

STUDY ON SORPTION OF SOME TOXIC AND HEAVY IONS IN DILUTE SOLUTIONS BY CLINOPTILOLITE

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Abstract

The deposits of clinoptilolite (CLI) in Iran after activation with sodium chloride or sodium hydroxide solution was subjected to ion exchange with some heavy and toxic cations. The results showed that the absorption for Ca^{2+} (7.5 ppm), Cu^{2+} (50 ppm), Zn^{2+} (40 ppm), Cd^{2+} (40 ppm), Pb^{2+} (500 ppm) and Al^{3+} (5 ppm) were 95.2, 96.70, 93.30, 99.12, 99.2 and 90.0 percents, respectively. The noteworthy of our method in eliminating of contamination and conversion of waste water to drinking water is discussed in this report.

Introduction

Molecular sieves are a class of porous open framework solids, which includes aluminosilicates (zeolites), aluminophosphates and silicoaluminophosphates of diverse structures. Zeolites either natural or synthetic are built from corner sharing SiO_4^{4-} and AlO_4^{5-} tetrahedral and contain regular systems of intracrystalline cavities and channels of molecular dimensions [1-4]. The natural clinoptilolite belongs to the heulandite group of minerals. Because of high content of silicon, it is known as high silica heulandite. Although negative charge of the clinoptilolite (CLI) framework arising from tetrahedrally coordinated aluminum is neutralized by monovalent cations, chiefly Na(I) and K(I) but there are some deposits of CLI containing dominantly divalent cations such as Ca(II) and Mg(II) [5-9].

According to our literature survey, CLI properties are divided in three different categories of ion exchanger,

Keywords: Clinoptilolite; Heavy and toxic cations; Ionic exchange molecular sieves and catalysts. Because of its great affinity for the ammonium ions, it is used for removal of

NH_4^+ ions from natural and waste water. It also acts as good absorbent for isotopic cations such as ^{137}Cs from waste water solutions. Its function as molecular sieve is evident on absorbing light hydrocarbons from heavier gases. It adsorbs SO_2 from dry flue gases as well. Another application of CLI is its catalytic ability in processes such as conversion of methanol to light hydrocarbons, hydrogenation of sun flower oil and isomerization reactions [10-15].

In this paper we report the results of our investigation on sorption ability of Iranian CLI in eliminating some heavy and toxic ions from dilute contaminated solutions.

Experimental Section

All chemicals were purchased from Merck Chemical Company. The concentration of ions in solution was determined by atomic absorption spectroscopy (AAS) with Philips, Pu 9100 series. The crystallinity of materials were estimated from X-ray diffraction (XRD) patterns recorded on Philips, Pw-1880 diffractometer, using Cu K α radiation type of scan continuous, V=40 KV, I=30 mA. Mineral CLI from province of Semnan was prepared and ground to a powder. The results of

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chemical analysis, and XRD pattern are given in Table 1 and Figure 1.

1. 25 ml of water (containing 4 ppm Ca^{2+}) was mixed with desirable amount of CLI (Table 2, Figure 2). After stirring for 2 h, the solution was filtered and concentration of Ca^{2+} in filtrate was determined by AAS.
2. One gram of CLI was added to 25 ml of water with different concentration of Ca^{2+} (Table 3, Figure 3). After stirring for 2 h, the percentage of its absorption in different filtrates was determined.
3. 0.5 g of CLI was treated with 25 ml of water (containing 10 and 50 ppm Ca^{2+}), after stirring for 2 h, the absorption of filtrate solution was determined; The same experiment was carried out, but the stirring time was extended to 24 h. The results are given in Table 4 and Figure 4.
4. Activation of CLI: Natural CLI (5g) was mixed with 25 ml of sodium chloride solution (2%) and stirred for four hours. After filtration, the filtered was washed with distilled water, and then was dried. Then 0.5 g of activated CLI was treated with 25 ml of city water and a solution containing 50 ppm of Ca^{2+} . We have included the results with natural CLI for comparison (Table 5).
5. 0.5 g of activated CLI was treated with 25 ml solution of Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Al^{3+} . After stirring for 2 h, the absorbance of filtrate solutions was determined by AAS. The results are given in Tables 6, 7, 8, 9, 10, respectively.
6. This experiment was similar to the experiment number 4, but instead NaCl, the CLI was treated with two different 2% and 5% solutions of NaOH. The results are shown in Tables 11, 12, respectively.

