



The removal of some rare earth elements from their aqueous solutions on by-pass cement dust (BCD)

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ABSTRACT

The sorption behavior of yttrium (Y^{3+}), neodymium (Nd^{3+}), gadolinium (Gd^{3+}), samarium (Sm^{3+}) and lutetium (Lu^{3+}) from their aqueous solutions by by-pass cement dust (BCD) has been investigated using a batch technique. The sorption on BCD was studied as a function of pH, shaking time, initial concentration, mass of BCD and temperature. It was found that the sorption capacity of BCD had the order of $Lu^{3+} > Sm^{3+} > Y^{3+} > Gd^{3+} \approx Nd^{3+}$ following Freundlich isotherm at the determined optimum conditions. The results also demonstrated that the sorption data fit well the pseudo-second-order kinetic model. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° indicated that the sorption of the investigated REEs on BCD was endothermic, favored at high temperature and spontaneous in nature.

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1. Introduction

Recently, more and more rare earth elements (REEs) enter the environment through various pathways as a result of rapid increase of the utilization of REE resources and their applications in many fields of modern industry and daily life [1–3]. Rare earth elements are used as petrogenetic tracers in internal geodynamic studies of the earth [4]. Moreover, millions of tons of fertilizers containing REEs are also used worldwide for increasing agricultural productivity [5]. The increased demand for REEs means increased public exposure to the REEs both from various commercial products and from production wastes/effluents. In regions with high levels of REEs, elevated levels of REEs are found in human [6] and other organisms [7]. REEs are entering the human body due to exposure to various industrial processes can affect metabolic processes. Trivalent ions, especially La(III) and Gd(III) can interfere with calcium channels in human and animal cells. They can also alter or even inhibit the action of various enzymes and when they found in neurons can regulate synaptic transmission, as well as block some receptors (for example, glutamate receptors) [8].

Numerous techniques are available for the separation and recovery of REEs such as chemical precipitation, ion exchange, solvent extraction and adsorption [9–12]. Adsorption represents the most

efficient and widely applied technique. During the last decade, research efforts have been directed towards using low cost alternative techniques or development of low cost sorbents applicable for the removal and separation of undesirable metal ions from an aqueous phase [13–15]. A variety of low cost sorbents such as fly ash [16], rice husk [17], peat [18], peat moss [19], red mud [20], teawaste [21], olive stones [22], date bits [23] have been tried. Recently, research efforts have been directed towards the use of wastes as sorbent materials in an attempt to minimize the processing costs and to protect the environment and public health [24].

By-pass cement dust (BCD) is the by-product of the manufacture of Portland cement. It is a fine grained material that is generated during the calcination process in the kiln. CaO is the major constituents of BCD composition. Other constituents include SiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , Na_2O , Cl, etc. Most of cement companies generate high quantities of BCD every year [25]. Potential effectiveness of BCD as a low cost sorbent for some pollutants has been demonstrated. For instance, BCD was used for removal; some heavy metals from textile industrial effluents [26], Cu(II), Ni(II), Zn(II), Fe(III), Co(III), U(VI) and Th(IV) from aqueous solutions [27–29], Cr(III) from tanning wastewater effluents [30] and in wastewater treatment [31].

Therefore, the objective of this research is to investigate the influence of various experimental parameters on sorption of some rare earth elements (including yttrium, neodymium, gadolinium, samarium, and lutetium) on BCD as an effective and low cost sorbent material in aqueous solutions. Moreover, the kinetics, isotherms and thermodynamics characteristics of the sorption

