



CATION EXCHANGE MECHANISM OF DIVALENT METALS IONS IN SYNTHETIC NaX AND LTA ZEOLITES: EFFICIENCY AND SELECTIVITY

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In this investigation, the removal of divalent heavy metals by two types of zeolites has been studied. The mechanism of cation exchange for Cu^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} on NaX Faujasite and Linde type A (LTA) zeolites was studied. Both zeolites are very efficient in divalent heavy metals removal from water. Ion exchange isotherms were performed and the thermodynamic parameters were calculated as well. Kielland plots showed that the order of selectivity is not the same for both the zeolites. For NaX it followed the following order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ while for LTA the order is $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. Exchange velocity (k_w) and the radii of the hydrated metals ions are involved in determining this order of selectivity.

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Introduction

Zeolites are cation exchangers that occur naturally, the Swedish mineralogist Axel Fredrick Cronstedt first discovered them in 1756.¹ The framework of zeolites is a three-dimensional arrangement of tetrahedral SiO_4 and AlO_4^- units. The aluminate units in the framework are responsible for its net negative charge which is balanced by the presence of extra framework cations located on defined crystallographic positions. These cations are responsible for zeolite exchange properties and the rich ion-exchange chemistry of these materials. The elevated cation exchange capacity made zeolite attractive for wastewater treatment especially for removing heavy metals.

Nowadays, many water resources are contaminated due to the direct release of industrial influents. Heavy metals are one of the most serious environmental pollutants since they accumulate in living organisms even at low concentration causing dangerous diseases.² Natural zeolites have been used to remove heavy metal from aqueous solutions because they are inexpensive and highly abundant. Several researches showed that zeolites have good cation-exchange capacities under different experimental conditions.³⁻⁵ One of the most frequently studied natural zeolites is Clinoptilolite.^{6,7} The cation exchange capacity is usually between 0.6 and 2.3 meq g^{-1} .⁸ Recently, a great deal of attention has been paid to synthetic zeolites due to their enhanced properties including higher cation exchange capacity compared to natural ones. Synthetic Faujasite zeolite, NaX ($\text{Na}_{88}\text{Al}_{88}\text{Si}_{104}\text{O}_{384}$ and Si/Al ratio = 1.18) and Zeolite A, LTA ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$ and Si/Al ratio=1) are more favourable for heavy metals adsorption since they contain more exchangeable Na^+ ions in their framework.

There are several studies dealing with divalent heavy metals adsorption onto synthetic zeolites,^{9,10} but no detailed analysis for the cation exchange mechanism is available. The current study highlights the theory of ion exchange in synthetic NaX and LTA zeolites. The efficiency and selectivity of divalent heavy metals binding (Cu^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+}) were analyzed in detail based on the cation exchange theory including calculation of thermodynamic parameters which allows better understanding the selectivity of these zeolites toward metal ions.

Experimental

Materials

The French Institute of Petroleum (IFP Energie Nouvelle) provided the synthetic NaX Faujasite and LTA zeolite samples. These samples were used as received without any further chemical modification. Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and anhydrous lead nitrate ($\text{Pb}(\text{NO}_3)_2$) were purchased from Sigma Aldrich, and used as received. Ultrapure water was used throughout.

Batch adsorption experiments

Metal ions solutions (Cu^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+}) were prepared from their corresponding nitrate salts in ultrapure water to obtain solutions of different concentrations. In batch studies, 20 mg of the solid zeolite powder was placed in 100 mL of a metal solution of desired concentration. For obtaining the isotherms, the initial metal ions concentrations were varied between 0.17 mmol L^{-1} and 5 mmol L^{-1} . The solutions were stirred for 120 min at 25 °C then filtered by a 0.45 μm syringe filter and the remaining metal ions were measured by AAS (Perkin Elmer AA200). The adsorption capacity (mmol g^{-1}) of the adsorbent at equilibrium was calculated by eqn. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where

C_0 is the initial concentration

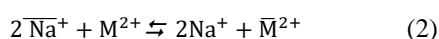
C_e is the concentration at equilibrium,

V is the volume of metal solution in litre and

m is the mass of the adsorbent in g.

