



Original Research Article

Synthesis and Characterization of Zeolite and Its Application in Adsorption of Nickel from Aqueous Solution

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ABSTRACT

The Synthesis and Characterization of Zeolite and its Application in Adsorption of Nickel from Aqueous Solution were investigated. Synthesis of zeolite was performed at 90 °C for 8 h. The size of the resulting crystals increased with an increase in the water content of the reaction mixture. The synthesized zeolite was characterized by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) techniques. Crystal structure of the product was determined as zeolite X by XRD. The concentration of the nickel ion was determined using atomic absorption spectrophotometer (AA 320 – ON). Removal efficiency of nickel ion was dependent on the contact time and adsorbent dosage. The effect of adsorbent dosage of 0.5-4.5 g showed that there was an increase in the adsorption capacity when the adsorbent dose was increased from 2.0-4.0 g. The effect of contact time at 10, 20, 30, 45, 60, 75 and 90 min was analysed and it was evident that adsorption of nickel was rapid in the first 40 min followed by a gradual increase until equilibrium was attained. Adsorption data was interpreted in terms of Langmuir and Freundlich isotherms. It was observed that the experimental data fitted better to Langmuir model with a correlation factor (R²) value of 0.993 compared to Freundlich with R² value of 0.980. The result showed that zeolite X was effective in the removal of Ni²⁺ ion from aqueous solution.

Keyword: Nickel ion; sodium hydroxide (NaOH); aluminium oxide (Al₂O₃); silicon dioxide; nickel nitrate

INTRODUCTION

In a classical sense, zeolites are crystalline aluminosilicates with a large variety of well-defined three dimensional framework. (SiO₄) [4] and (AlO₄) [5] tetrahedra are the primary building units. They form different secondary building

units depending on their spatial arrangement and have been used extensively as ion exchangers, adsorbents, separation materials and catalyst [1-8]. Zeolites with different structures are known to be obtained by

synthesis either from aluminosilicate by hydrogel or by conversion of clay minerals [9-11].

Zeolite synthesis is known to be complex because the gel composition, alkalinity temperature, time and nature of starting materials do contribute in a specific way to the success of its crystallization [12]. Some works have been reported for the synthesis of zeolites [13]. Synthesized large crystals of zeolite X from gels with the composition of 4.76- Na₂O, 1- Al₂O₃, 3.5- SiO₂, 45-4H₂O and 5-8.3 TEA [14]. Synthesized zeolite X, P, hydroxysodalite etc. from waste sandstone cake via alkali fusion method [15]. Synthesized zeolite X from waste metals using silicon sludge and Al (OH)₃ from aluminum dross [16]. Synthesized zeolite X, from low grade bauxite using alkali fusion activation and hydrothermal reaction.

Zeolite X is a very attractive material for technological and environmental application. As a commercial material, zeolite X is used in separation of gases in permanent gas flow, aerobic digestion process, mild hydrocracking of maphthenic compound, hydrocracking of vacuum gas oil and especially in detergents as a water softening builder [17-21].

In this work, zeolite X was synthesized using hydrothermal method. The obtained zeolite X was applied in the adsorption of nickel²⁺ ion from aqueous solution.

MATERIALS AND METHODS

All reagents were of analytical grade. Sodium metasilicate (SiO₂. 95%), sodium hydroxide pellets (99%) and aluminatrichydrate (65% Al₂O₃), were purchased from Sigma Aldrich and used as received without further purification.

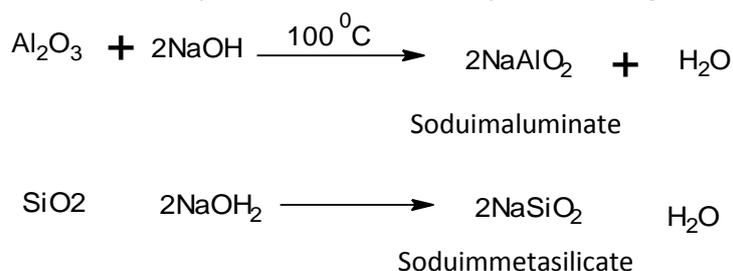
Nickel nitrate (M&B) purchased from Joe-Chem. in form of green colour crystals was used for the heavy metal analysis. Distilled water was used throughout the study.

