy of transfer of one mole of solute from infinity to the surface of St-DVB. The numerical value of E evaluated from equation (18) is 18.257 ± 0.75 kJ mol^{-1} which is excepted for chemisorption based on ion exchange (32).

Influence of Temperature

The effect of temperature on the adsorption of lead ions (1.45×10^{-2} mol L^{-1}) on St-DVB beads was also checked using 0.15 g of adsorbent and other optimized conditions. The temperature was varied from 283 to 323 K. The amounts of lead ion adsorbed at various temperatures are shown in Table 1, which reveals that the uptake of lead increases with the rise in temperature, indicating better adsorption at a higher temperature. These observations are in accordance with the findings of lead adsorption on lateritic minerals (21).

The amounts of lead adsorbed at equilibrium at different temperatures have been utilized to evaluate the thermodynamical parameters for the sorption system. The van't Hoff plot of ln K_c vs. $1/T$ was a straight line (Fig. 9). The slope and intercept of this line were equal to ($-\Delta H/R$) and ($\Delta S/R$) respectively, thus allowing us to calculate ΔH and ΔS by using the equation (7). The estimated ΔH value for the present system was -1.586 ± 0.054 kJ mol^{-1} (Table 2). The values of free energy "ΔG" and entropy "ΔS" of specific adsorption at various temperatures were calculated by using equations (8) and (9) and have been reported in Table 2. The

Table 1. Adsorption studies of lead ions on St-DVB beads as a function of temperature

Temp. (K)	$1/T$ (K^{-1})	Concentration adsorbed (mol L^{-1})	Concentration in bulk (mol L^{-1})	K_c	ln K_c
283	3.534×10^{-3}	11.385×10^{-3}	3.094×10^{-3}	3.680	1.303
293	3.413×10^{-3}	11.448×10^{-3}	3.031×10^{-3}	3.777	1.329
302	3.311×10^{-3}	11.496×10^{-3}	2.983×10^{-3}	3.854	1.349
313	3.195×10^{-3}	11.539×10^{-3}	2.939×10^{-3}	3.926	1.368
323	3.096×10^{-3}	11.597×10^{-3}	2.881×10^{-3}	4.025	1.392
333	3.003×10^{-3}	11.622×10^{-3}	2.857×10^{-3}	4.068	1.403

St-DVB—150 mg, shaking time—02 min, volume equilibrated 10 mL, concentration of HNO_3 0.001 mol L^{-1}, concentration of lead 1.45×10^{-2} mol L^{-1}.

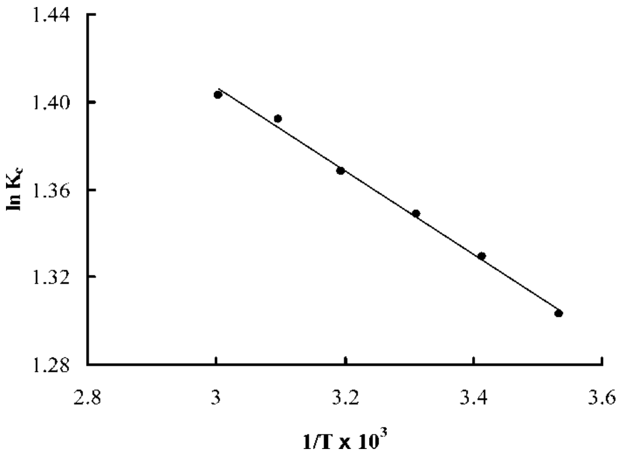

Figure 9. van't Hoff plot for the adsorption of lead ions on St-DVB beads.

negative values of ΔG indicate that the adsorption of lead on St-DVB beads occurs via a spontaneous process. The increase in the numerical value of $-\Delta G$ with the rise in temperature indicates that the sorption process of lead ions on St-DVB beads is more favorable at higher temperatures. The negative value of enthalpy change (ΔH) confirms the exothermic adsorption of lead on St-DVB beads. The positive value of ΔS suggests the increased randomness at the solid-solution interface during the adsorption of lead ions on St-DVB beads, thus suggesting that lead ions replace some hydrogen ions in aqueous solution previously adsorbed on the surface of adsorbent.

Effect of Foreign Ions

The presence of other cations and anions in the adsorptive medium may change the environment and solution chemistry of the metal of interest,

Table 2. Thermodynamic parameters for adsorption of lead ions on St-DVB beads

Temperature (K)	ΔG (kJ · mol^{-1})	ΔH (kJ · mol^{-1})	ΔS (JK^{-1} · mol^{-1})
283	−3.066	−1.586	16.438
293	−3.238		16.464
302	−3.387		16.467
313	−3.560		16.441
323	−3.738		16.483
333	−3.884		16.426

which effects the adsorption efficiency of an adsorbent. Therefore, using the optimized parameters, the adsorption of 4.83×10^{-5} mol L^{-1} of lead ions on St-DVB beads was also studied in the presence of high concentrations of various cations and anions. The results are shown in Table 3. All the anions were used as their sodium salts, whereas for cations the nitrate salts were used. The perusal of the data shows that the adsorption of lead on St-DVB beads was almost quantitative in the presence of all the ions studied. The adsorption of lead ions on St-DVB beads was significantly affected by 53 and 91% in presence of iron and calcium ions respectively. This decrease in the adsorption of lead ions could probably be due to the utilization of the adsorption sites on the surface of St-DVB beads by cations used.