Theory of cation exchange in zeolites

The sodium–divalent metal ion exchange process in zeolite can be expressed by eqn. (2)



The bar above the symbols represents the ion exchanger phase. The thermodynamic equilibrium constant, K , of the reversible ion-exchange reaction is defined by eqn. (3).¹¹

$$K = \frac{[[\text{Na}^+]^+]^2 \bar{X}_M \gamma_{\text{Na}}^2 f_M}{[\text{M}^{2+}] \bar{X}_{\text{Na}}^2 \gamma_M f_{\text{Na}}^2} \quad (3)$$

$[\text{Na}^+]$ and $[\text{M}^{2+}]$ are the molarities of the ions in solution, γ_i and f_i are the activity coefficients in the aqueous phase and in the ion-exchanger phase, respectively. The standard states for the ion-exchanger phase are taken as the exchanger in its pure Na^+ and M^{2+} forms, and the activity coefficients, f_{Na} and f_M , are chosen as unity when the exchanger is at the standard state of the Na^+ form and the M^{2+} form, respectively. \bar{X}_i is an equivalent fraction of ion i in the ion-exchanger phase, defined by Eqns. (4) and (5).

$$\bar{X}_{\text{Na}} = \frac{[\overline{\text{Na}}^+]}{2[\overline{\text{M}}^{2+}] + [\overline{\text{Na}}^+]} \quad (4)$$

$$\bar{X}_M = \frac{2[\overline{\text{M}}^{2+}]}{2[\overline{\text{M}}^{2+}] + [\overline{\text{Na}}^+]} \quad (5)$$

The equivalent fractions of the ions in the solution (X_i) can replace the molarities $[\text{Na}^+]$ and $[\text{M}^{2+}]$ leading to eqns. (6 – 8).

$$X_{\text{Na}} = \frac{2[\text{Na}^+]}{2[\text{M}^{2+}] + [\text{Na}^+]} \quad (6)$$

$$X_M = \frac{2[\text{M}^{2+}]}{2[\text{M}^{2+}] + [\text{Na}^+]} \quad (7)$$

$$[\text{Na}^+] + 2[\text{M}^{2+}] = TN \quad (8)$$

where TN represents the total normality of the solution. By using a corrected selectivity coefficient, K_{Na}^M , the thermodynamic equilibrium constant can be rewritten eqn. (9).¹²

$$K_{\text{Na}}^M = \frac{X_{\text{Na}}^2 \bar{X}_M \gamma_{\text{Na}}^2}{X_M \bar{X}_{\text{Na}}^2 \gamma_M} [2(TN)] \quad (9)$$

where,

$$K = K_{\text{Na}}^M \frac{f_M}{f_{\text{Na}}^2} \quad (10)$$

When the total normality, $TN = [\text{Na}^+] + 2[\text{M}^{2+}]$, is lower than 0.01 N, $\gamma_{\text{Na}}^2/\gamma_M$ will be close to unity. K_{Na}^M depends on the total normality. When the corrected selectivity coefficient is larger than unity ($\ln K_{\text{Na}}^M > 0$), the zeolite is selective for the ion M^{2+} . If K_{Na}^M is smaller than unity ($\ln K_{\text{Na}}^M < 0$), Na^+ ions are more preferred. When K_{Na}^M is equal to unity ($\ln K_{\text{Na}}^M = 0$), there will be no preference between these ions. K_{Na}^M is also related to the Kielland coefficient as given below. Kielland plots show the details of the ion exchange selectivity as a function of the equivalent fraction \bar{X}_M .

$$\log K_{\text{Na}}^M = \sum_{m=1} (m+1) C_m \bar{X}_M^m + \log(K_{\text{Na}}^M)_{\bar{X}_M \rightarrow 0} \quad (11)$$

The coefficient, C_m , is called generalized Kielland coefficient. These plots often give linear relationships with a slope $2C_1$.

$$\log K_{\text{Na}}^M = 2C_1 \bar{X}_M + \log(K_{\text{Na}}^M)_{\bar{X}_M \rightarrow 0} \quad (12)$$

If the Gibbs–Duhem equation is applied to the ion-exchange reaction, the thermodynamic equilibrium constant, K , is given by the integration of Kielland plot from $\bar{X}_M = 0$ to $\bar{X}_M = 1$.

$$\ln K = (Z_{\text{Na}} - Z_M) + \int_0^1 \ln K_{\text{Na}}^M d\bar{X}_M + \Delta \quad (13)$$

Thus, the thermodynamic equilibrium constant is determined by the valences of the exchanged and exchanging cations, the generalized Kielland coefficient C_1 and the intercept of Kielland plot, $(K_{\text{Na}}^M)_{\bar{X}_M \rightarrow 0}$.