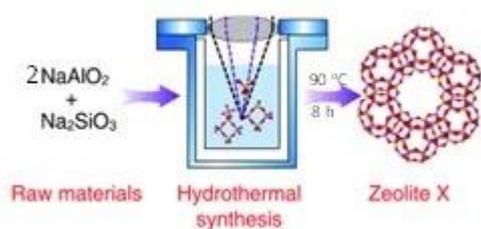
Zeolite synthesis

The synthesis of zeolite was carried out according to the method reported by [22]. The synthesis gel was prepared from two separate solutions. Solution A was prepared by reacting sodium hydroxide (NaOH) with aluminium oxide (Al₂O₃). The solution was stirred at 100 °C until dissolved and then cooled to 25 °C. Solution B was prepared by reacting sodium hydroxide with of silicon dioxide solution. The solution was stirred until dissolved.

Solution A was quickly added to solution B and stirred vigorously for 30 min. The mixture turned into a thick opaque gel which was then transferred into a cylindrical poly (tetraflouroethylene vessel) (PTFE vessel 90 mm length, 27 mm) placed in a tight PTFE pressure (MLS GmbH, HPV80, 100 mL).

Crystallization took place without agitation within 8–10 h. After crystallization, the pressure vessel was cooled in ice before opening. The upper part of the clear, strongly alkaline solution was decanted. The white residue was washed several times with hot distilled water and centrifuged until the pH of the supernatant became less than 10. The product was then air dried for approximately 14 h at 100 °C and equilibrated over saturated aqueous NaCl. Also increasing the H₂O content results in increasingly larger zeolite crystals with smoother surface because viscosity of the synthesis gel decreases and therefore transport of the species in the gel becomes faster.





Scheme 1: Synthesis of zeolite X

Batch equilibrium studies

Batch adsorption experiment was carried out according to the method reported by [23]. Batch adsorption experiment was conducted for the removal of nickel. Stock solution of nickel (1000 mg/L) was prepared with distilled water using nickel nitrate. All other solutions were prepared by diluting stock solution. Synthesized zeolite was left in contact with nickel ion solution. Samples were collected at 10, 20, 30, 45, 60, 75 and 90 min to determine the optimal contact time. The effect of adsorbent dosage of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 g per test solution were studied. The test bottles were agitated on a multifix mechanical shaker.

Characterization

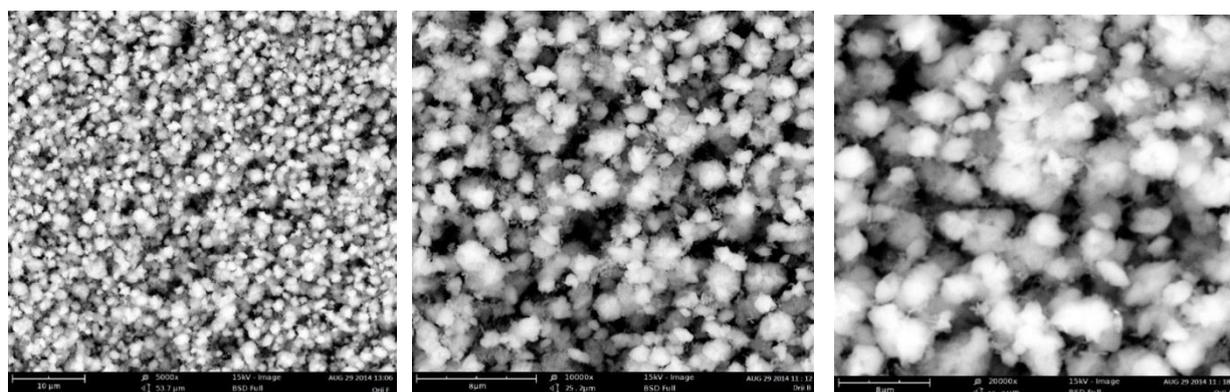
Characterization experiment was carried out according to the method reported by [24].

