

The Removal of Cadmium, Cobalt, and Nickel by Adsorption with Na-Y Zeolite

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ABSTRACT: *The article aims to study the removal of heavy metal ions Cd^{2+} , Co^{2+} and Ni^{2+} from aqueous solution using faujasite NaY. The adsorption studies were carried out in the single and binary component system. Sorption experiments were performed in batch at pH (5–6), adsorbent dosage (0.15 g), and initial concentration (0.1–10 mmol/L). The single-ion equilibrium adsorption data were fitted to three isotherm models: Langmuir, Freundlich, and Dubinin-Radushkevich. Results showed that the Langmuir isotherm fits sorption data better than the Freundlich equation. The maximum adsorption capacities (Q_{max}) were 0.81, 0.85 and 0.92 mmol/g for Cd^{2+} , Ni^{2+} and Co^{2+} ions, respectively. Besides, the study of the competitive sorption of ions in a binary system showed that faujasite NaY preferentially adsorbs cations in the following order: $Co^{2+} > Ni^{2+} > Cd^{2+}$. The obtained R_L (separation factor or Langmuir parameter) values were in the range of 0–1 indicating that Cd^{2+} , Co^{2+} and Ni^{2+} sorption were favorable. The obtained mean free energy value for adsorption of Co^{2+} and Ni^{2+} were in the range of 8–16 kJ/mol, indicating that ions were uptaken through an ion exchange process.*

KEYWORDS: *Faujasite NaY; Competitive adsorption; Heavy metals; Isotherm modeling.*

INTRODUCTION

What is evident is that aquatic environments need a deeper look as they are being menaced by industrial operations [1]. In addition, the problem of industrial waste water, often discharged into receiving waters without treatment, does not cause only degradation of the physicochemical and biological quality of the environment but also generates many waterborne diseases [2-5].

The heavy metals are non-biodegradable toxic pollutants [1], hence their removal is very important in terms of protecting the public health and the environment [6]. Various purification techniques are presented in the literature for the purpose of proving a remedy for this, among them we can list biological treatment [7], the membrane processes [8], the coagulation-flocculation [9],

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the chemical precipitation [10], liquid-liquid extraction and the adsorption [11-13]. Several researchers have studied the removal performance and selectivity sequence of heavy metal ions using different adsorbents such as: ion exchange [14, 15], clay minerals [16], activated carbon [17] and Zeolites [6, 18-20]. In this context, the zeolites have been received much attention for the treatment of waste water due to their remarkable properties leading to many applications, particularly in the fields of catalysis, adsorption and cation exchange [21]. The use of zeolites as adsorbents for the removal of heavy metals has been studied by many researchers: *Erdem et al.* [22] have studied the adsorption behavior of a natural zeolite (clinoptilolite) and found that adsorption phenomena depend on the charge density and the diameter of hydrated ions. The selectivity sequence can be given as $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. *Wang et al.* [23] have studied the removal of Cu^{2+} and Zn^{2+} from aqueous solution using zeolite A and X. They showed that zeolite A had higher removal efficiency than zeolite X. The adsorbed amount of Cu^{2+} and Zn^{2+} onto zeolite A was 37.99 and 29.68 mg/g, respectively. *Franus et al.* [24] indicated that zeolite NaP1, obtained from fly ash, showed high efficiency of the removal of zinc ions compared to zeolite X. However, zeolite NaX was used successively by *Shibata* and *Steff* [25] for Pb^{2+} exchange at different pH. They found that over exchange increases with increasing pH from 5 to 7. In another study, zeolite NaX was found to be an efficient adsorbent for the removal of Pb^{2+} from aqueous solution with adsorption capacity of 14.42 mg/g at 25°C and pH=6 [26]. In 2016, *Shakur et al.* [27] introduce a novel PAN/NaX/ZnOnanocomposite to remove uranium from radioactive contaminated waters. It was found that this nanocomposite exhibited excellent adsorption selectivity for uranium ions in comparison with bulk NaX zeolite and NaXnanozeolite. A maximum chromium uptake was found to be 3.61 meq/g in batch system at 30°C using zeolite NaX [28]. However, several studies have developed the possibility of using MFI-type zeolite for wastewater treatment [29-32]. *Kumar and Pugoventi* [33] prepared MFI zeolite membrane for the removal of toxic chromium from aqueous medium with a maximum removal of 78%. The behaviour of a NaY zeolite during the adsorption of heavy metals was described by *Oliveira et al.* [34], that studied the adsorption of Cr^{3+} , Cu^{2+} and Zn^{2+} . *Tavares et al.* [35] investigated the behaviour

