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Removal of Nickel(II) from Aqueous Solutions by Adsorption with Modified ZSM-5 Zeolites

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Abstract: The sorptive removal of nickel ion from aqueous solutions using modified ZSM-5 zeolites was investigated. Experiments were carried out as a function of solute concentration and different temperatures. Mesoporous material of ZSM-5 zeolite was modified with phosphoric acid by wet method. The modified zeolite was converted to Na⁺ form using aqueous NaHCO₃ solution. The Na⁺ form of modified zeolite, represented as PNa₂-ZSM-5 was characterized by XRD, BET, SEM and AAS techniques. It was then tested for ion exchange with aqueous Ni(SO₄) solution. The Ni²⁺ content of the solution was analyzed by AAS. Phosphoric acid modified PNa₂-ZSM-5 zeolite shows higher adsorption capacity than the parent Na-Y zeolite. Equilibrium modeling data were fit to linear Langmuir model then the Freundlich model. These parameter confirmed that sorption of Ni²⁺ is feasible spontaneous and endothermic.

Keywords: Nickel removal, Modified zeolites, Ion exchange, Isotherms.

Introduction

Several environmental and health problems, associated with the metal contamination of the natural systems (soil and water) are arising from mining industries, smelting, brass, metal coating, silver refineries, electroplating and several other industrial activities¹⁻². The main symptoms of nickel causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness³. Among the methods such as precipitation, oxidation, ultrafiltration, reverse osmosis and elctrodialysis, ion exchange on natural zeolites seems to be more attractive method. Zeolites have been intensively studied recently because of their applicability in removing trace quantities of heavy metal ions from aqueous solution by utilizing the ion exchange phenomenon⁴⁻⁶.

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates”. The structure of zeolites consists of three dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atom, while the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice⁷. But hitherto only unmodified zeolites have been examined for ion exchange capacity, in which one mole of sodium ion is exchanged for every mole of Al^{3+} present in the framework of zeolite. There have been reports of modification of zeolite with H_3PO_4 , for catalytic application. In the present study, ZSM-5 zeolite has been modified for removal of Ni^{2+} ion from aqueous solution. Each mole of phosphoric acid introduced into the zeolite provides two moles of exchangeable protons, which can be replaced by Na^+ ions using mild base like NaHCO_3 ⁸. The results obtained from this study are important for ion exchange and water softening applications.

Experimental

HZSM-5 zeolite was purchased from Sud-Chemie India Ltd, Mumbai, India. Nickel Sulphate was obtained from Qualigens Fine Chemicals Ltd., Mumbai, India. All other chemicals used were of analytical reagent grade, procured from Rankem Fine Chemicals Ltd, New Delhi, India.

Preparation of modified zeolite

About 4 g of HZSM-5 zeolite in 40 mL of double distilled water was mixed with 0.385 g of phosphoric acid. The mixture was kept under vigorous stirring at 60 °C for 3 h and then evaporated to dryness in an air oven at 120 °C. Phosphoric acid modified zeolite was contacted with 30 mL of aqueous NaHCO_3 solution under vigorous stirring at 60 °C for 3 h to obtain the disodium form of an PNa_2 -ZSM-5 zeolite. It was then filtered, washed with water and dried in air oven at 120 °C overnight before use. Figure 1 illustrates the sequence of occurrences in the above treatment. The Na- ZSM-5 zeolite was prepared by adding NaHCO_3 solution directly with H ZSM-5 zeolite.

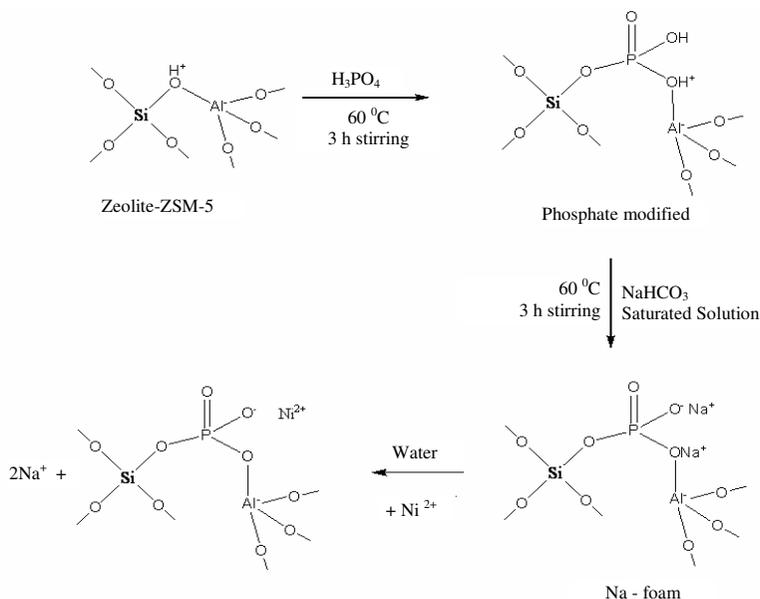


Figure 1. Reaction schemes illustrating modification of PNa_2 -ZSM-5 zeolites.