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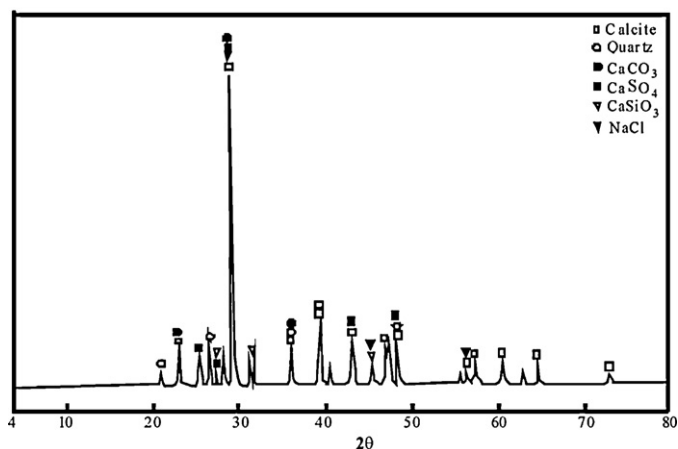


Fig. 1. X-ray diffraction of by-pass cement dust.

process of the investigated elements from their aqueous solutions on BCD will be discussed.

2. Experimental

2.1. Materials

2.1.1. By-pass cement dust (BCD)

By-pass cement dust (BCD) was brought from National Cement Co., Egypt. The received BCD was placed in a glass container which in turn was kept in a desiccator all the time of the experiments. BCD chemical composition (Table 1) was identified using X-ray fluorescence (PANalytical Axios advanced, The Netherlands). The constituents' phases of BCD were identified by X-Ray diffraction analysis (XRD brucker axs D8 advance, Germany) with $\text{CuK}\alpha$ radiation (1.5406 \AA) with a typical scanning begin at 2θ equal to $20\text{--}80^\circ$ and scan rate of 20 min^{-1} . X-Ray diffraction pattern of BCD is shown in Fig. 1. It indicates that BCD mainly consists of calcite, calcium sulfate, mono calcium silicates, calcium carbonate, quartz and sodium chloride (where $\text{CaCO}_3 = 38.34\%$, $\text{NaCl} = 3.77\%$, $\text{KCl} = 5.54\%$, $\text{CaSO}_4 = 4.93\%$, $\text{SiO}_2 \text{ free} = 7.08\%$, $\text{CaSiO}_3 = 5\%$, $\text{CaO free} = 12.20\%$). The cation exchange capacity (CEC) of BCD was determined using ammonium acetate saturation method [32] and it was 6.53 meq/g .

2.1.2. Reagents

Standard individual REE solutions (1000 mg/L) for Y(III), Nd(III), Gd(III), Sm(III) and Lu(III) were prepared from the corresponding oxides (Aldrich Co., Germany) by dissolving 0.254, 0.162, 0.231, 0.116 and 0.26 g, respectively in 10 mL of perchloric acid. The solutions were heated till complete evaporation and another 5 mL of perchloric acid was added, then the solutions were diluted to volume with 0.1 N perchloric acid. Arsenazo (III) was obtained from Aldrich Co, Germany. All other reagents used were analytical reagent grade. In all experiments, doubled distilled water was utilised for preparation and dilution of solutions.

2.2. Sorption experiments

The sorption experiments were studied by a batch technique. In the experiments, BCD was separately shaken with each REE solution at various experimental conditions. Separating of solid phase from liquid was done by centrifuging at 4000 rpm for 15 min. The pH of the solutions was maintained by thiel buffer [33] in the range (2–7). After equilibration, the REEs' concentrations were determined spectrophotometrically employing Shimadzu UV–Vis160A Spectrophotometer using Arsenazo III (0.05%, w/v) as a

complexing agent at 655 nm against reagent blank [34]. Uptake percentage (%E) and distribution constant K_D (mL/g) were calculated from the equations:

$$\%E = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$K_D \text{ (mL/g)} = \left(\frac{C_o - C_e}{C_e} \right) \frac{V}{m} \quad (2)$$

where C_o and C_e are the initial and equilibrium REE concentration in the solution (mg/L), respectively. V is the volume of the aqueous solution (mL) contacted with BCD and m is the mass of BCD in grams.

2.3. Sorption kinetics

To examine the controlling mechanism of the sorption process, two kinetic models were used to test experimental data.