Philips Pan analytical, X'PERT PRO X-ray diffractometer (XRD) was used for the qualitative phase analysis, determination of the degree of crystallinity and unit cell dimension. Operating conditions involved the use of $\text{CuK}\alpha$ radiation of 40kV and 50mA. The samples were scanned from $5.0 - 99.9^\circ (2\theta)$. Scanning electron micrographs (SEM) were taken using camscan Apollo 200 to determine the particle morphology. The concentration of the residual heavy metal in the sorption medium was determined using fully automated pc controlled atomic adsorption spectrophotometer (AA 320-ON).

RESULT AND DISCUSSION

Composition and Structure

The progress of zeolitization reaction was observed through changes in the morphology of the starting material and synthesis products. The morphology of the synthesized sample as observed in the micrograph of figure 1 are similar to those presented by Kacirek and Lechert [22] and Ozgul D. O. et al [24]. Figure 1 shows the scanning electron micrograph of zeolite X from a starting gel composition (21.8 NaOH-9.75 $\text{Al}_2\text{O}_3 - 21.97 \text{SiO}_2 - \text{dH}_2\text{O}$) and increasing the amount of H_2O ; 1 = 110 mL; 2 = 118 mL; 3 = 120 mL 4= 125 mL; 5 = 127 mL; 6=132 mL and 7=140 mL.