Results and Discussion

Recent discovery of deposits of CLI in Iran prompted us to study its sorption properties in dilute solutions. The XRD and chemical analysis of CLI are given in Figure 1 and Table 1. On the basis of XRD, the major mineral is clinoptilolite. The effect of the amount of CLI on sorption of Ca^{2+} in very dilute solutions is shown in Table 2 and Figure 2. According to the results of Table 2, increasing amount of CLI from 0.8 to 1 g does not change the capacity of absorption in dilute solutions. By increasing the concentration of Ca^{2+} in solution from 7.5 to 125 ppm, the percentage of absorbance of Ca^{2+} was reduced from 95.2 to 28% (Table 3, Fig. 3).

In order to increase the cationic exchange capacity of CLI, it was treated with sodium chloride solution. Comparison of the results of natural and activated CLI (Table 5), shows that the activated CLI capacity for Ca^{2+} in water (13 ppm Ca^{2+}) increases from 71% to 92.3% and for 50 ppm solution of Ca^{2+} from 42.6 to 76%. Therefore the activation increases the sorption ability by

the amount of 30%. The results given in Table 4 show that the increasing time from 2 to 24 h doesn't show additional effect on CLI capacity.

On the basis of the results shown in Table 6 and Figure 5, it is evident that up to 25 ppm solution of Cu^{2+} ion, about 97.14% absorbance is observed. By increasing to 70 ppm the absorbance is decreased to 87.55%. In a similar manner the capacity of activated CLI was studied in absorbance of Zn^{2+} . The results show that up to 40 ppm solutions, 93.30% absorbance is observed (Table 7, Fig. 6).

The tendency for absorbance of Cd^{2+} is shown in Table 8 and Figure 7. According to the results shown in Table 9 and Figure 8, it is evident that up to (500 ppm) solution of Pb^{2+} ion, about 99.2% absorbance is observed which indicates very good tendency for absorbance of Pb^{2+} ions from contaminated solutions. The capacity for absorbance of Al^{3+} ions in solution is much less than Pb^{2+} . The results are given in Table 10 and Figure 9.

If CLI is activated by sodium hydroxide solution (2%), its absorbance ability is increased so that 100% of Ca^{2+} ions are absorbed in 50 ppm solution. By increasing the concentration of Ca^{2+} from 125 to 500 ppm, the absorbance varies from 73.12 to 25.6% (Table 11). The absorbance results with CLI activated by 5% solution of sodium hydroxide are also shown in Table 12. In this table, the results are compared with those obtained from the activated CLI by 5% NaCl solution. Comparison of the results shown in Tables 11 and 12, indicated that although the absorbance ability of CLI activated with NaOH solutions of 2% and 5% is similar, but activation with sodium hydroxide solution of 5% is much better than sodium chloride solution of 5%.

Finally it should be mentioned that using NaCl as activator of CLI, is recommended instead of NaOH in the case of drinking water purification although, the latter is a more effective activator, since NaCl does not change the quality of water.

Conclusion

In this report, we have shown that the natural Iranian clinoptilolite activated with NaCl solution successfully eliminates some heavy and toxic metal ion from contaminated water. Our results clearly indicate that around 99% of these metal ions are removed when dilute solutions are treated with activated CLI. Moreover, we showed that when we used sodium hydroxide solution for activation, the absorption of Ca^{2+} in dilute solutions (up to 125 ppm) was about twice more than CLI activated by sodium chloride solution.