The Lagergren pseudo first-order equation is a simple kinetic analysis of sorption in the following form [35]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303} \right) \quad (3)$$

where q_e and q_t are the sorbed concentration of REE at equilibrium and at any time t , respectively and k_1 is the overall rate constant of first-order sorption. The slope of the plot of $\log(q_e - q_t)$ as a function of t can be used to determine the first-order rate constant k_1 . The activation energy of the sorption process can be determined using Arrhenius equation. It can be calculated from the slope of a plot of $\log k$ and $1/T$, since the slope equal to $(-E_a/2.303R)$.

In addition, the pseudo second-order equation based on sorption equilibrium capacity may be expressed in the following form [35]:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (4)$$

where k_2 is the rate constant of the second-order sorption. Eq. (4) can be rearranged to:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Similarly, the slope of the plot of t/q_t as a function of t was used to determine the second order rate constant k_2 that is used to determine the activation energy of the sorption process using Arrhenius equation.

2.4. Thermodynamic parameters

Determination of thermodynamic parameters were based on experiments that carried out by shaking 0.02 g BCD with solutions of each REE of concentration (100 mg/L) adjusted at $\text{pH } 7 \pm 0.1$ for 5 min at different temperatures. The thermodynamic parameters (ΔH° , ΔG° and ΔS°) were calculated from the sorption results.

3. Results and discussion

3.1. Sorption experiments

The parameters which may affect the uptake of REEs by pass cement dust, such as shaking time, temperature, pH, initial concentration of REE and sorbent mass were investigated. The results showed that the equilibrium reached to its maximum within 9 min of shaking, while uptake percentage only slightly increased on raising temperature up to 60°C . Therefore, the sorption experiments were carried out at room temperature for 9 min.

Table 1
Major chemical constituents of BCD.

Mass (%)	Constituents										
	CaO	SiO ₂	P ₂ O ₅	Na ₂ O	Fe ₂ O ₃	MgO	K ₂ O	Al ₂ O ₃	Cl ⁻	SO ₃	LOI
	44.24	10.54	6.35	2.00	1.92	1.45	3.5	4.7	4.93	2.9	17.47

Table 2
Variation of the K_D with the REEs' initial concentrations for their sorption on BCD.

[REE]	$K_D \times 10^4$				
	Y ³⁺	Nd ³⁺	Gd ³⁺	Sm ³⁺	Lu ³⁺
50	6.12	6.12	6.12	6.12	6.12
100	0.61	0.68	6.12	6.12	0.74
200	0.08	0.06	6.12	6.12	0.11
300	0.03	0.04	6.12	6.12	0.05
400	0.02	0.02	0.07	0.92	0.03
500	0.02	0.02	0.03	0.28	0.03

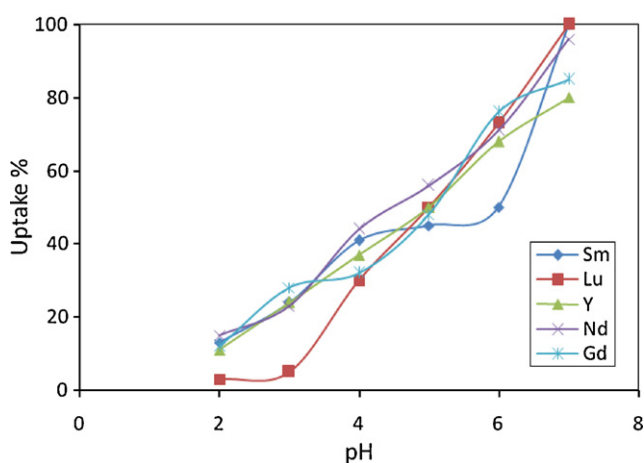


Fig. 2. Variation of the uptake percentage with pH for REEs sorption on BCD. Operating conditions: 50 mL solution, [REE]=100 mg/L, 0.02 g BCD, and shaking time =9 min.