Ion-exchange equilibrium experiments

The ion exchange capacity of Ni^{2+} ion with modified Na-ZSM-5 and PNa_2 -ZSM-5 zeolites were studied using a batch method. The batch experiments were carried out with 20 mL of 50 m mol Ni^{2+} solution. About 65 mg of the adsorbent was added and the uptake of the zeolite was determined. The pH of the solution was measured using a pH meter (Elico Model LI-120, Hyderabad, India). Adjustments of pH were made with 0.1 M HCl and 0.1 M NaOH solutions. The screw cap bottle containing the adsorbate and adsorbent were placed in the thermostatic orbital shaker (Neolab, Mumbai, India) and were shaken at a constant speed of 200 rpm. After equilibrium time, the samples were centrifuged and the filtrates were analyzed. The kinetic studies were carried out in magnetic stirrer 50 m mol Ni^{2+} solutions. About 50 mg of the adsorbent was added. The samples were withdrawn from the stirrer at a regular time intervals and the samples were centrifuged. The absorbance of supernatant solution was measured using Atomic absorption spectrophotometer (SHIMADZU, AA-6300). The uptake and the amount of Ni^{2+} ion exchanged by the modified zeolites were computed using the following equations.

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

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2)$$

Where, q_e is the amount of exchanged Ni^{2+} ions (m mol/g), C_o and C_e are the initial and equilibrium concentration of Ni^{2+} ion in solution (m mol/L) respectively V is the solution volume and m is mass of the adsorbent (g).

Results and Discussion

Characterization of modified zeolite

The BET surface areas of both modified Na-ZSM-5 and PNa_2 -ZSM-5 zeolites were measured using Smart Sorbs 92 Surface area analyzer where N_2 gas was used as adsorbate. The surface areas of modified Na-ZSM-5 and PNa_2 -ZSM-5 zeolites were 385 and 422 m^2/g respectively. The XRD analysis of the modified Na-ZSM-5 and PNa_2 -ZSM-5 zeolites was measured using D-Max / 111 -VC Model with nickel filtered and Cu $K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The X-ray analysis reveals the absences of structural degradation during modification are shown in Figure 2.

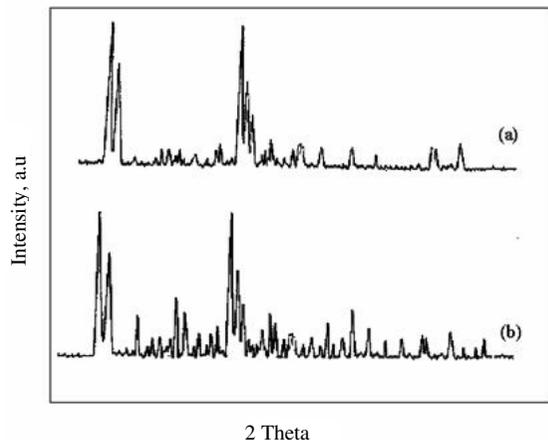


Figure 2. X-ray powder diffraction patterns of (a) Na-ZSM-5 (b) PNa_2 -ZSM-5 zeolites.

Scanning electron microscope (SEM) images were taken to study the surface morphology of zeolite particles using a Joel Jsm-6360 scanning electron microscope. The SEM pictures of the parent H-ZSM-5, Na-ZSM-5 and PNa₂-ZSM-5 zeolites are shown in Figure 3 (a, b and c) respectively. The modification of PNa₂-ZSM-5 zeolite might not have resulted any structural degradation of the parent zeolite.