The Gibbs standard free energy change ΔG° can be calculated by eqn. (14).

$$\Delta G^\circ = -RT \ln K \quad (14)$$

Results and Discussion

Exchange equilibrium curves for NaX Zeolite

The exchange isotherms are shown in Figure 1 and are represented as the equivalent fraction of the divalent metal ions fraction (\bar{X}_M) inside the NaX zeolite as a function of the equivalent ion fraction in the solution (X_M).

The obtained exchange isotherms almost have the same shape, they showed a steeper increase in the initial stage of $X_M^{2+} < 0.2$ and then the isotherms increased more gently. This shape is characteristic of a favourable exchange process.

For $2\text{Na}^+ \rightarrow \text{Pb}^{2+}$ exchange reaction, the isotherm proceeds more steeply up to $\bar{X}_{\text{Pb}} \sim 0.6$ which indicates higher selectivity for Pb^{2+} than for the other three heavy metals (Figure 1). The theoretical exchange capacity was calculated from the Na^+ ions contained in NaX ($\text{Na}_{88}\text{Al}_{88}\text{Si}_{104}\text{O}_{384}$). 1 g of NaX zeolite contains 6.54 mmol Na^+ , so theoretically, it has a maximum adsorption capacity for divalent ions equals to 3.27 mmol g^{-1} since every two Na^+ ions are exchanged for

one divalent metal cation so this value was supposed to be the theoretical exchange capacity of NaX. The ion exchange capacities for all metal ions were determined from their corresponding isotherms and were found to be 93, 87, 95, and 96% of the theoretical exchange capacity for Cu^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} respectively. These values were calculated from the equivalent fraction of cations in zeolite when the maximum exchange capacity was reached.

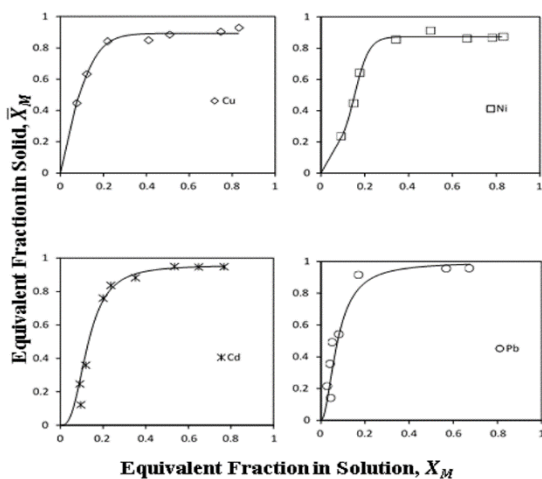


Figure 1. Cation exchange isotherm for $2\text{Na}^+ \rightarrow \text{M}^{2+}$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Cd}$ and Pb) exchange on the NaX zeolite.

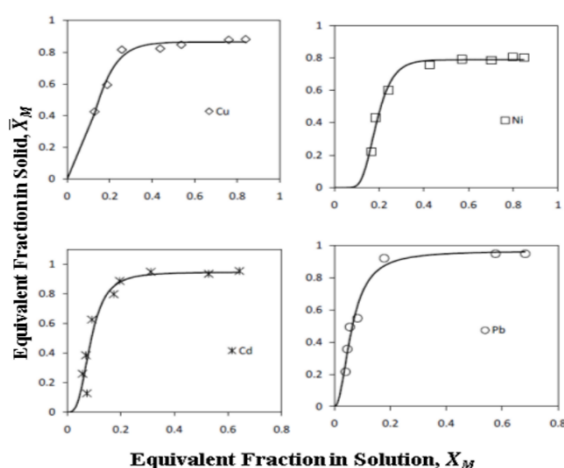


Figure 2. Cation exchange isotherm for $2\text{Na}^+ \rightarrow \text{M}^{2+}$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Cd}$ and Pb) exchange on the LTA zeolite.