Application of the Procedure

In order to check the applicability of the developed procedure on some real samples, the uptake of lead ions from two battery wastewater samples on

Table 3. Effect of foreign ions on the adsorption of lead ions on St-DVB beads

Ions	Concentration of foreign ions (mol · L^{-1})	K_d	Adsorption (%)
None	—	2.21×10^4	99.7
NO_3^-	8.064×10^{-3}	4.10×10^3	98.4
ClO_4^-	5.028×10^{-3}	2.83×10^3	97.7
SO_4^{2-}	5.205×10^{-3}	2.71×10^3	97.6
Cl^-	1.410×10^{-4}	5.06×10^3	98.7
Br^-	6.257×10^{-3}	2.50×10^3	97.4
CO_3^{2-}	8.332×10^{-3}	9.59×10^2	93.5
CH_3COO^-	8.468×10^{-3}	6.60×10^3	99.0
NO_2^-	1.087×10^{-4}	3.85×10^3	98.3
Cit.	2.644×10^{-3}	4.70×10^3	98.6
EDTA	1.723×10^{-3}	4.70×10^3	98.6
Na^+	2.175×10^{-4}	4.10×10^3	98.4
K^+	1.279×10^{-4}	3.44×10^3	98.1
Ca^{2+}	1.248×10^{-4}	6.00×10^0	08.7
Mg^{2+}	2.057×10^{-4}	1.03×10^3	93.9
Fe^{3+}	8.953×10^{-3}	6.00×10^1	47.4
Cd^{2+}	4.448×10^{-3}	1.95×10^3	96.7
Cr^{3+}	9.616×10^{-3}	1.35×10^3	95.3
Cu^{2+}	7.868×10^{-3}	1.64×10^3	96.1
Co^{2+}	8.484×10^{-3}	6.00×10^2	90.0
Mn^{2+}	9.101×10^{-3}	1.19×10^3	94.7
Ni^{2+}	8.518×10^{-3}	1.32×10^3	95.2

St-DVB beads has also been studied by using the optimized sorption conditions. The results are reported in Table 4 along with the determined composition of the samples, which shows that an average of 95.7% of lead can be removed from such samples under the existing concentrations of the determined cations and anions. It is, therefore, concluded that St-DVB beads have good potential as a decontaminant for lead ions from aqueous media.

Regeneration of the Beads

To be use in metal ion recycling process, metal ions adsorbed should be easily desorbed under suitable conditions. The desorption of the adsorbed lead ions from St-DVB beads was also studied in a batch experimental setup. The loaded St-DVB beads were shaken for 7.5 minutes in the desorption medium i.e., 30mL of 1.0 mol L^{-1} of the nitric acid solution. The desorbed amount of lead was quantified by atomic absorption spectrometry. The regenerated beads were reused for the adsorption of lead. Figure 10, shows the adsorption-desorption values of lead ions by St-DVB beads after several

Table 4. Determined composition of battery water samples

	Concentration (mg L^{-1})	
Ions	B1	B2
Ca	26.20	38.20
Mg	15.30	33.69
Na	85.60	156.30
K	5.80	8.37
Fe	0.22	0.31
Mn	0.02	0.05
Zn	0.18	0.21
Cu	0.01	0.02
Cd[a]	10.00	8.30
CO_3^{-2}	0.96	4.00
HCO_3^{-2}	140.00	112.0
Cl^-	11.00	19.6
SO_4^{-2}	18.00	14.00
Pb	13.42	8.70
Pb[b]	0.52	0.41

[a] μg L^{-1}.

[b] Concentration after decontamination on St-DVB beads.

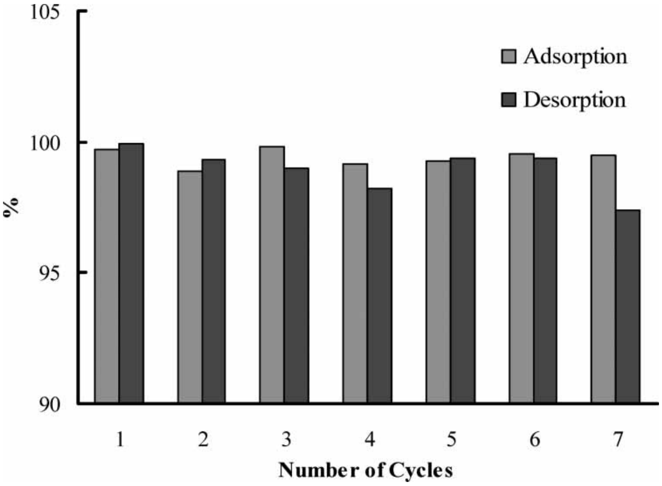

Figure 10. Adsorption-desorption efficiency of lead ions on St-DVB beads.

consecutive adsorption cycles, which shows clearly that St-DVB beads can be used repeatedly without loosing their exchange capacity ($\geq$98%) even after seven cycles.

CONCLUSIONS

Quantitative adsorption of lead ions from aqueous solutions on St-DVB beads can be achieved within a short contact time of two minutes without any prior chemical treatment or time consuming adjustments. The reaction was found to be exothermic and occurs in the presence of a variety of anions and cations, with maximum adsorption noted in the presence of 0.001 mol L^{-1} of nitric, hydrochloric, sulphuric and perchloric acid solutions. The adsorption data obeyed the Freundlich, Langmuir, and Dubinin-Radushkevich isotherms. The data will be useful in understanding the sorption mechanism of lead on St-DVB beads. This study also concludes that the St-DVB beads have great potential to be utilized for the removal of lead from aqueous solutions with good recyclability.

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