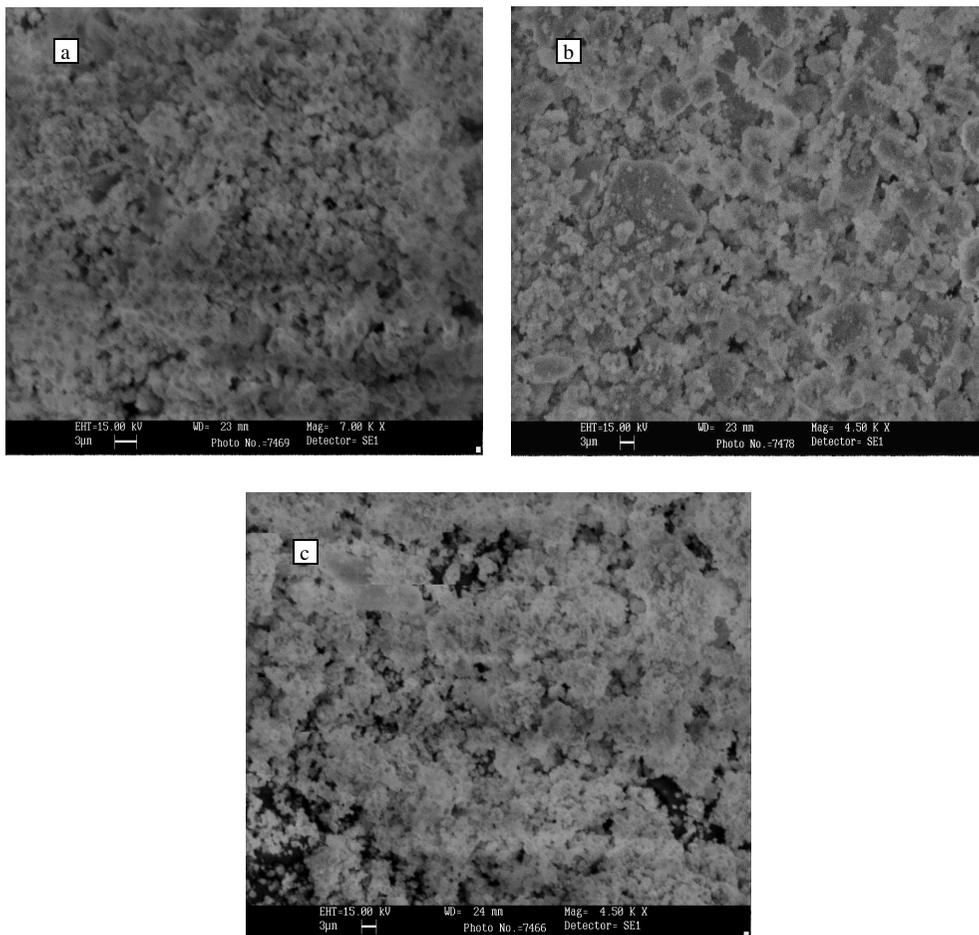


Figure 3. SEM image of (a) H-ZSM-5, (b) Na-ZSM-5 (c) PNa₂-ZSM-5 zeolites.

Effect of pH

The effect of pH of the suspending medium on nickel removal was studied by performing equilibrium sorption experiments at different pH values. The results are illustrated in Figure 4. For the PNa₂-ZSM-5 zeolite the uptake efficiency gradually increases as the pH increases from 3 to 4 in Ni²⁺. But above pH 4 Ni²⁺ uptake was observed which could be attributed to precipitation. The Na-ZSM-5 zeolite also exhibited similar the behavior. Hence optimum pH range for the removal of Ni²⁺ was found to be 4. The PNa₂-ZSM-5 zeolite showed higher uptake than the Na-ZSM-5 zeolites as shown in Figure 4 as it contains more exchangeable Na⁺ ions than latter.