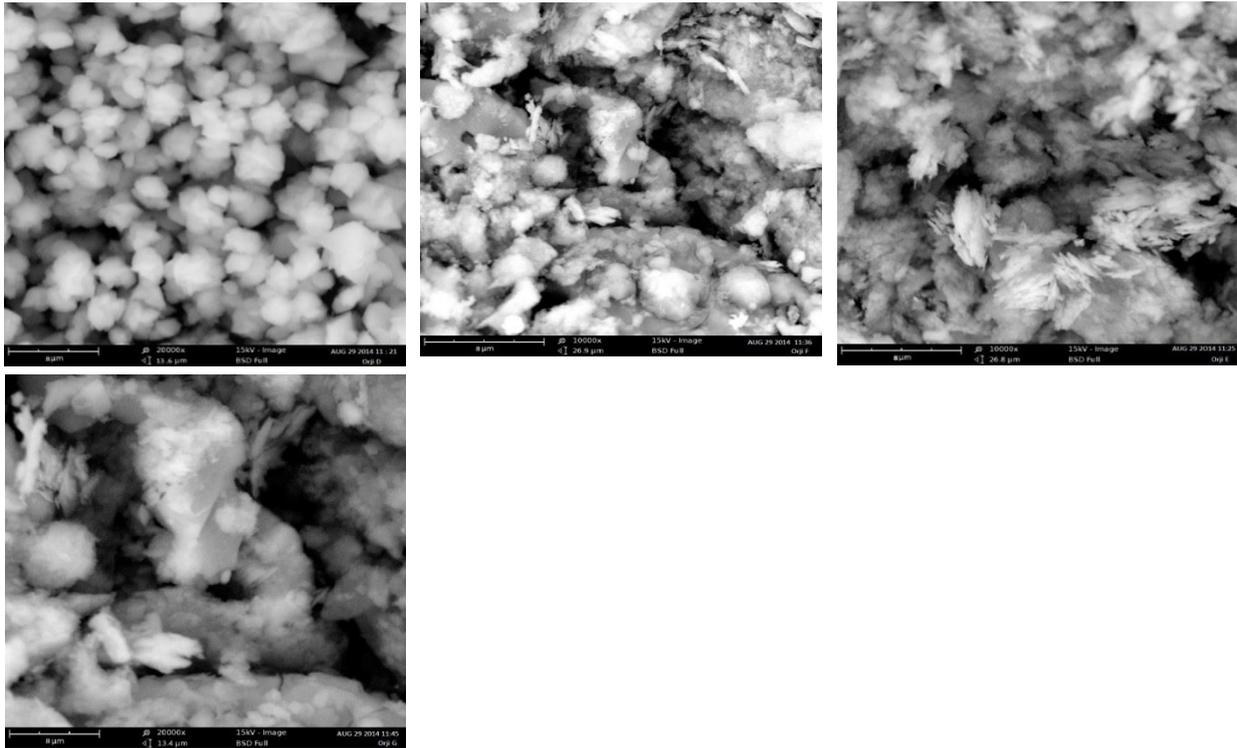


Fig. 1: Scanning Electron Micrograph (SEM) image of the synthesized zeolite

The X-Ray diffraction analysis gave useful information about the crystalline and amorphous changes of an adsorbent. The mineral phases present in figure 2 were

identified by comparison with the Joint Committee in Powder Diffraction Standard - International Centre for Diffraction [JCPDS – ICD] reference library [24].

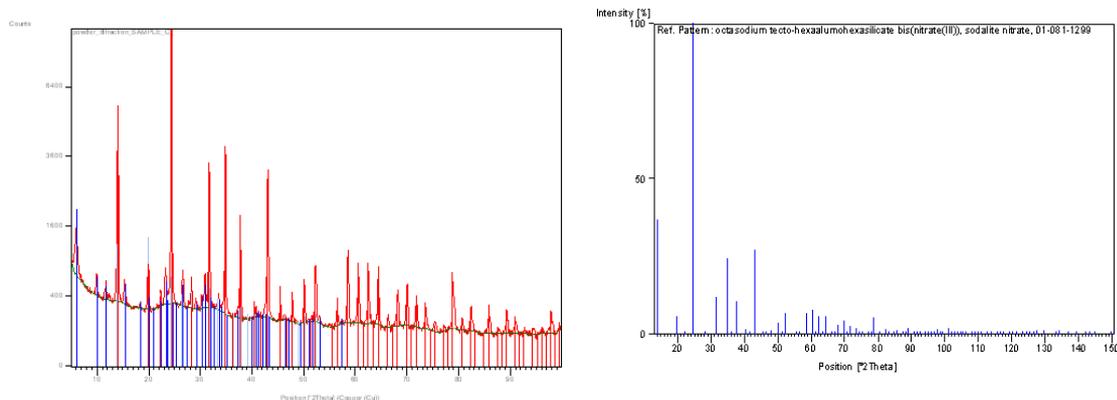


Fig. 2: X-Ray diffraction result of the synthesized zeolite

Effect of amount of adsorbent

The effect of amount of adsorbent on the uptake of nickel was examined. Nickel ion removed versus amount of zeolite showed that the removal of the metal ions increases with an increase in the amount of zeolite. For nickel,

there was a substantial increase when the dose of zeolite was increased from 2.0 to 4.5 g because there were more sites for the adsorbate to be adsorbed. The increase in the removal efficiency was not so significant when the zeolite amount was further

increased as could be seen from figure 3 because competition for bonding sites between molecules of the adsorbate decreases with

increase in the dosage of the adsorbent. Table 1 and Figure 3 shows the adsorption capacity of Ni^{2+} ion using different zeolite dosage.

Table 1: Adsorption capacity of Ni^{2+} ion using different zeolite dosage.