3.1.1. Effect of pH

Fig. 2 shows the influence of pH on the sorption of the investigated REEs. The data reveals that the percentage of sorption steeply increases with increasing pH up to 7 ± 0.1 . Consequently, in the subsequent work, the sorption experiments were carried out at pH 7.

Generally, below pH 2 dissolution of BCD was occurred. Above pH 7 the formation of a precipitate was observed. Low REEs uptake at low pH values is most probably due to the protonation of the active sites in BCD, which inhibits their binding ability towards the REEs [36]. In addition, as pH increases, surface positive charge decreases, this would result in lower columbic repulsion of the adsorbed REE ions [37]. In aqueous solution, the hydrolysis of trivalent lanthanides begins at pH as low as 6 and various species can be formed, such as $\text{Ln}(\text{OH})_2^{2+}$, $\text{Ln}(\text{OH})_2^+$, $\text{Ln}(\text{OH})_3$, $\text{Ln}(\text{OH})_4^-$ [38]. Thus, as pH increases, hydrolysis precipitation most probably would start due to the formation of various hydrocomplexes in aqueous solution.

The observed reduction in the percentage of REE uptake on BCD at low pH by the sorbent indicates that the interaction between them is most probably due to an ion exchange process [39].

3.1.2. Effect of initial concentration of REE

The sorption of each REE as a function of their initial concentrations was studied at room temperature by varying the REE initial concentration from 50 to 500 mg/L. Table 2 shows the calculated

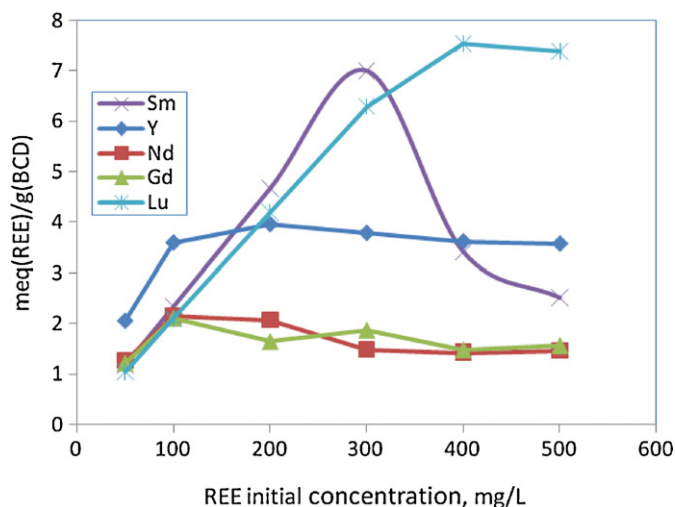


Fig. 3. Variation of the meq(REE)/g BCD with the REEs' initial concentrations for their sorption on BCD. Operating conditions: 50 mL solution, 0.04 g BCD, pH=7, and shaking time =9 min.

distribution coefficients (K_D) at different REE initial concentrations. Over the studied range, the distribution coefficients vary by more than 6 orders of magnitude. The inverse correlation between REE initial concentration and distribution coefficient reflects the greater partitioning of REEs into the solid phase (up to 100 mg/L for Y³⁺, Nd³⁺, Gd³⁺ and 300 mg/L for Sm³⁺ and Lu³⁺). With increasing REEs concentration, the distribution coefficients stabilize, owing to saturation of the BCD surface.

These results indicate that energetically less favorable sites become involved with increasing REEs concentration in the aqueous solution.

Additionally, the results were expressed in terms of meq of REE sorbed per unit mass of BCD (Fig. 3) to investigate the difference in affinity of BCD towards each REE. It is obvious from this figure that the sorption capacity of BCD has the order of $\text{Lu}^{3+} > \text{Sm}^{3+} > \text{Y}^{3+} > \text{Gd}^{3+} \approx \text{Nd}^{3+}$. The amount of REE sorbed per unit mass of BCD increased with the initial REE concentration as expected. The plateau values for Lu³⁺, Y³⁺, Gd³⁺, and Nd³⁺ represent saturation of the active sites on BCD available for interaction. The decrease in Sm³⁺ sorption at high concentration may be due to the Sm³⁺ affinity to sorbate-sorbate interaction than sorbate-sorbent one. This is more or less in agreement with the sorption of Sm³⁺ by natural clinoptilolite-containing Tuff [40].

