



Characterizations of Co (II) and Pb (II) removal process from aqueous solutions using expanded perlite

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ABSTRACT

In this study, the adsorption of cobalt and lead ions from aqueous solutions by expanded perlite (EP) has been investigated. The effects of several parameters such as pH, adsorbent dosage, and contact time on adsorption process have been investigated. The results of experiments showed that adsorption of both metal ions increased by increasing pH values up to 6.5. Adsorption process was initially fast. The adsorption rate decreased then until reached to equilibrium concentration at 150 and 90 min for cobalt and lead ions, respectively. About 46 and 99% of cobalt and lead were adsorbed onto expanded perlite at equilibrium conditions. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption models were used to determine the isotherm parameters associated with the adsorption process. Maximum adsorption capacities of cobalt and lead were 1.05 and 6.27 mg/g, respectively. Thermodynamic parameters for both sorption systems were determined at four different temperatures. The negative values of Gibbs free energy change indicated the spontaneous nature of adsorption process.

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1. Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. The presence of heavy metal in streams, lakes, and groundwater reservoirs has been responsible for several health problems with plants, animals, and human being.

Studies proved that metals such as copper, lead, zinc, cobalt, nickel, chromium, and mercury which have been considered as hazardous heavy metals are very toxic elements and they are commonly found in water and wastewater. So, the removal of these metals from wastewater is necessary.

A number of processes exist for the removal of metal pollutions from wastewater, viz. precipitation, electroplating, ion-exchange, solvent extraction, and membrane separation. These processes have several disadvantages such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge/waste products that require disposal and further treatment. This led to the need to develop an effective, low-cost, and environment friendly

process for wastewater treatment. Adsorption is an efficient and economical process used for the removal of heavy metals from industrial wastewater.

A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. The review concluded that these low-cost processes involved the use of activated carbon and ion-changers. The cost of these biomaterials and mineral materials are negligible compared with the cost of activated carbon or ion-exchange resins. The removal of heavy metals from industrial wastewater is considered an important application of adsorption processes using suitable adsorbent [1,2].

Lead is harmful to humans, plants and animals. Lead poisoning can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects and language difficulties. Lead pollution occurs through the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields, caulking and bearings [3].

Lead ions concentrations approach 200–500 mg/L in the industrial wastewaters. This value is very high in relation to the water quality standards and it should be reduced to a range of 0.1–0.05 mg/L [3].

Cobalt containing compounds are widely used in many industrial applications such as mining, metallurgical, paints, pigment, and electronics [4]. Cobalt is also present in the wastewater of nuclear power plants. The permissible limits of cobalt in the irrigation water and livestock wastewater are 0.05 and 1.0 mg/L, respectively

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(Environmental Bureau of Investigation, Canadian Water Quality Guidelines) [5]. The acute cobalt poisoning in humans may cause serious health effects e.g. asthma like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Cobalt may cause mutations (genetic changes) in living cells. Exposure to ionizing radiation is associated with an increased risk of developing cancer [5].

Perlite is a naturally occurring dense glassy volcanic rhyolitic rock and can be expanded up to 20 times its original volume when heated rapidly at 800–1200 °C [6]. Expanded perlite (EP) acts as an excellent insulator, both thermal and acoustical, resists fire and is classified as an ultra-light weight material. The expanded perlite is white in color, and has a density of about 32 kg/m³. Perlite is generally chemically inert and has a pH of approximately 7. Perlite is very cheap and easily available in Iranian markets. The cost of expanded perlite is less than US\$ 0.2 per kg in Iran. This could make it a viable candidate as an economical adsorbent for removing heavy metals such as lead, copper, cadmium and chromium [7–9].

In our previous studies [10,11], the adsorption characteristics of Cd, Ni, Ag, Cu, and Hg onto expanded perlite were investigated. In the present work, the adsorption behavior of expanded perlite (EP) in the removal of Pb (II) and Co (II) ions from aqueous solutions has been investigated.

2. Experiments

2.1. Adsorbent characterization

Expanded perlite samples were obtained from KanehAzar Co. (Tabriz, Iran). The expanded perlite was used without any chemical treatment for the sorption reported here. The chemical composition of the perlite which was determined by XRF is given in Table 1. It is mainly composed of silica as SiO₂ (79.6%), aluminum as Al₂O₃ (11.5%), and potassium as K₂O (4.8%). The specific surface area of expanded perlite is 1.89 m²/g. It was measured by BET-N₂ adsorption.