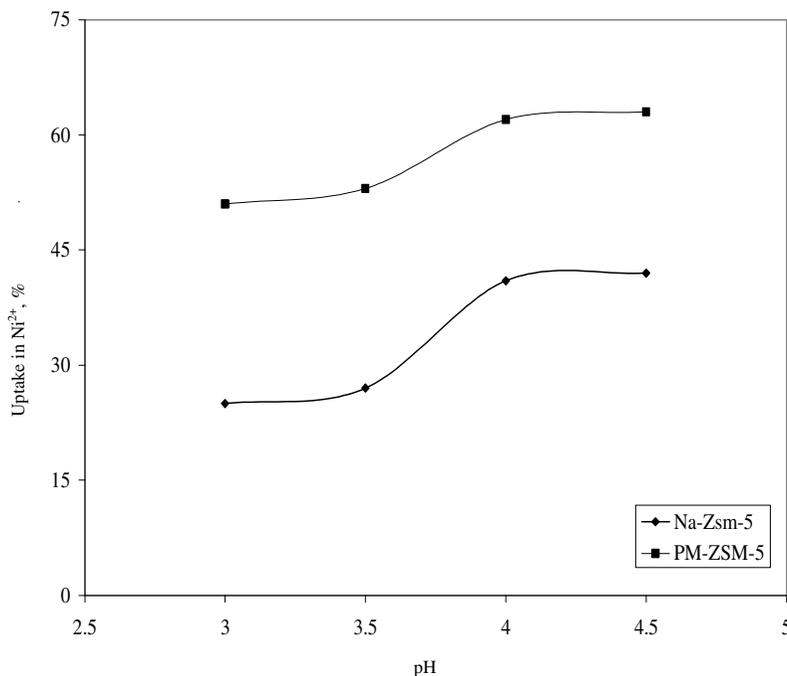


Figure 4. Effect of pH in Ni^{2+} ions from aqueous solutions onto (\blacklozenge) Na-ZSM-5 and (\blacksquare) PM-ZSM-5 zeolites.

Sorption isotherms

The sorption isotherms for the removal of Ni^{2+} at different temperatures were studied. It provides information on uptake capabilities and reflects the usual equilibrium process behavior. The Langmuir isotherm could be written⁹ as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where Q_0 is the monolayer adsorption capacity (m mol/g) and b is the constant related to the free energy of adsorption. The logarithmic form of Freundlich equation is given¹⁰ as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f is the relative adsorption capacity of the adsorbent (m mol/g) and $1/n$ is the constant indicative of the intensity of the adsorption process. The Langmuir isotherm correctly fitted than the Freundlich. The Langmuir as shown in Figure 5. The corresponding Langmuir and Freundlich parameters along with their correlation coefficients are given in Table 1.

The Langmuir constants Q_0 and b are increases with increase of temperature showing that the sorption capacity and intensity of the sorption are enhanced at higher temperatures. Hence, the active surface available for sorption has increased with increase of temperature. Recently there have been many reports on the sorption of Ni^{2+} with different adsorbents and the results are presented in Table 2.

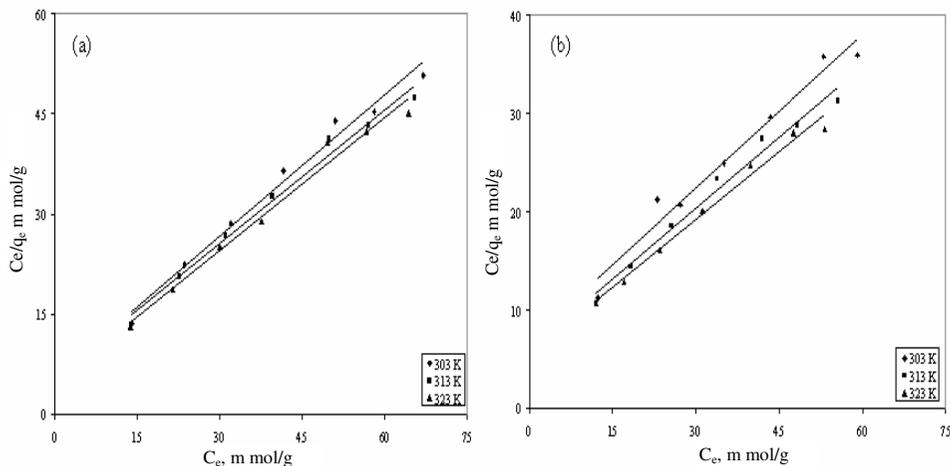


Figure 5. Langmuir isotherm plots for the sorption of Ni²⁺ ions from aqueous solutions onto (a) Na-ZSM-5 (b) PNa₂-ZSM-5 zeolites.

Table 1. Langmuir and Freundlich isotherm plots for the sorption of Ni²⁺ ions from aqueous solutions onto Na-ZSM-5 and PNa₂-ZSM-5 zeolites.

| Temp (K) | Langmuir isotherm | | | Freundlich isotherm | | |
|---------------------|--------------------------|------------|-----------------------------|---------------------|--------------------------|-----------------------------|
| | Q ₀ , m mol/g | b, L/m mol | R ² _L | 1/n | K _f , m mol/g | R ² _F |
| Na-Y | | | | | | |
| 303 | 0.82 | 0.981 | 0.989 | 0.28 | 0.52 | 0.931 |
| 313 | 0.98 | 0.102 | 0.987 | 0.26 | 0.61 | 0.952 |
| 323 | 1.04 | 0.115 | 0.992 | 0.24 | 0.72 | 0.962 |
| PNa ₂ -Y | | | | | | |
| 303 | 1.25 | 0.121 | 0.993 | 0.20 | 0.37 | 0.928 |
| 313 | 1.32 | 0.135 | 0.996 | 0.18 | 0.40 | 0.975 |
| 323 | 1.48 | 0.148 | 0.997 | 0.17 | 0.51 | 0.992 |