The data from Fig. 3 reveals that the sorption capacity of Sm³⁺ and Lu³⁺ was higher than CEC of BCD which reflects again that sorption mechanism of these elements is a mixed mechanism of ion exchange and hydrolysis precipitation as well.

3.1.3. Effect of sorbent mass

Effect of sorbent mass on the sorption process of the investigated REEs is represented in Fig. 4. The experimental results reveal that the sorption efficiency of REEs increases up to the optimum mass of 0.04 g BCD for Y³⁺, Gd³⁺, Nd³⁺ and 0.01 g for Sm³⁺ and Lu³⁺ beyond which the sorption efficiency does not change with the sorbent mass.

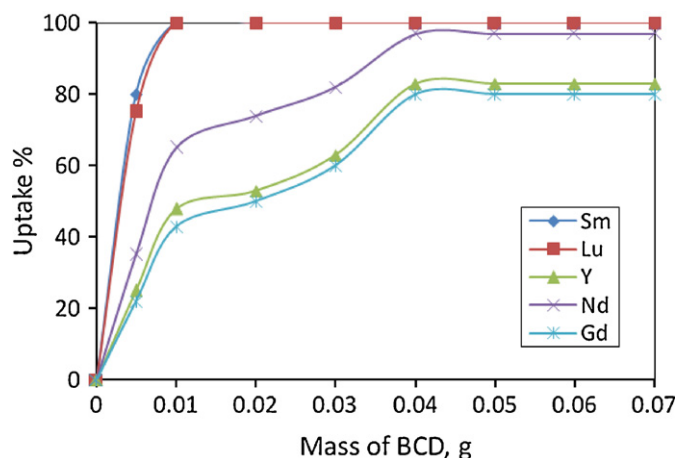


Fig. 4. Variation of the uptake percentage with the sorbent mass for REEs sorption on BCD. Operating conditions: 50 mL solution, [REE] = 100 mg/L, pH = 7, and shaking time = 9 min.

The increase in uptake percentage with increasing the BCD mass may be due to increasing number of sorbent particles in the solution that allows more REEs ions to interact with more binding sites.

3.2. Sorption kinetics

For simplicity, the kinetics experiments were carried out for Gd^{3+} and Sm^{3+} . The studies shows that the pseudo-first-order kinetic model did not fit the data for the sorption process since the values of correlation factor R^2 were small. Therefore, the pseudo-second-order kinetic model was applied. The calculated values of k_2 and E_a with the values of the linear correlation coefficients (R^2) are represented in Table 3. The values of correlation factor R^2 of the pseudo-second-order were better than those of pseudo-first-order model indicating second-order kinetics of the sorption process on BCD.

The natural logarithms of the rate constants (k) were used according to the Arrhenius equation to calculate the activation energy of sorption process. It was found that the activation energy was within the range of 0–40 kJ/mol, which means that the sorption process is a physical one [41].

3.3. Thermodynamic parameters

For better understanding the mechanism of the sorption process of REEs on BCD, thermodynamic parameters were determined. They were calculated using the equation:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where K_D is the distribution coefficient (mL/g), ΔS° is standard entropy (J/mol K), ΔH° is standard enthalpy (kJ/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol K). The standard Gibbs free energy ΔG° values (kJ/mol) were calculated from the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

The values of ΔH° , ΔS° and ΔG° were calculated from the slopes and intercepts of plots of $\ln K_D$ versus $1/T$. The values are presented in Table 4. The positive value of enthalpy change ΔH° for the process confirms the endothermic nature of the process, while the positive entropy of sorption ΔS° reflects the affinity of BCD towards these elements. The obtained values of ΔG° point to that the feasibility of the sorption process of the investigated elements on BCD and its spontaneous nature without an induction period.