of a biofilm of *Arthrobacter viscosus* supported on NaY zeolites on the removal of Cr^{6+} . *Mekatel et al.* [36] used the faujasite NaY for the retention of heavy metals such as Ni^{2+} , Pb^{2+} , Zn^{2+} , Cr^{6+} , Cd^{2+} and Co^{2+} . Recently, *Efome et al.* [37] used nanofibrous metal-organic frameworks membrane for lead and mercury sequestration from aqueous medium. They demonstrate that removal percents of Pb and Hg are up to 98% at a pH>10. It has been found that the membrane can remove Pb^{2+} with a permeance of 248.57 L/m².h.bar for a membrane thickness of 650 μm. *Quintelas et al.* [38] have studied the performance of an *Escherichia coli* biofilm supported on NaY zeolite for the retention of Cr^{6+} , Cd^{2+} , Fe^{3+} and Ni^{2+} .

The present study deals with a series of experiments to assess the utility of NaY zeolite for the removal of Cd^{2+} , Co^{2+} and Ni^{2+} ions from aqueous solutions under batch conditions, in single and binary component system. The equilibrium adsorption data for single component were fitted with Langmuir, Freundlich and Dubinin–Radushkevich models. The NaY zeolite was chosen for the present study due to its textural properties and characteristics of regeneration. Indeed, NaY zeolite belongs to faujasite structure characterized by a good thermal stability and a hierarchical porosity generating an important specific area [39,40]. Furthermore, the synthetic zeolites can be prepared from a number of sources materials such as clay material, waste materials and natural zeolites [24, 41]. These materials are local abundant and low cost resources.

EXPERIMENTAL SECTION

Reagents

All chemicals used were of the highest grade and supplied by Sigma-Aldrich. All solutions were prepared with deionized water (resistivity of 18.2 MΩ).

In order to perform this study, Cd^{2+} , Co^{2+} and Ni^{2+} synthetic solutions were prepared from cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) salts. The solution pH was adjusted using nitric acid HNO_3 (0.1 mol/L).

The adsorbent used in this study was the faujasite NaY, obtained from Sigma-Aldrich. It is a synthetic zeolite of formula: $\text{Na}_{56} [\text{Al}_{56}\text{Si}_{136}\text{O}_{384}]250\text{H}_2\text{O}$ (Si/Al = 2.43). The faujasite structure is described as a cube-octahedra assembly connected to each other by hexagonal prisms. The cation exchange capacity is 3.24 meq/g. The zeolite was used without prior treatment.

Adsorbate solution

The stock solutions of Cd^{2+} , Co^{2+} and Ni^{2+} were achieved by weighing out an appropriate mass of corresponding nitrate salt of metal and diluting it with deionized water to a final concentration of 10 and 20 mmol/L for single component sorption and two component sorption, respectively.

Sorption experiments

Sorption experiments were performed in batch at $25 \pm 2^\circ\text{C}$. 20 mL of the solution containing the desired quantity of the metal ion, ranging from 0.1 to 10 mmol/L, was treated with 0.15g of faujasiteNaY, solution pH (5-6) to avoid any possible hydroxide precipitation. The solution and appropriate blanks were stirred slowly for 12h to reach apparent equilibrium based on kinetic studies reported in the literature [11, 42] (Table 1).