Table 1. Chemical compositions of CLI

Elements	%W/W ^a
SiO_2	67.85

Al ₂ O ₃	10.35
CaO	4.20
MgO	0.37
Na ₂ O	1.15
K ₂ O	0.94
TiO ₂	0.16
Fe ₂ O ₃	0.56
SO ₃	0.01
L.O.I	14.16

^a%W/W. g of a certain type of atoms in oxide from/100g

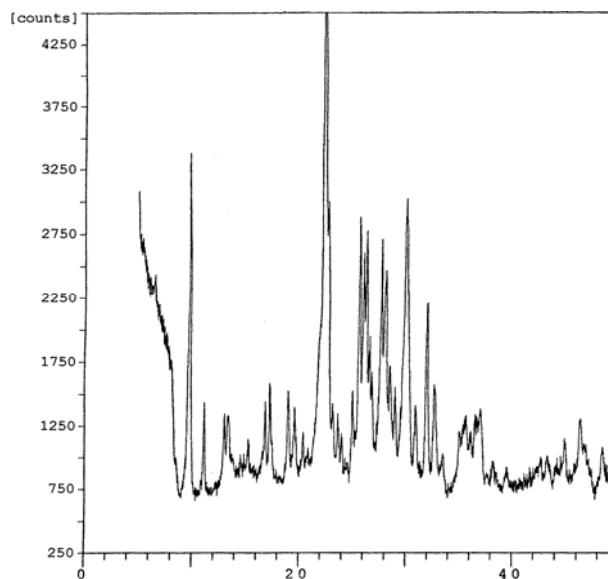


Figure 1. XRD pattern of natural CLI.

Table 2. Effect of amount of CLI on absorption of Ca²⁺ in very dilute solutions (4ppm)

Number	CLI (g)	Concentration of Ca ²⁺ absorbed (ppm)	Percent of absorption
1	0.2	0.889	22.20
2	0.4	2.680	66.67
3	0.6	3.000	75.00
4	0.8	3.305	82.62
5	1.0	3.305	82.62

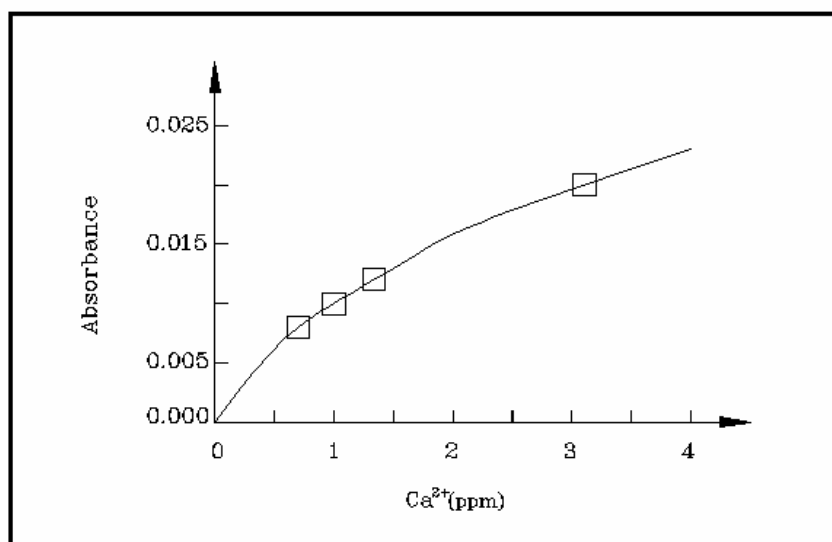
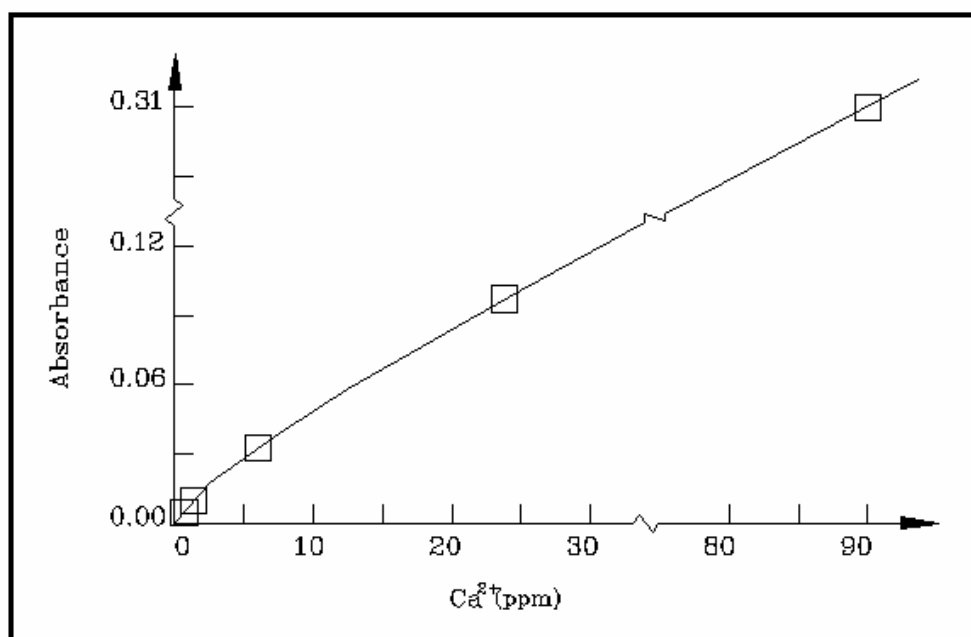