In the surface hydroxyl groups, the silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. The different types of silanol groups and alumina's hydrous oxide surface groups in EP are shown in Fig. 1 [12,13]. These groups give the adsorption property to perlite.

2.2. Experimental studies

Solutions containing 1000 mg/L of Pb (II) and Co (II) were prepared using analytical grade Pb(NO₃)₂ and Co(NO₃)₂ salts, respectively. All other solutions were diluted from these stock solutions.

Several experiments were carried out to identify the optimum values of pH, contact time and adsorbent dosage. The initial solution pH values were adjusted at 2, 3, 4, 5, 6.5 and 8 using 0.1 M NaOH or HNO₃ solution. The effect of adsorbent dosage on removal of metal

Table 1
Chemical composition of expanded perlite.

Constituent	Percentage (wt.%)
SiO ₂	79.6
Al ₂ O ₃	11.5
K ₂ O	4.8
CaO	0.8
Fe ₂ O ₃	0.8
Na ₂ O	0.5
MgO	0.5
SO ₃	0.2
TiO ₂	0.1
MnO ₂	0.065

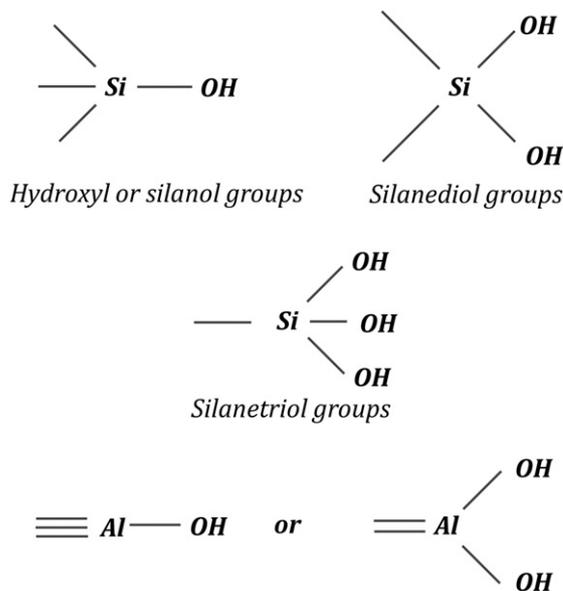


Fig. 1. The types of silanol groups and alumina's hydrous oxide surface groups in EP.

ions from solutions was studied by using 5 mg/L as an initial solution in conjunction with 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18 g/L of EP. At an optimum dosage, other experiments were done. Samples were collected at 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 240 and 360 min to determine the optimum value of shaking time. Isotherm studies were carried out at 5, 10, 20, 30, 40 and 50 mg/L as initial solution concentrations and optimum EP dosage and adsorption time. Other adsorptions experiments were also conducted at 20, 30, 40, and 50 °C to determine the effect of temperature on the adsorption process and to evaluate the adsorption thermodynamic parameters.

Experiments were carried out at a 250 mL conical flask filled with 100 mL of test solution. Necessary amount of adsorbent material was added. The flask was then shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 110 rpm. The contents of flasks were filtered through a filter paper. The filtrate was analyzed for metal concentration using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The adsorption percentage of metal ions was calculated as follows:

$$\text{Adsorption}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively.

The amount of metal ions adsorbed per unit mass of adsorbent (q_e) was calculated using the following equation:

$$q_e = \frac{V}{M} (C_i - C_e) \quad (2)$$

The average absolute value of relative error, AARE, was used to compare the predicted results with experimental data. This is defined as follows:

$$\text{AARE} = \frac{1}{NDP} \sum_{i=1}^{NDP} \frac{|\text{Predicted Value} - \text{Experimental Value}|}{\text{Experimental Value}} \times 100 \quad (3)$$

in which NDP is the number of data points.

3. Results and discussion

3.1. Effect of pH

The pH of solution has an important role in metal ions adsorption. This is partly because hydrogen ions themselves are strongly competing with metal ions [9]. Surfaces possessing highly charged groups in aqueous solvents are especially sensitive to environmental conditions such as pH. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive or less negative [14,15].