Analytical methods

The equilibrium concentrations (C_e , mmol/L) of Cobalt, Nickel and Cadmium were determined using a Metrohm model 850 Professional ionic Chromatography for ion analysis equipped with an IC conductivity detector. A Metrosep C4-250/4.0 column was used for cobalt, nickel and the exchanged sodium Na^+ ions analysis and the mobile phase was a mixture of Nitric acid (0.9 mM) and Oxalic acid (1.6 mM). A Metrosep C3-250/4.0 column was used for Cadmium analysis and the mobile phase was a mixture of tartaric acid (6 mM) and Oxalic acid (4 mM). A constant flow rate of 1 mL/min was used. The adsorbed amounts of ion at equilibrium time (Q_e , mmol/g) were calculated using the following equation [43]:

$$Q_e = \frac{(C_i - C_e)V}{m_s}$$

Where C_i and C_e are the initial and equilibrium ion concentrations in solution (mmol/L), respectively. V was the total solution volume (mL) and m_s was the weight of adsorbent (faujasiteNaY) (g).

Adsorption Isotherms

The adsorption isotherms describe the relationship between the adsorbed amount and the solute concentration at adsorption equilibrium. Several models have been proposed for the study of the adsorption. In this study, equilibrium data were analyzed by using the Langmuir, Freundlich and Dubinin–Radushkevich isotherm model.

Langmuir isotherm model

The Langmuir model (the uptake of metal ions on a homogenous surface by monolayer adsorption, all sites are identical and energetically equivalent, the adsorbent is structurally homogeneous without interaction between molecules adsorbed on neighboring sites) was expressed in the below equation [11, 44-46]:

$$Q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (\text{Non-linear form})$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \cdot K_L} \quad (\text{Linear form})$$

Where Q_e presented the amount of adsorbed solute per unit weight of adsorbent at equilibrium, Q_{\max} was the maximum adsorption capacity (mmol/g), C_e indicated the equilibrium concentration of solute (mmol/L) in the solution, and K_L was the Langmuir constant related to a free energy adsorption (L/mmol).

The essential characteristics of the Langmuir isotherm can be expressed in term of a dimensionless constant called equilibrium parameter R_L as follows [47]:

$$R_L = \frac{1}{1 + K_L \times C_i}$$

When C_i was the initial ion concentration. R_L indicates the shape of isotherm to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

Freundlich isotherm model

The Freundlich model[48](the uptake of metal ions on a heterogeneous surface done by multilayer adsorption with interaction between adsorbed molecules) was expressed in below equation:

$$Q_e = K_F \cdot C_e^{1/n_F} \quad (\text{Non-linear form})$$

$$\ln Q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (\text{Linear form})$$

Where Q_e presented the amount of the solute adsorbed per unit weight of adsorbent (mmol/g), C_e is the equilibrium concentration of the solute (mmol/L), K_F was the Freundlich constant indicative of the relative adsorption capacity of the adsorbent, and n_F was an empirical constant that represents the parameter characterizing the heterogeneity of the adsorbent surface. For a favourable adsorption, $0 < 1/n_F < 1$, an unfavorable adsorption, $1/n_F > 1$, and $1/n_F = 1$ indicates a linear adsorption. If $n_F = 0$, the adsorption process is irreversible [48, 49].

Table 1: Variation of concentration and pH of samples.

Sample	Concentration (mmol/L)	Co ²⁺		Ni ²⁺		Cd ²⁺	
		pH _i	pH _f	pH _i	pH _f	pH _i	pH _f
1	0.125	5.49	6.20	5.22	6.01	5.31	6.09
2	0.25	5.50	6.01	5.36	6.12	5.43	6.11
3	0.375	5.26	6.03	5.45	6.22	5.14	6.37
4	0.5	5.33	6.11	5.28	6.23	5.20	6.15
5	1	5.32	6.24	5.17	6.15	5.23	6.33
6	2	5.45	6.19	5.36	6.42	5.51	6.22
7	3	5.66	6.45	5.12	6.34	5.19	6.51
8	4	5.48	6.12	5.41	6.21	5.27	6.29
9	5	5.53	6.31	5.23	6.33	5.48	6.38
10	6	5.50	6.20	5.34	6.17	5.41	6.61
11	7	5.51	6.01	5.23	6.19	5.31	6.58
12	8	5.28	6.03	5.41	6.20	5.49	6.33
13	9	5.31	6.14	5.45	6.23	5.67	6.12
14	10	5.75	6.32	5.23	6.42	5.37	6.17