Figure 2. Ion exchange isotherm plot for desirable amount of CLI in very dilute solutions.

Table 3. Amount of Ca^{2+} ions (in Solution) absorbed by CLI

Number	Concentration of Ca^{2+} (ppm)	Concentration of Ca^{2+} absorbed (ppm)	Percent of absorption
1	7.5	7.14	95.2
2	12.5	11.50	92.0
3	25.0	18.93	75.7
4	50.0	26.16	52.3
5	125.0	34.95	28.0

**Figure 3.** Ion exchange isotherm plot for $\text{Ca}^{2+} \leftrightarrow \text{Na}^+$ exchange in CLI.**Table 4.** The effect of time on absorbance of CLI in very dilute solutions^a

Number	Time (h)	Concentration of Ca^{2+} (ppm)	Concentration of Ca^{2+} absorbed (ppm)	Percent of absorption
1	2	10	7.65	76.50
2	24	10	7.86	78.60
3	2	50	24.10	48.10
4	24	50	24.40	48.87

^ain each experiment 0.5 g of CLI were used

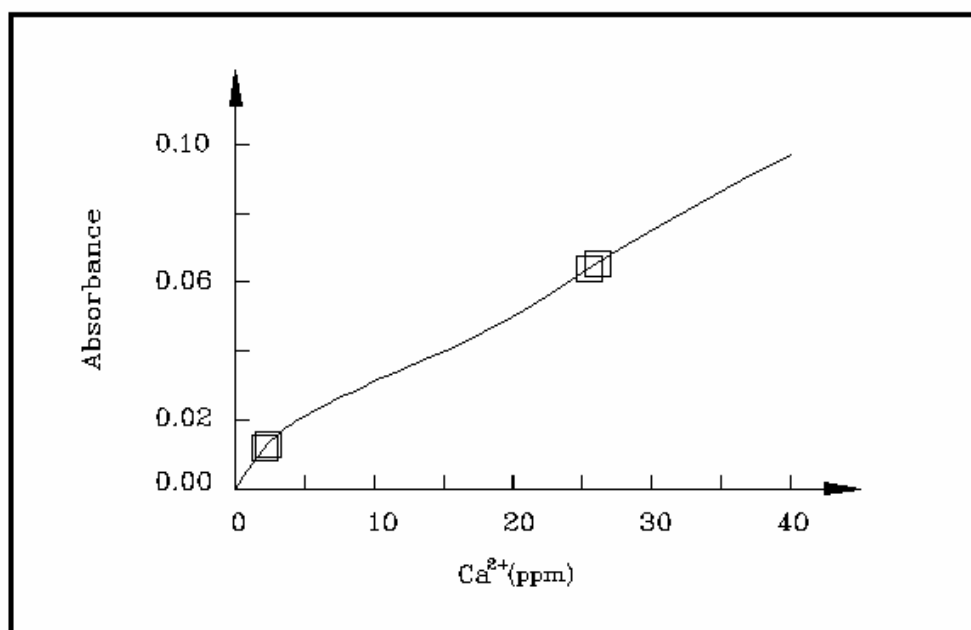


Figure 4. Ion exchange isotherm plot of water containing 10 and 50 ppm Ca^{2+} solution after 2 and 24 h.