Amount of adsorbent (g/l)	Amount adsorbed (mg/g)
0.5	11
1	12
1.5	13
2	15
2.5	23
3	30
3.5	38
4	44
4.5	44.5

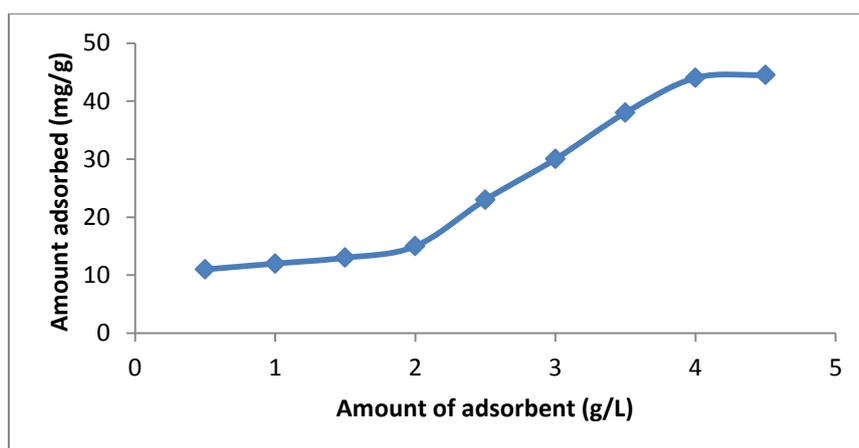


Fig. 3: Effect of amount of adsorbent on Ni^{2+} ion adsorption

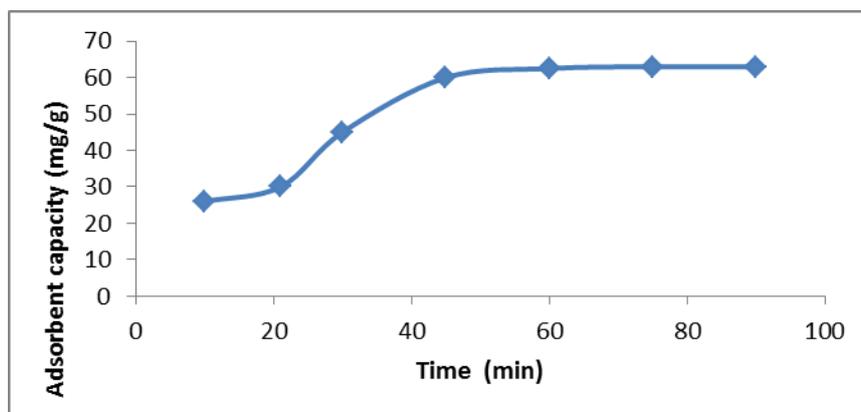
Effect of contact time

The effect of contact time on the adsorption of nickel was examined. The result showed that adsorption was rapid in the first 40 min followed by a gradual increase with time until equilibrium was attained. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in the solution and the number of vacant sites

available on the adsorbent surface. The attainment of equilibrium adsorption might have been due to reduction in the available active adsorption sites on the adsorbent with time resulting to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbent. Table 2 and Figure 4 Shows the adsorption capacity of Ni^{2+} ion onto zeolite at different contact time.

Table 2: Adsorption capacity of Ni²⁺ ion onto zeolite at different contact time

S/N	Time (min)	Adsorbent capacity
1	10	26
2	21	30
3	30	45
4	45	60
5	60	62.5
6	75	63
7	90	63.1