Dubinin–Radushkevich isotherm model

The empirical Dubinin–Radushkevich model isotherm [50] was used to distinguish between physical and chemical adsorption of metal ions and to calculate the free energy of adsorption. The model is shown as:

$$\ln Q_e = \ln Q_{max} - \beta \varepsilon^2$$

Where Q_{max} is the maximum amount of ion that can be sorbed onto unit weight faujasite NaY, (mmol/g), β the constant related to the sorption energy (mol^2/kJ^2); and ε is the Polanyi potential = $RT \ln(1 + 1/C_e)$, where R is the gas constant (kJ/mol K), and T is the absolute temperature (K). ε was expressed in below equation:

$$\varepsilon = RT \ln(1 + 1/C_e)$$

The values of the adsorption energy, E , was obtained from the relationship in below equation:

$$E = 1/\sqrt{2\beta}$$

The magnitude of E can be related to the reaction mechanism. If E is in the range of 8-16 kJ/mol, sorption is governed by ion exchange. In the case of $E < 8.0$ kJ/mol, physical forces may affect the sorption mechanism [51, 52].

RESULTS AND DISCUSSION

Monocomponent sorption isotherms

Fig. 1 shows the equilibrium sorption behavior of the faujasite NaY, in single-component solutions of Cadmium, Cobalt or nickel ions in water.

The adsorption isotherms obtained that belongs to the class H according to Giles classification [53], characteristic of high affinity between adsorbate and adsorbent, and the amount adsorbed appears important at low concentrations. The presence of a bearing shows that the maximum adsorption capacity of the faujasite NaY is reached. The results obtained show that the affinity of faujasite Na-Y for the studied ions varies as follows: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. The results can be explained by the physical and chemical properties of the metal ions as the ionic radii of metals. This last is an important factor for the exchange in terms of diffusion and site of adsorption in the zeolite structure. The atomic radii of Co^{2+} and Ni^{2+} cations are 0.082 and 0.080 nm, respectively. These cations are easily exchanged with those of Na^+ of faujasite Na-Y (0.098 nm) (Table 2).

Also, from the same table, the metal with the highest free energy of hydration should therefore prefer to remain in the solution phase. Thus, according to the free energy of hydration, the selectivity sequence is $\text{Co}^{2+} > \text{Ni}^{2+}$.

Table 2: Radii and hydration energies of different metal ions.

Metals ions	Hydrated radius(Å)	Unhydrated radius(Å)	Free energy of hydration (kcal/g-ion)
Co ²⁺	4.23	0.82	-479.5
Ni ²⁺	4.04	0.80	-494.2
Cd ²⁺	4.26	1.03	-430.5
Na ⁺	3.58	0.95	

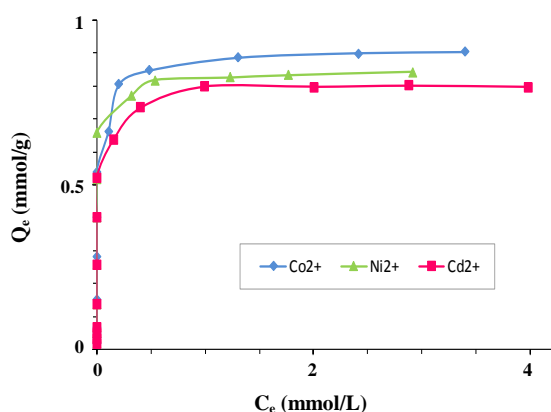


Fig. 1: Monocomponent equilibrium sorption data for Co²⁺, Ni²⁺ and Cd²⁺ for initial concentrations (10 mmol/L) of metal and pH (5-6).