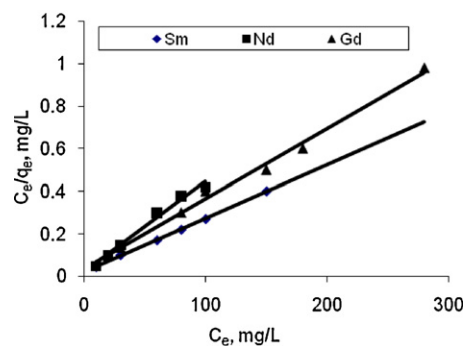


Fig. 5. Langmuir sorption isotherm of REEs sorption on BCD.

3.4. Sorption isotherms models

The sorption data of Sm^{3+} , Gd^{3+} and Nd^{3+} have been subjected to different sorption isotherms models namely Langmuir and Freundlich over a range of 100–300 mg/L for Nd^{3+} and 100–400 mg/L for Gd^{3+} and Sm^{3+} . The goodness-of-fit between experimental data and the model predicted values was expressed by the correlation coefficient (R^2 , values close or equal 1). When the value of R^2 is close to 1, it does not mean that the fit is necessarily good [42]. Therefore, the conformity between experimental data and the model predicted values was expressed by the total mean error ($\varepsilon\%$), which is the discrepancy between the experimental data and the predicted values [43]:

$$\varepsilon\% = \frac{\sum_{i=1}^n |q_{e(exper.)} - q_{e(calc.)}|}{\sum_{i=1}^n q_{e(exper.)}} \quad (8)$$

A relatively low ($\varepsilon\%$) value indicates which model can be successfully used to describe the sorption equilibrium on BCD.

3.4.1. Langmuir isotherm

The Langmuir isotherm was applied for the sorption equilibrium on BCD according to the equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ_e} + \frac{C_e}{Q_e} \quad (9)$$

where C_e is the equilibrium concentration of REE in solution (mg/L), q_e is the amount of solute sorbed per unit mass of BCD at equilibrium (mg/g) and Q_e (mg/g) and b (L/mg) are the Langmuir constants related to monolayer sorption capacity and free energy of sorption, respectively.

From Table 5, it can be concluded that Q_e parameter for Sm^{3+} was 8.32 meq/g, which was higher than the CEC of BCD. These data reflects again the mixed mechanism of sorption on BCD of ion exchange process and hydrolysis precipitation as well. According to the Langmuir model, sorption occurs uniformly on the active sites of the sorbent and once a sorbate occupies a site, no further sorption can take place at this site. A plot of C_e/q_e versus C_e would result in a straight line with a slope of $(1/Q_e)$ and intercept of $1/bQ_e$ as shown in Fig. 5. The values of the slopes, intercepts of the plots and total mean errors are presented in Table 5. The values of total mean error ($\varepsilon\%$) between this model and the experimental data for Sm^{3+} , Gd^{3+} and Nd^{3+} were 3.76, 1.38 and 6.31, respectively.

3.4.2. Freundlich isotherm

The simple Freundlich isotherm is often used for heterogeneous surface energy systems according to the equation:

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (12)$$

where q_e is the amount of solute sorbed per unit mass of BCD at equilibrium (mg/g) and C_e is the equilibrium concentration of REE

Table 3The calculated parameters of the pseudo-second order kinetics model for sorption of Gd³⁺ and Sm³⁺ on BCD at different temperatures.