Doğan and Alkan [16] emphasized that the negative surface charge of perlite samples increased with an increase in pH. Electro-kinetic studies have also shown that the perlite samples have no iso-electric point and have negative zeta potential and surface charge [16]. The variation of surface charge density of perlite samples with increasing pH can be result of the ionization of surface silanol groups [17]. With increasing adsorption density hydrogen ions pass from surface to solution, and thus change the pH of the bulk solution [15]. The process can be written as follows, e.g. for Pb:

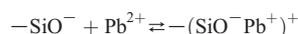
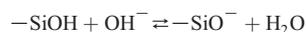


Fig. 2 demonstrates the dependency of adsorption percentage of cobalt and lead ions on initial pH of solution. The adsorption of metal ions increased significantly as pH increased and adsorption reached its maximum at pH equal to 6.5. More increase in pH values leads to metal precipitation and metal accumulation on EP surface deteriorated the adsorption mechanism. Therefore, kinetic studies above pH 8 were not attempted due to the precipitation of metal ions as hydroxides.

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Co and Pb ions is shown in Fig. 3. These data have been obtained at initial metal concentration, pH and temperature equal to 5 mg/L, 6.5 and 20 °C, respectively. This figure illustrates that adsorbent dosage has an important role in adsorption process. Increasing adsorbent dosage has increased Co (II) and Pb (II) adsorption to more than 42 and 92%, respectively.

The increase in the removal efficiency may be attributed to the fact that with an increase in the adsorbent dosage, more adsorbent surface will be available for the solute adsorbed [18]. The adsorption percentages of Co (II) and Pb (II) reached their maximum values at 16.0 and 10.0 g/L adsorbent dosage, respectively.

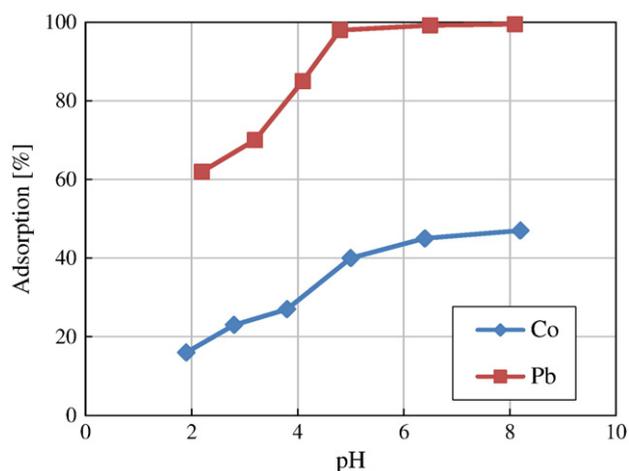


Fig. 2. Effect of pH on the adsorption of Co and Pb onto EP.

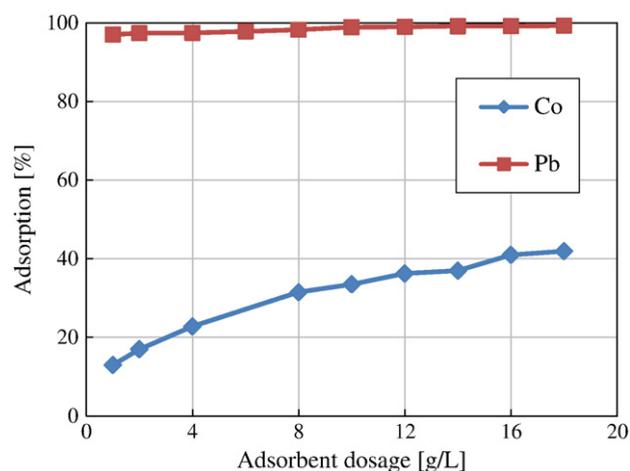


Fig. 3. Effect of adsorbent dosage on the adsorption of Co (II) and Pb (II) ions onto EP.

Fig. 4 shows that the capacity of cobalt and lead sorption increased with decreasing quantity of EP introduced. This is in agreement with those reported in the literature [19,20]. This is due to the fact that a higher amount of metal contact per unit weight of expanded perlite was available in smaller amount of EP. In other words, a shortage of metal concentration takes place at a higher adsorbent dosage.

3.3. Effect of contact time and adsorption kinetics

Fig. 5 illustrates the adsorption percentage of Co (II) and Pb (II) metal ions as a function of contact time. As shown in Fig. 5, the adsorption is so fast at initial contact time. At first 5 min of contact time the concentration of cobalt and lead ions in aqueous solution reached 81.8 and 95.7% of their equilibrium concentration, respectively. The adsorption of these metal ions increased slightly when contact time increased and reached a maximum. The adsorption of Co and Pb onto EP approached their equilibrium value at 150 and 90 min, respectively.