The atomic radius of Cd²⁺ is 0.103 nm. This metal cation has also the greatest atomic weight. This probably explains the decrease in the amount of adsorbed Cd²⁺. The metal affinity to faujasite NaY was found to follow the sequence of Co²⁺>Ni²⁺> Cd²⁺. This is in agreement with results from literature: Mekatel *et al.* [36] demonstrated that the selectivity sequence is as follows: Co²⁺>Ni²⁺> Zn²⁺> Pb²⁺>Cr⁶⁺>Cd²⁺. Quintelas *et al.* [38] have studied the performance of an Escherichia coli biofilm supported on faujasite Na-Y and the selectivity sequence is given as follows: Fe³⁺> Ni²⁺> Cd²⁺> Cr⁶⁺. The mechanism involved was ion exchange between metal cations (Co²⁺, Ni²⁺, Cd²⁺) in the solution and sodium ions in the zeolite NaY. The ratio (amount of Na⁺ released/ amount of cation adsorbed) as a function of initial concentration was shown in Fig. 2.

The relation between released and loaded equivalents of positive charges was found to be stoichiometric ((amount of Na⁺ released/ amount of cation adsorbed) ≈ 2). This implies an ion exchange process for the uptake of Co²⁺, Ni²⁺ and Cd²⁺ onto zeolite NaY. During this process metal ions move through the pores of zeolite and channels of the lattices and they replace Na⁺ cations [22, 55].

The equilibrium data obtained for the adsorption of Co²⁺, Ni²⁺ and Cd²⁺ ions onto faujasite NaY were analyzed by considering the Langmuir and Freundlich isotherm models (Fig. 3).

Based on the values of correlation coefficients (R²) shown in Table 3, Langmuir model describes better the sorption data than the Freundlich model. Thus, indicating the homogeneity of the active sites of adsorbent. The maximum sorption capacities (Q_{max}) are 0.81, 0.85 and 0.92 mmol/g for Cd²⁺, Ni²⁺ and Co²⁺ ions, respectively.

The R_L values (Table 3) were found to be less than 1 and greater than 0 indicating the favorable adsorption of Co²⁺, Ni²⁺ and Cd²⁺ onto Faujasite NaY.

The Freundlich constant (1/n_F) was less than unity, indicating that an increasing tendency of adsorption process occurred with ion concentration increasing. This should be attributed to the fact that with progressive surface coverage of faujasiteNaY [11, 51]. The K_F value for Co²⁺ and Ni²⁺ were greater than for Cd²⁺, confirming a greater adsorption tendency of the adsorbent towards Co²⁺ and Ni²⁺.

Fig. 4 shows Dubinin-Radushkevich isotherm for the batch adsorption of different metal ions using faujasite NaY as adsorbent.

A linear plot was obtained when lnQ_e was plotted against ε² over the entire concentration range. The obtained E value for adsorption of Ni²⁺ and Co²⁺ was 8.27 and 10 kJ/mol (Table 4), respectively, indicating that both ions were uptake through an ion exchange process. On the other hand, the value of the free energy of adsorption for Cd²⁺ is in the case of E < 8.0 kJ/mol, indicating that the sorption process is done through physical sorption [52].

Bicomponent sorption isotherms

Three bicomponent adsorption systems (Co²⁺ + Cd²⁺), (Co²⁺ + Ni²⁺) and (Cd²⁺ + Ni²⁺) were studied. Fig. 5 shows bicomponent sorption isotherms obtained with equimolar initial concentration of cations.