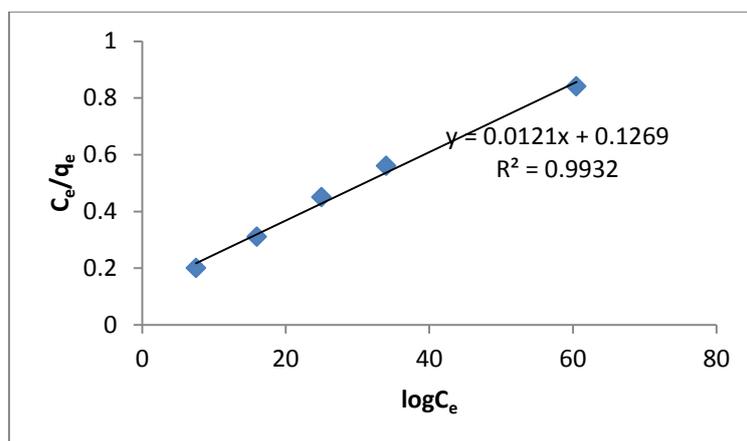
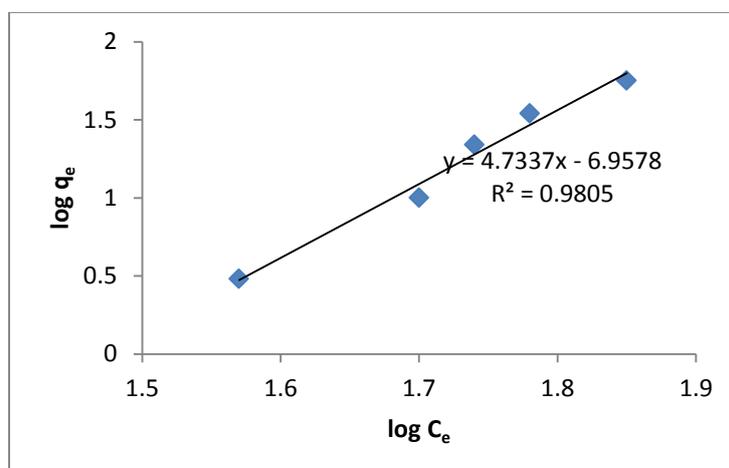
**Figure 4: Effect contact time on Ni²⁺ ion adsorption****Adsorption isotherm**

Adsorption isotherms are very important in describing the adsorption behaviour of solutes on specific adsorbents. Langmuir sorption isotherm models the monolayer coverage of the sorption surface and assumes that sorption occurs on a structurally homogenous adsorbent and all the sorption sites are energetically identical. The plot of (C_e/q_e) versus C_e showed that the experimental data fitted well in the linearized equation of the Langmuir isotherm over the whole Ni (II) ion concentration range studied. Linear plots of $\ln q_e$ versus $\ln C_e$

showed that Freundlich isotherm was also representative for the Ni adsorption by zeolite X. A plot of $\ln q_e$ versus $\ln C_e$ enables the empirical constants K_f and $1/n$ to be determined from the intercept and slope of the linear regression. In this study, Langmuir isotherm has a better fitting model than Freundlich as the former have higher correlation regression coefficient than the latter thus indicating the applicability of monolayer coverage of the Ni (II) ion on the surface of adsorbent. Table 3 Figure 5 Shows the Langmuir and Figure 6 the Freundlich isotherm data.

Table 3: Langmuir and the Freundlich isotherm data

c_e	c_e/q_e	q_e	$\log q_e$	$\log c_e$
7.1	0.2	37.5	1.57	0.88
16	0.31	51	0.70	1.20
25	0.45	55	1.74	1.39
34	0.56	60.34	1.78	1.53
60.4	0.84	72	1.85	1.78

**Fig.5: Langmuir isotherm plot for adsorption of Ni²⁺****Fig. 6: Freundlich isotherm plot for adsorption of Ni²⁺****CONCLUSION**

In this study, zeolite X was successfully synthesized by adding sodium metasilicate to aluminate solutions and was used as an adsorbent for Ni²⁺ ion removal from aqueous solution. The process parameters were optimized: contact time and adsorbent dose were found to have significant effects on Ni²⁺ ion adsorption. The adsorbent dose and contact

time showed increase in adsorption capacity until equilibrium was attained. The adsorption process fitted better in Langmuir isotherm model. The study showed that zeolite X is a good adsorbent for Ni²⁺ ion removal from wastewater.