Exchange Equilibrium Curves for LTA Zeolite

The exchange reactions of the four heavy metals ions Cu^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} were done for LTA zeolite as well under the same conditions. The corresponding isotherms are shown in Figure 2. As in the case of NaX zeolite, the exchange isotherms for LTA showed a favourable exchange process with a steep increase in the initial stage of $X_{\text{M}^{2+}} < 0.2$ that proceeds more gently afterwards. Similarly, for $2\text{Na}^+ \rightarrow \text{Pb}^{2+}$ exchange reaction, the isotherm proceeded more steeply up to $\bar{X}_{\text{Pb}} \sim 0.6$ which indicates higher selectivity for Pb^{2+} than for the other three heavy metals. The theoretical exchange capacity was calculated from the Na^+ ions contained in LTA ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$). 1 g of LTA zeolite contains 7 mmol Na^+ . So theoretically, it has a maximum adsorption capacity for divalent ions equals to 3.5

mmol g^{-1} since every two Na^+ ions are exchanged for 1 metal divalent cation so this value was supposed to be the theoretical exchange capacity of LTA. The ion exchange capacities for all were determined from their corresponding isotherms and were found to be 88, 82, 96, and 95% of the theoretical exchange capacity for Cu^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} respectively. These values were calculated from the equivalent fraction of cations in zeolite when the maximum exchange capacity was reached.

Cation exchange selectivities: $2\text{Na}^+ \rightarrow \text{M}^{2+}$

The selectivity of both NaX and LTA zeolites is further analyzed through Kielland plots where the logarithm of the selectivity coefficient is plotted as a function of the equivalent fraction of cations in zeolites (X_{M}).

Table 1. Thermodynamic data for $2\text{Na}^+ \rightarrow \text{M}^{2+}$ exchange on NaX at 25 °C.

M^{2+}	$\ln(K_{\text{Na}}^{\text{M}})_{\bar{X}_{\text{M}} \rightarrow 0}$	C_1	ΔG^0 (kJ mol^{-1})
Cu^{2+}	2.32	1.10	-5.80
Ni^{2+}	1.69	1.50	-4.20
Cd^{2+}	1.77	1.70	-4.40
Pb^{2+}	2.65	1.60	-6.40

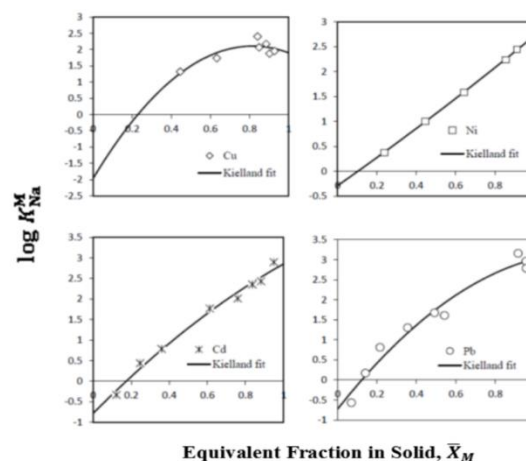


Figure 3. Kielland plots for $2\text{Na}^+ \rightarrow \text{M}^{2+}$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Cd}$ and Pb) exchange on the NaX zeolite.

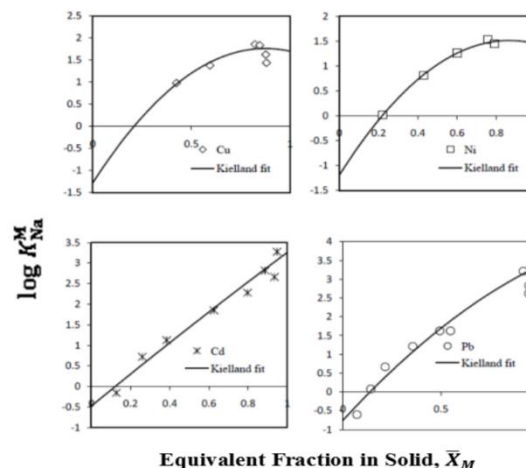
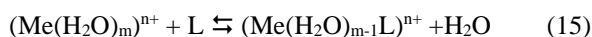


Figure 4. Kielland plots for $2\text{Na}^+ \rightarrow \text{M}^{2+}$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Cd}$ and Pb) exchange on the LTA zeolite.