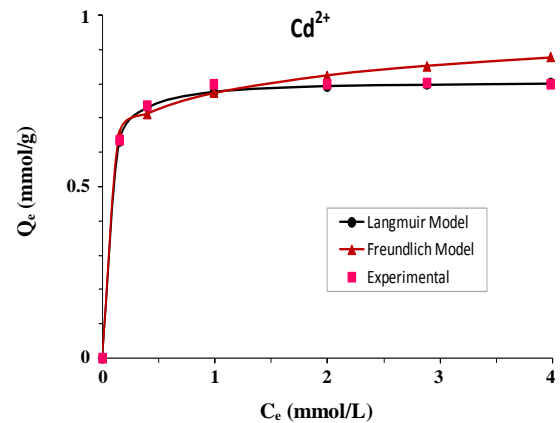
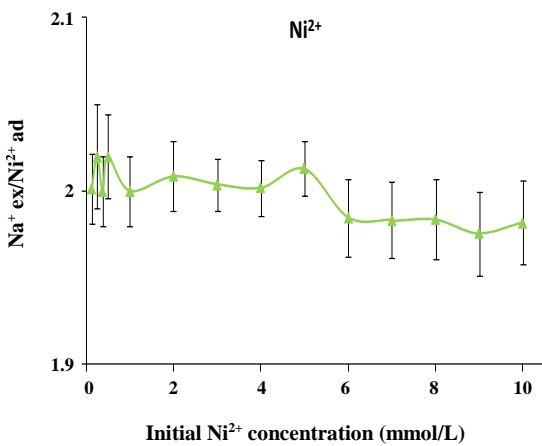
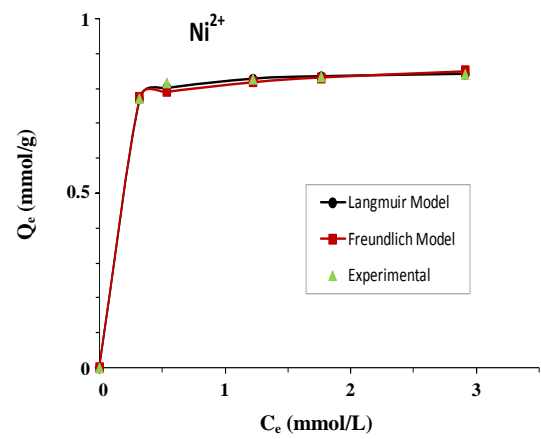
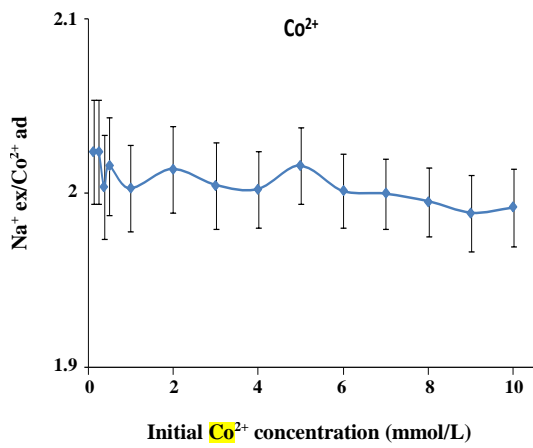
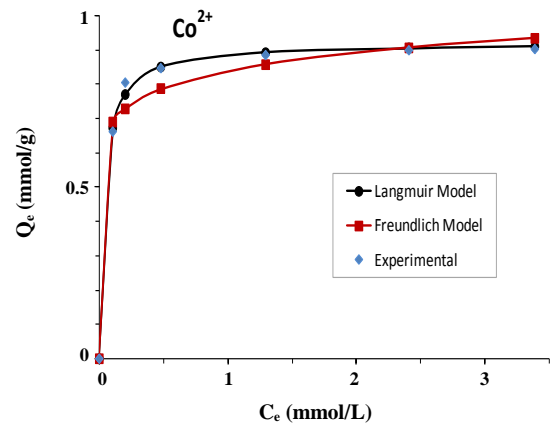
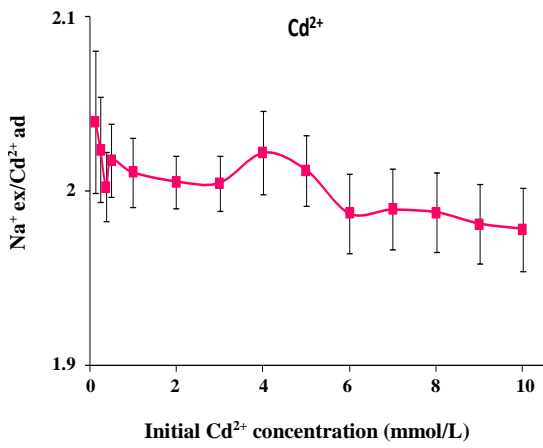


Fig. 2: (Amount of Na⁺ released/ amount of cation adsorbed) as a function of the initial cation concentration.

Fig. 3: Langmuir and Freundlich isotherms fitted to experimental sorption of Ni²⁺, Co²⁺ and Cd²⁺ onto Faujasite NaY.