REFERENCES

1. Apak R, Tutem E, Hugul M. Heavy metal cation retention by unconventional sorbent (red mud and fly ashes). *J Wat Res* 1998; 32: 430-434.
 2. Banerjee K, Cheremisinoff P N, Cheng SL. Adsorption kinetics of o-xylene by fly-ash. *J Wat Res* 1997; 31: 249-250.
 3. Danis TG, Albanis TA, Petrakis DE, Pomonis PJ. Removal of heavy metal mesoporous aluminum phosphate water. *J Wat Res* 1998; 32: 295-298.
 4. Panday KK, Prasad G, Singh VN. Copper II removal from aqueous solutions using fly ash. *J Wat Res* 1985; 19: 869-872.
 5. Williams CJ, Aderhold D, Edyvean RG. Novel biosorbents for the removal of metals from aqueous effluents. *J Wat Res* 1998; 32: 216-219.
 6. Baltpurvins KA, Burns RC, Lawrence GA, Suart AD. Effect of electrolyte composition on zinc hydroxide precipitation by lime. *J Wat Res* 1997; 31: 973-978.
 7. Rangel MJ, Streat M. Adsorption of cadmium by activated carbon cloth: influence of surface oxidation and solution pH. *J Wat Res* 2002; 42: 1244-1252.
 8. Halil H. Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk. *J Haz Mat* 2003; 97: 49-57.
 9. Aly HM, Daifullah AM. Potential use of bagasse pith for the treatment of wastewater containing metals. *J Adsorp Sci Technol* 1998; 16: 33-38.
 10. Vinod K, Gupta CK, Jain I, Ali M, Sharma VK. Removal of cadmium and nickel from wastewater using bagasse fly ash-a sugar industry waste water. *J Wat Res* 2003; 37: 4038-4044.
 11. Daneshvar N, Salari D, Aber S. Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions using soya cake. *J Haz Mat* 2002; 94B: 49-61.
 12. Dimitrova SV, Mehandgiev DR. Lead removal from aqueous solution using granulated blast furnace slag. *J Wat Res* 1998; 32: 3289-3292.
 13. Warzywoda J, Bac N, Jordan AS. Synthesis of large zeolite X crystals. *J Cryst Growth* 1990; 204: 539-541.
 14. Wajima T, Yashizuka K, Hiria T, Ikegami Y. Synthesis of zeolite X from waste sand-stone cake using alkali fusion method. *J Mat Transact* 2008; 49: 612-618.
 15. Hiraki T, Nosaka A, Okinaka N, Akiyama T. Synthesis of zeolite X from waste metals. *ISIJ Int* 2009; 49: 1644-1648.
 16. Wang C, Zhou J, Wang Y, Yang M, Li T, Meng C. Synthesis of zeolite X from low grade bauxite. *J Chem Technol Biotechnol* 2013; 88: 1350 – 1357.
 17. Denny AF, Geoffrey AJ, Sherman JD. Sequestering of Ca²⁺ and Mg²⁺ in aqueous media using zeolite mixtures. *US Patent* 4094778. 1978;125: 203-209
 18. Barakat MA. New trends in removing heavy metals from industrial waste water. *J Arab Chem* 2010; 44: 209- 219.
 19. Novembre D, Sabatino D, Gimeno D. Synthesis of the Na-X zeolite from tripolaceous deposit (Cortina Italy) and volcanic zeolitized rocks (Visco Volcanom Italy). *Microp Mesop Mater* 2004; 75: 1-11.
 20. Stucky GD, Dwyer FG. *ACS Symposium Series* 218. Washington DC: American Chemical Society; 1983, p 20.
 21. Holler A, Barth-Wirsching U. Zeolite Formation from Fly Ash. *Fortschritte der Miner.* *Fortschritte der Miner* 2010; 63: 21-43.
 22. Lechert H, Kacirek H. The kinetics of nucleation of X zeolites. *Zeolites* 1992; 13: 192-200.
 23. Surinder S, Lokesh KV, Sambhi SS, Sharma S. K. Adsorption behavior of Ni(II) from water onto zeolite X: kinetics and equilibrium studies. *Proceed of the World Congress on*
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Engineering and Computer Science; 2008, 1-6.

24. PDF - 2 Data Base JCPDS - ICDD, JCPDS - Newton Square, PA, USA: International Centre for Diffraction Data; 1997.

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