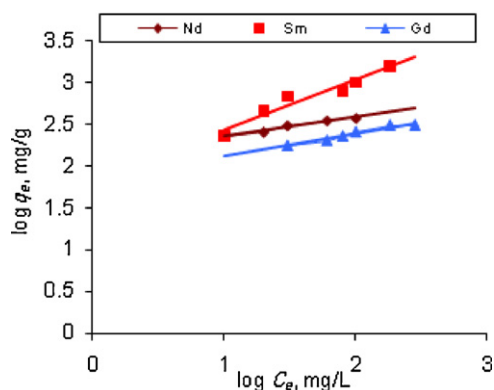
Temperature (K)	Gd ³⁺			Sm ³⁺		
	k_2 ($\times 10^{-3}$ g/mg min)	R^2	E_a (kJ/mol)	k_2 ($\times 10^{-3}$ g/mg min)	R^2	E_a (kJ/mol)
303	3.22	0.9927	27.96	10.23	0.9987	9.97
313	5.51	0.9843		11.31	0.9928	
323	7.04	0.9813		12.04	0.999	
333	8.99	0.9908		13.98	0.9941	

Table 4Thermodynamic parameters for sorption of Y³⁺, Nd³⁺, Gd³⁺, Sm³⁺ and Lu³⁺ on BCD.

REE	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)			
			303 K	313 K	323 K	333 K
Y ³⁺ , Gd ³⁺ , Nd ³⁺	50.72	0.250	-24.90	-27.03	-30.03	-32.53
Sm ³⁺ , Lu ³⁺	19.99	0.124	-17.60	-18.82	-20.06	-21.30

Table 5Isotherms constants and values of correlation factors (R^2) for sorption of Sm³⁺, Nd³⁺ and Gd³⁺ on BCD.

REE	Freundlich isotherm				Langmuir isotherm				
	1/n	log k	R^2	$\varepsilon\%$	Q_e (meq/g)	b	R^2	R_L	$\varepsilon\%$
Sm ³⁺	0.599	1.828	0.9388	2.83	8.32	0.123	0.9835	0.010	3.76
Nd ³⁺	0.220	2.130	0.9722	0.50	4.44	0.089	0.9892	0.0270	2.31
Gd ³⁺	0.260	1.860	0.9541	0.68	5.87	0.096	0.9945	0.075	1.38

**Fig. 6.** Freundlich sorption isotherm of REEs sorption on BCD.

in solution (mg/L). K and n are constants characteristics of the system. $\log k$ and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity of the sorbent, respectively. A plot of $\log q_e$ as a function of $\log C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\log k$ as shown in Fig. 6. The values of $1/n$, $\log k$ and $\varepsilon\%$ are presented in Table 5. The values of $1/n < 1$ correspond to a heterogeneous surface with an exponential distribution of energy of the sorption sites [44].

The total mean error ($\varepsilon\%$) between this model and the experimental data represents the best fit of experimental data than Langmuir one. The fit of the data to Freundlich isotherm indicates that the sorption process is not restricted to one specific class of sites and assumed surface heterogeneity [45]. This trend is due to the high surface area of the sorbent and multilayer of sorption on the BCD. This trend was also investigated by M. Al-Meshragi et al. [46] for sorption of Cr(III) on BCD.

4. Conclusions

- The efficiency of BCD for the sorption of Y³⁺, Nd³⁺, Gd³⁺, Sm³⁺ and Lu³⁺ from their aqueous solutions was investigated. It was

found that maximum sorption capacity was achieved at pH 7 using thiel buffer and the sorption capacity of BCD has the order of Lu³⁺ > Sm³⁺ > Y³⁺ > Gd³⁺ \approx Nd³⁺. The sorption of these elements on BCD was found to follow pseudo-second-order kinetics.

- The thermodynamic parameters ΔH° , ΔS° and ΔG° values of the REEs sorption onto BCD show endothermic heat of sorption, favored at high temperatures. The positive entropy value is an indication of the probability of favorable nature of sorption and the process is spontaneous.
- The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The Freundlich isotherm was demonstrated to provide the best correlation and the lowest total error for sorption of the studied elements on BCD.
- BCD may be successfully used as effective, low cost and abundant source for the removal of Y³⁺, Nd³⁺, Gd³⁺, Sm³⁺ and Lu³⁺ from their aqueous solutions and may be used as alternative to more costly materials.

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