Table 3: Langmuir and Freundlich isotherm constants for single component adsorption of Co²⁺, Ni²⁺ and Cd²⁺ on FaujasiteNaY.

Langmuir Parameters				
System	R ²	Q _e (mmol/g)	K _L (L/mmol)	R _L (× 10 ²)
Co ²⁺ alone	0.9615	0.92	25.17	0.4216-0.8029
Ni ²⁺ alone	0.9996	0.85	29.96	0.3056-0.5246
Cd ²⁺ alone	0.9888	0.81	23.22	0.2676-0.5331
Freundlich Parameters				
System	R ²	1/n _F	K _F	
Co ²⁺ alone	0.8661	0.0887	0.84	
Ni ²⁺ alone	0.9569	0.0422	0.81	
Cd ²⁺ alone	0.8900	0.0904	0.77	

Table 5: Langmuir and Freundlich isotherm constants for binary-component adsorption of Co²⁺, Ni²⁺ and Cd²⁺ on FaujasiteNaY.

Langmuir Parameters				
System	R ²	Q _e (mmol/g)	K _L (L/mmol)	Q ^{mix} /Q _{max}
Cd (Cd-Ni)	0.9264	0.53	3.71	0.65
Ni (Cd-Ni)	0.8625	0.73	7.15	0.85
Cd (Co-Cd)	0.9987	0.58	2.54	0.71
Co (Co-Cd)	0.9355	0.79	3.08	0.85
Ni (Ni-Co)	0.9354	0.53	10.06	0.62
Co (Ni-Co)	0.9805	0.65	13.86	0.70
Freundlich Parameters				
	R ²	1/n _F	K _F	K _F ^{mix} /K _F
Cd (Cd-Ni)	0.7858	0.0831	0.44	0.77
Ni (Cd-Ni)	0.7818	0.0473	0.65	0.80
Cd (Co-Cd)	0.9431	0.1105	0.45	0.58
Co (Co-Cd)	0.7762	0.1017	0.62	0.73
Ni (Ni-Co)	0.9519	0.0597	0.48	0.59
Co (Ni-Co)	0.9366	0.0151	0.64	0.76

In multicomponent system, the adsorption is complicated because the interactions between solutes are involved. The interaction effects on the sorption process may be represented by the ratio of the sorption capacity for one metal ion in the presence of the other metal ion (Q^{mix}) to the sorption capacity for the same metal ion when it is present alone in the solution (Q_{max}) such that for [56, 57]:

(Q^{mix} / Q_{max}) > 1: the sorption is promoted by the presence of other metal ions;

(Q^{mix} / Q_{max}) = 1: there is no observable net interaction.

(Q^{mix} / Q_{max}) < 1: sorption is suppressed by the presence of other metal ions.

The values of Q^{mix} / Q_{max} for the three cations are found to be less than unity (Table 5). This explains that the cation adsorption was suppressed in binary system.

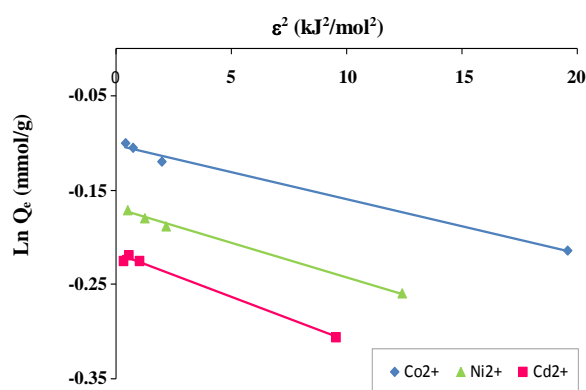


Fig. 4: Dubinin–Radushkevich isotherm plots for adsorption of Co²⁺, Ni²⁺ and Cd²⁺.