Table 5. Comparison between activated CLI and natural CLI

Number	Sample	Concentration of Ca^{2+} absorbed (ppm)	Percent of absorption
1	CLI with 13 ppm Ca^{2+} solution	9.25	71.0
2	CLI with 50 ppm Ca^{2+} solution	21.30	42.6
3	Activated CLI with 13 ppm Ca^{2+} solution	12.00	92.3
4	Activated CLI with 50 ppm Ca^{2+} solution	38.00	76.0

Table 6. Amount of Cu^{2+} ions (in solution) absorbed by activated CLI

Number	Concentration of Cu^{2+} (ppm)	Concentration of Cu^{2+} absorbed (ppm)	Percent of absorption
1	5	4.66	93.13
2	15	14.42	96.13
3	25	24.29	97.14
4	50	48.35	96.70
5	60	54.63	91.04
6	70	61.29	87.55

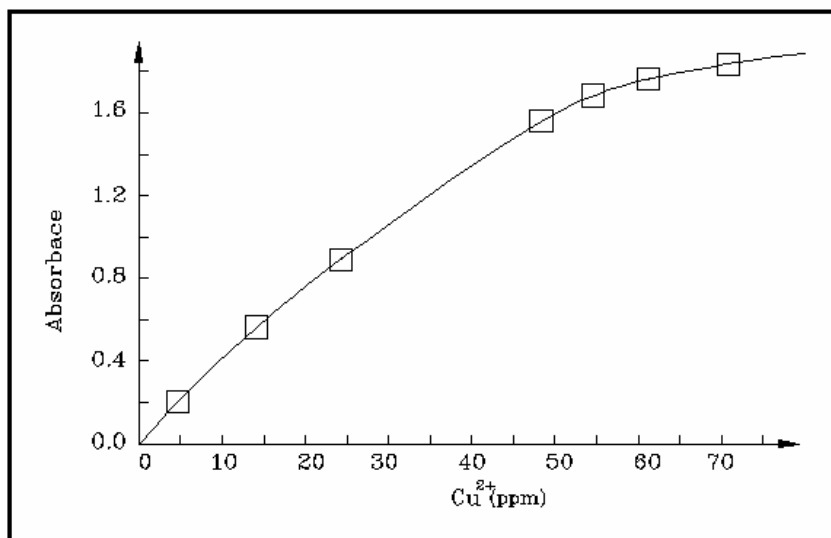


Figure 5. Ion exchange isotherm plot for $\text{Cu}^{2+} \leftrightarrow \text{Na}^+$ exchange in CLI.

Table 7. Amount of Zn^{2+} ions (in solution) absorbed by activated CLI

Number	Concentration of Zn^{2+} (ppm)	Concentration of Zn^{2+} absorbed (ppm)	Percent of absorption
1	5	4.86	97.14
2	15	14.85	98.94
3	25	24.49	97.96
4	40	37.32	93.30