Lagergren first-order and Ho et al.'s pseudo-second-order rate equations were used to describe the kinetics of these metal ions adsorption onto EP. The first-order Lagergren rate equation used by researchers to study the kinetics of heavy metal adsorption is as follows [9,12]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

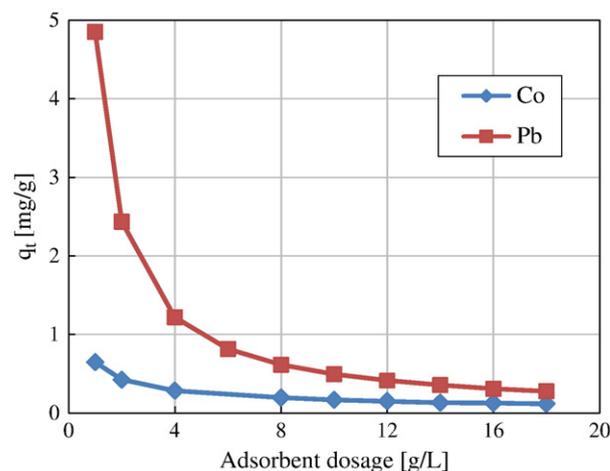


Fig. 4. Effect of adsorbent dosage on the adsorption of Co (II) and Pb (II) ions onto EP.

The empirical Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model in linear form is given as follows [14]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

Where K_f is related to the adsorption capacity and $1/n$ is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of material.

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. Dubinin–Radushkevich (D–R) isotherm is commonly used to describe the sorption isotherms of single solute systems [25]. The D–R isotherm, apart from being an analogue of the Langmuir isotherm, is more general than the Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential [3,25]. The D–R isotherm is expressed as:

$$q_e = q_{mt} \cdot e^{-\beta \varepsilon^2} \tag{9}$$

Where ε (Polanyi Potential) is equal to Eq. (10). The constant β gives the mean free energy, E , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using Eq. (11):

$$\varepsilon = RT \cdot \ln \left(1 + \frac{MW}{C_e} \right) \tag{10}$$

$$E = \frac{1}{\sqrt{2\beta}} \tag{11}$$

These three correlations fitted in their non-linear form on experimental data. Correlation coefficients, r^2 and AARE% are reported in Table 3. Figs. 8 and 9 show the comparison of experimental data with the q_e values obtained by applying Eqs. (7–9). From r^2 and AARE% values in Table 3, it is clear that the Langmuir model predicts experimental data as well as D–R isotherm model.

The shape of the isotherm may also be considered to predict if an adsorption system is “favorable” or “unfavorable”. The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or an equilibrium parameter R , which is defined by the following equation [3,7]:

$$R = \frac{1}{1 + K_L C_e} \tag{12}$$

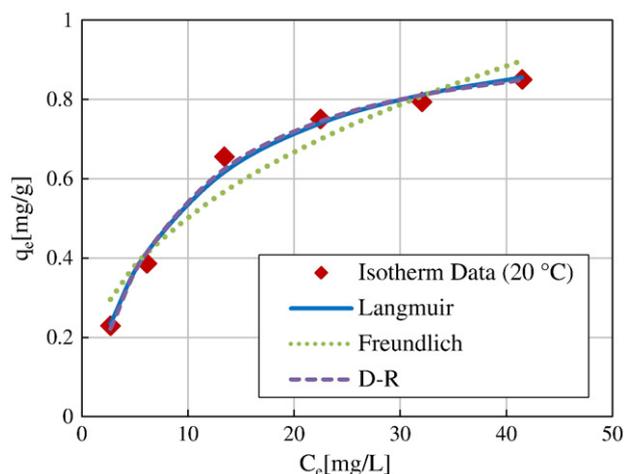


Fig. 8. Isotherms models of Co ion adsorption onto EP.

According to the value of R , the isotherm shape may be interpreted as follows:

- $R > 1$: Unfavorable adsorption
- $R = 1$: Linear adsorption
- $0 < R < 1$: Favorable adsorption
- $R = 0$: Irreversible adsorption

The values of R for cobalt and lead have been calculated as 0.18–0.77 and 0.26–0.95, respectively. Hence, the adsorption of Co (II) and Pb (II) ions onto EP is favorable.