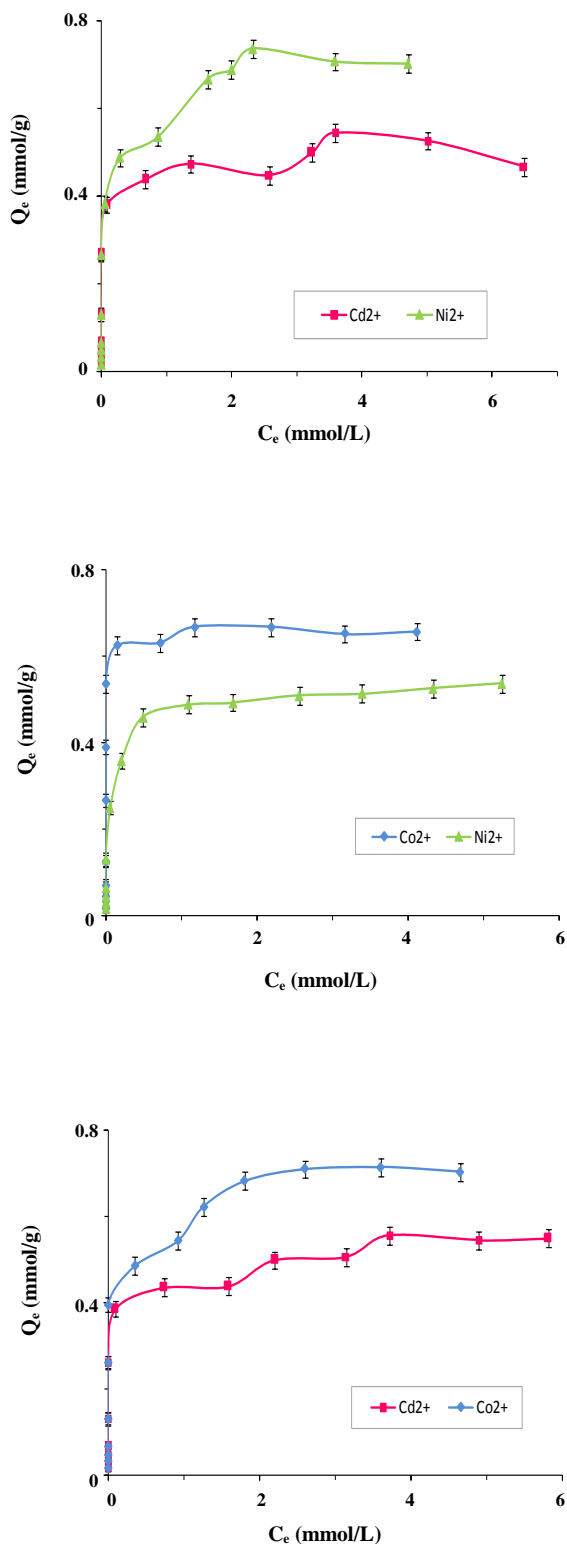


Fig.5: Equilibrium sorption data for Co^{2+} , Ni^{2+} and Cd^{2+} in binary system.

CONCLUSIONS

The equilibrium data have been analysed for each metal ion in single component using Langmuir, Freundlich and Dubinin–Radushkevich isotherms. In binary system, the equilibrium data have been analysed using Langmuir and Freundlich models. The Langmuir isotherm was demonstrated to provide the best correlation for the sorption of the three metal ions onto faujasiteNaY. In single component, the maximum sorption capacities (Q_{max}) are 0.81, 0.85 and 0.92 mmol/g for Cd^{2+} , Ni^{2+} and Co^{2+} ions, respectively. The obtained R_L values were in the range of 0–1 indicating that Cd^{2+} , Ni^{2+} and Co^{2+} sorption was favorable. The free energy of adsorption value calculated from D-R isotherm is in the range of 8–16 kJ/mol for Ni^{2+} and Co^{2+} indicates that the sorption process is done through an ion exchange interaction. On the other hand, the free energy of adsorption value for Cd^{2+} is in the case of $E < 8$ kJ/mol, indicating that the sorption process is done through physical sorption. Competitive sorption isotherm confirmed that Cd^{2+} , Ni^{2+} and Co^{2+} sorptions are inhibited and the sorption capacities varied as $Co^{2+} > Ni^{2+} > Cd^{2+}$. These reported results showed that faujasiteNaY is an efficient low cost ion exchange material for the removal of Cadmium, Cobalt and Nickel ions from aqueous solutions in both single and multicomponent systems.

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