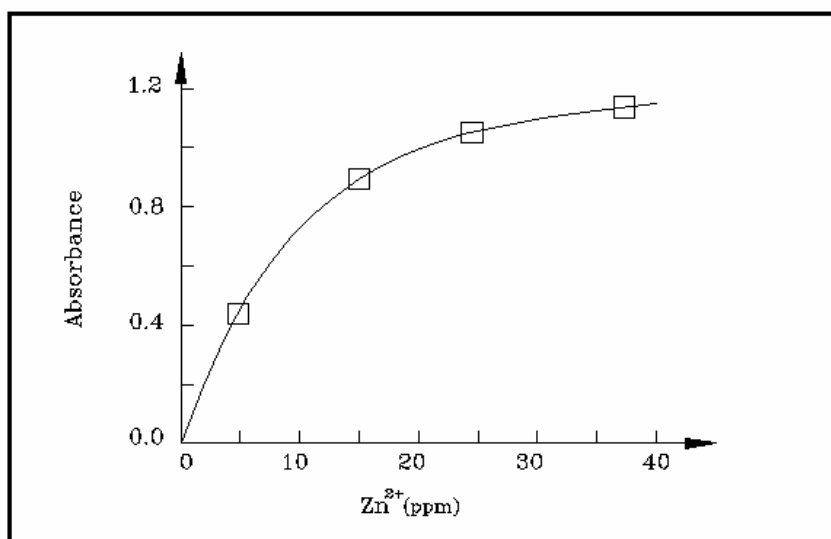
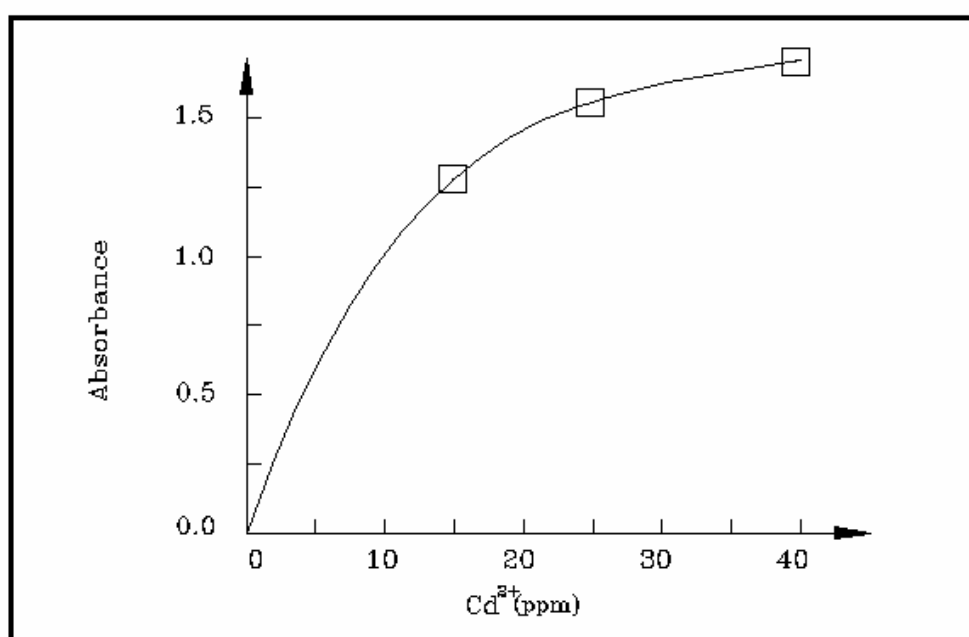


Figure 6. Ion exchange isotherm plot for $\text{Zn}^{2+} \leftrightarrow \text{Na}^+$ exchange in CLI.

Table 8. Amount of Cd^{2+} ions (in solution) absorbed by activated CLI

Number	Concentration of Cd^{2+} (ppm)	Concentration of Cd^{2+} absorbed (ppm)	Percent of absorption
1	5	–	~100.00
2	15	14.90	99.30
3	25	24.85	99.38
4	40	39.65	99.12

**Figure 7.** Ion exchange isotherm plot for $\text{Cd}^{2+} \leftrightarrow \text{Na}^+$ exchange in CLI.**Table 9.** Amount of Pb^{2+} ions (in solution) absorbed by activated CLI

Number	Concentration of Pb^{2+} (ppm)	Concentration of Pb^{2+} absorbed (ppm)	Percent of absorption
1	50	49.5	99.0
2	200	199.4	99.7
3	350	348.8	99.6
4	500	490.0	99.2