The results of D–R isotherm model obtained at four different operating temperatures can be expressed in a single equation. The average values of q_{mt} and β parameters at the range of 20–50 °C are listed in Table 4. The values of AARE% obtained by using these values for cobalt and lead ions are 6.2 and 11.4%, respectively.

A comprehensive coverage of different adsorbents under different environmental conditions can be found in the format of several publications. It may be seen that q_m values differ widely for different adsorbents. From Table 5 it can be concluded that EP exhibits moderate adsorption capacity toward Pb (II) and Co (II) ions. The fresh adsorbent price and the cost of regeneration/disposal of adsorbent are important issues must be considered when selecting an adsorbent. For example, commercial activated carbon cost about US\$ 4000–6000 per tonne in Iran, yet EP cost less than US\$ 200 per tonne. Having low price, expanded perlite may be a good candidate for a practical process. However, a

Table 3 Isotherm models for the adsorption of Co and Pb onto EP.

	20 °C				30 °C				40 °C				50 °C			
	q_m	K_L	R^2	AARE%												
Langmuir isotherm model																
Co	1.050	0.1059	0.991	3.3	1.007	0.1004	0.988	3.5	0.9493	0.09253	0.994	3.0	0.8986	0.08431	0.996	2.3
Pb	6.269	0.9381	0.997	7.5	5.986	0.7964	0.995	5.1	5.925	0.5887	0.999	1.6	5.818	0.507	0.999	1.2
Freundlich isotherm model																
	$1/n$	K_f	R^2	AARE%												
Co	0.4073	0.1968	0.942	10.6	0.4120	0.1830	0.938	10.8	0.4248	0.1613	0.949	10.0	0.4399	0.1410	0.958	9.1
Pb	0.5005	2.777	0.984	12.0	0.4828	2.409	0.950	23.3	0.5056	2.047	0.979	17.0	0.5035	1.868	0.971	19.2
Dubinin–Radushkevich isotherm model																
	q_{mt}	β	R^2	AARE%												
Co	0.9544	2.53E–8	0.993	3.0	0.9101	2.44E–8	0.991	4.0	0.8475	2.40E–8	0.996	2.6	0.7905	2.37E–8	0.998	1.54
Pb	11.41	8.13E–9	0.995	6.9	9.257	7.11E–9	0.974	17.6	10.07	8.11E–9	0.994	5.7	9.014	7.45E–9	0.992	9.7

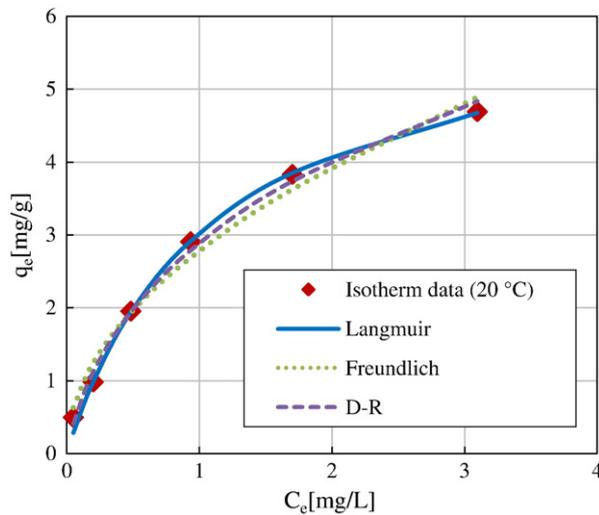


Fig. 9. Isotherms models of Pb ion adsorption onto EP.

detailed economic analysis is required to determine the most economical adsorbent.

3.5. Adsorption thermodynamics

In engineering practice entropy and Gibbs free energy factors should be considered in order to determine what process will occur spontaneously. Thermodynamic parameters such as enthalpy change (ΔH°), Gibbs free energy (ΔG°) and entropy change (ΔS°) can be estimated by using equilibrium constant changing with temperature. The values of standard Gibbs free energy change for the adsorption process were evaluated by using K_L values obtained from the Langmuir model at different temperatures.