The Kielland plots are represented in figure 3 and 4 for NaX and LTA respectively. The plots gave a linear relation for all metals except for Cu²⁺. The line at 0 indicates that the corrected selectivity coefficient is equal to unity ($K_{Na}^M = 1$) where there is no preference between Na⁺ and M²⁺ ions. If the plots fall below this line this means that the zeolite is more selective for Na⁺ while if they fall above it this indicates that the zeolite is more selective for M²⁺. From these Kielland plots, it can be deduced that for Cd²⁺ and Pb²⁺ ions the zeolite becomes more selective for the metal ions at $\bar{X}_M > 0.2$ since all Kielland plots fall above the 0 line above this value. For Cu²⁺ and Ni²⁺, M²⁺ ions are more preferred almost throughout the $2Na^+ \rightarrow M^{2+}$ exchange reaction. From the Kielland plots, the Kielland coefficient C_1 , and ΔG^0 values were estimated. The obtained values are listed in Table 1.

For NaX, ΔG^0 value for Pb²⁺ was the smallest while that of Ni²⁺ was the highest. Based on this results, the order of selectivity will be Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ which is in accordance with what was found before using the distribution coefficient K_d . The Kielland coefficient, C_1 , is related to the energy of the steric limitation or jumping barrier for the exchanging ions in the sodalite cages. In general, the energy term for the steric limitation is larger as the $|C_1|$ value is larger. For NaX zeolite, the energy of the steric limitation increases in the order of Cd²⁺ > Pb²⁺ > Ni²⁺ > Cu²⁺ but the order of selectivity didn't follow the same order. These findings are related to the nature of the metal ions and mainly to the exchange velocities between the ligands and the aqueous metal ions which is generally expressed as eqn. (15).¹³



where L represents H₂O or other ligands and Me the metal ion. The exchange velocity constant (k_w) of water molecules with metallic ions (Table 2) is the fundamental step controlling the rate of ions removal from water.

Table 2. The exchange velocity constant (k_w) and Hydrated ionic radius (R) for the four studied metal ions.

Cation	k_w (s ⁻¹)	R (nm)
Ni ²⁺	3.10 ⁴	0.302
Cd ²⁺	3.10 ⁸	0.275
Cu ²⁺	1.10 ⁹	0.297
Pb ²⁺	7.10 ⁹	0.261

Table 3. Thermodynamic data for $2Na^+ \rightarrow M^{2+}$ exchange on LTA at 25 °C.

M ²⁺	$\ln(K_{Na}^M)_{\bar{X}_M \rightarrow 0}$	C_1	ΔG^0 (kJ mol ⁻¹)
Cu ²⁺	1.6	0.870	-4.162
Ni ²⁺	0.985	1.27	-2.44
Cd ²⁺	2.27	1.85	-5.62
Pb ²⁺	2.60	2.07	-6.45

The obtained selectivity results vary with the order of the exchange velocity (k_w) values which seem to be the main parameter that controls their adsorption. Pb²⁺ has the greatest exchange velocity (k_w) so it is the first to be

adsorbed while Ni²⁺ has the lowest k_w value so its adsorption is less favorable compared to Pb²⁺, Cu²⁺ and Cd²⁺.

For LTA zeolite, the energy of the steric limitation increases in the order of Pb²⁺ > Cd²⁺ > Ni²⁺ > Cu²⁺ (Table 3) but the order of selectivity didn't also follow the same order. The order of selectivity according to ΔG^0 values will be Pb²⁺ > Cd²⁺ > Cu²⁺ > Ni²⁺. LTA is more selective for Pb²⁺ and less selective for Ni²⁺ like in the case of NaX zeolite but the selectivity of Cu²⁺ and Cd²⁺ is reversed. So in the case LTA zeolite, the selectivity might be affected by the radii of the hydrated metal ions (Table 2) in addition to exchange velocity (k_w) since the pore size of LTA are smaller than that of NaX zeolite.

Conclusions

NaX and LTA zeolites were found to be very efficient in the removal of heavy metals from water. The theory of cation exchange was applied in order to understand the mechanism of heavy metals adsorption. For both zeolites, Kielland plots showed that Cd²⁺ and Pb²⁺ have higher selectivity over Ni²⁺ at $\bar{X}_M > 0.2$ while for Cu²⁺ and Ni²⁺, M²⁺ ions are more preferred almost throughout the $2Na^+ \rightarrow M^{2+}$ exchange reaction.

For NaX, the order of selectivity is Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ while for LTA the selectivity order is Pb²⁺ > Cd²⁺ > Cu²⁺ > Ni²⁺. This order was directly controlled by exchange velocity (k_w) for NaX and the radii of the hydrated metal ions for LTA.

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