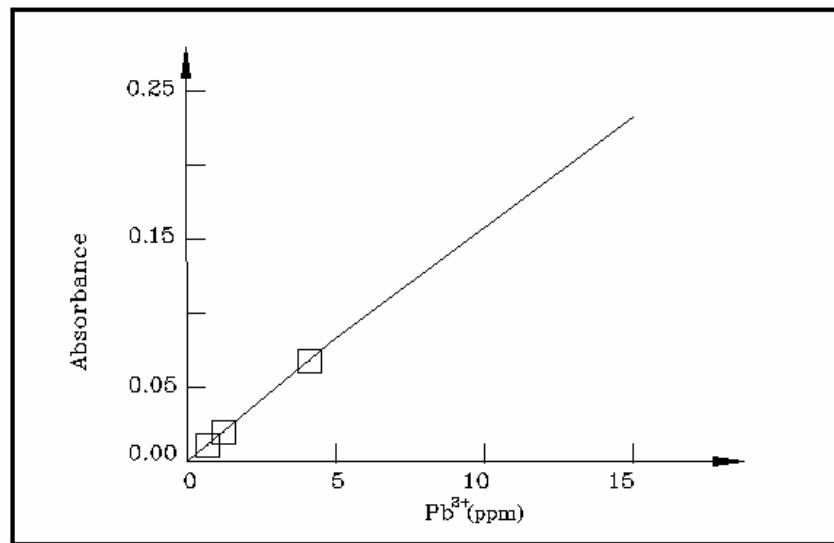


Figure 8. Ion exchange isotherm plot for $Pb^{2+} \leftrightarrow Na^+$ exchange in CLI.

Table 10. Amount of Al^{3+} ions absorbed by activated CLI

Number	Concentration of Al^{3+} (ppm)	Concentration of Al^{3+} absorbed (ppm)	Percent of absorption
1	5	4.50	90.00
2	15	12.43	82.85
3	25	15.23	61.20
4	35	20.00	57.14

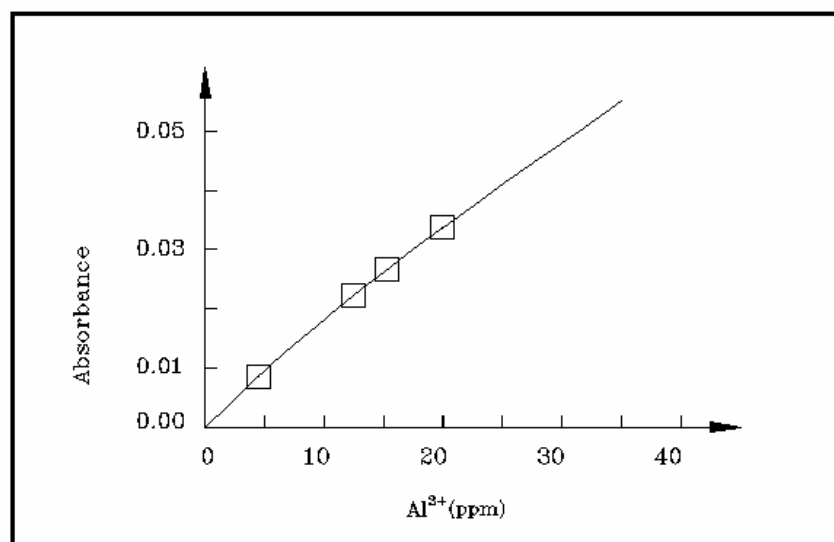


Figure 9. Ion exchange isotherm plot for $Al^{3+} \leftrightarrow Na^+$ exchange in CLI.

Table 11. The capacity of activated CLI with NaOH (2%)

Number	Concentration of Ca ²⁺ (ppm)	Concentration of Ca ²⁺ absorbed (ppm)	Percent of absorption
1	500	128.0	25.60
2	250	113.5	45.40
3	125	46.0	73.12
4	50	50.0	100.00

Table 12. Comparison of activated CLI with two different reagents (NaCl 5% and NaOH 5%)

Number	Concentration of Ca ²⁺ (ppm)	Percent abso. of Ca ²⁺ (activated CLI with NaCl)	Percent abso. of Ca ²⁺ (activated CLI with NaOH)
1	500	16.68	25.72
2	250	25.60	40.60
3	125	37.20	71.96

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