The equilibrium constant may be expressed in terms of enthalpy change of adsorption and temperature as follows [44]:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13-a)$$

or

$$\frac{\partial \ln K_L}{\partial T} = \frac{\Delta H^\circ}{RT^2} \quad (13-b)$$

According to Eq. (13-a), (ΔH°) and (ΔS°) parameters can be individually calculated from the slope and intercept of the plot of $\ln K_L$ versus $1/T$ (Fig. 10). Gibbs free energy (ΔG°) may be written in terms of entropy and enthalpy:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

The ΔH° for the adsorption of Co (II) and Pb (II) ions are equal to -6.0 and -16.9 kJ/mol, respectively. These negative values indicate the exothermic nature of the adsorption of all metal ions onto EP in temperature range of $20-50$ °C. The values of ΔS° are found

Table 4
D-R isotherm model parameters in the range of $20-50$ °C.

		Co (II)	Pb (II)
q_{mt}	(mg/g)	0.8756	9.938
β	(mol ² /J ²)	2.435E-08	7.699E-09
E	(kJ/mol)	4.531	8.059
AARE%		6.2	11.4

Table 5
Comparison of adsorption potential of various adsorbents for cobalt and lead removal from aqueous solutions.

Adsorbent	Co (II)	Pb(II)	Reference
Attapulgit	0.16		[26]
Kaolinite	0.92	–	[27]
Alginate–chitosan hybrid gel	3.2	–	[28]
Activated carbon	13.9	–	[29]
Natural zeolites	14.4	–	[30]
Bentonite	22.0	–	[31]
Lemon peel	22.0	–	[32]
MF-bentonite	34.3	–	[31]
Natural vermiculite	49.5	–	[33]
Lichen	–	1.0	[34]
Waste tea leaves	–	2.1	[35]
Sawdust	–	3.2	[36]
Modified peanut husk	–	4.7	[37]
Ulmus carpinifolia	–	4.8	[38]
Olive stone	–	5.9	[39]
Siderite	–	10.3	[40]
Expanded perlite	–	13.4	[9]
Activated carbon (Merck)	–	21.5	[41]
Zeolite	–	70.6	[42]
Valonia tannin resin	–	138.3	[43]
HQ–bentonite	–	139.1	[3]
Expanded perlite	1.05	6.27	This study

to be 52.3 and 43.7 J/mol K for the adsorption of Co (II) and Pb (II), respectively.

The values of Gibbs free energy (ΔG°) can be calculated directly from Eq. (14). It was found as -21.3 , -22.2 , -22.4 , and -22.9 kJ/mol for the adsorption of cobalt and -29.7 , -30.3 , -30.5 , and -31.0 kJ/mol for the adsorption of lead ions. The negative ΔG° values indicate that adsorption of Co (II) and Pb (II) are thermodynamically feasible and naturally spontaneous at $20-50$ °C.

4. Conclusions

The adsorption behavior of cobalt (II) and lead (II) onto expanded perlite was investigated in the batch experiments. The adsorption was found to be drastically dependent on pH, adsorbent dosage, and contact time. The optimum pH for the adsorption of both metal ions was found to be 6.5. The rate of adsorption of these metal ions was rapid. The cobalt–perlite and lead–perlite systems attained equilibrium in 150 and 90 min, respectively. Isotherm analysis of the data showed that the adsorption pattern of both metal ions onto EP followed the Langmuir model as well as Dubinin–Radushkevich (D–R) isotherm model. Using the Langmuir model equation, the maximum capacity of EP was found to be 1.05 and 6.27 mg/g for Co (II) and Pb

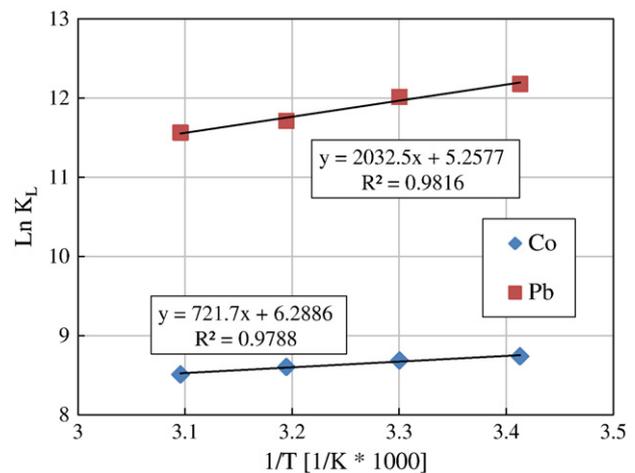


Fig. 10. $\ln K_L$ vs. $1/T$ for estimation of ΔH° and ΔS° .