Table 2. Adsorption capacities Q⁰ (mg/g) for some zeolite materials

| Adsorbent | Ni(II), mg/g |
|---|--------------|
| Kaolinite ¹¹ | 0.003 |
| Ball Clay ¹¹ | 0.41 |
| Kaolinite ¹² | 1.70 |
| Na-Montmorillonite ¹³ | 3.63 |
| Exfoliated Clay ¹¹ | 5.91 |
| Clay treated with HC ¹⁴ | 10.9 |
| Natural zeolite ¹² | 12.5 |
| Clay treated with NaC ¹⁴ | 14.5 |
| Natural zeolite ¹² | 19.3 |
| Modified Na-ZSM-5 zeolite ^a | 28.08 |
| H ₃ PO ₄ - modified ZSM-5zeolite ^a | 39.96 |

(^aPresent study)

Kinetic studies

Pseudo-first order kinetic model

The linear form of Lagergren's first order expression¹⁵ is written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where, k_1 (min^{-1}) is the first order adsorption rate constant, q_e is the amount of metal adsorbed at equilibrium and q_t is the amount adsorbed at time ' t '. The first order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the sorption processes¹⁶. The first order rate constant is given in Table 3.

Pseudo second order kinetic model

The linear form of pseudo- second -order rate model and¹⁷ is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where, plotting t/q_t against " t " for Ni^{2+} removal at different temperatures is presented in Figure 6. The relationship is linear, and the correlation between the parameter also explains that the process of sorption of each ion follows pseudo second order kinetics. The product $k_2 q_e^2$ is the initial sorption rate represented as $h = k_2 q_e^2$ from Table 3. It can be shown that the values of the initial sorption rate ' h ' and the rate constant ' k_2 ' increase with increase in temperature.

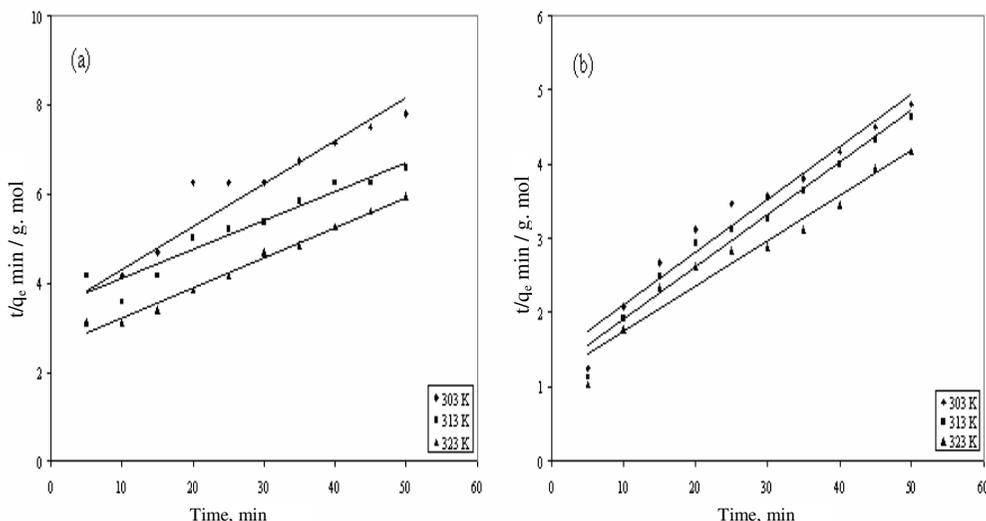


Figure 6. Pseudo-second-order kinetics plots for the sorption of Ni^{2+} ions from aqueous solutions onto (a) Na-ZSM-5 (b) PNa₂-ZSM-5 zeolites.

The correlation coefficient R^2 has an extremely high value, and its calculated equilibrium sorption capacity ' q_e ' is consistent with the experimental data. The results suggest that the pseudo-second order sorption mechanism is predominant and that the overall rate constant of each ion appears to be controlled by the chemisorption process¹⁷.

Table 3. The calculated parameters of the pseudo-first order and pseudo-second order kinetic models of Ni²⁺ ions from Na-ZSM-5 and PNa₂-ZSM-5 zeolites.

| Temp, K | Pseudo-first order | | | Pseudo-second order | | | |
|---------------------|---------------------------------------|-----------------------------|-----------------------------|-----------------------------|---------------|---------------------------------|-----------------------------|
| | k ₁ , min ⁻¹ | q _e , m mol/g | R ² ₁ | q _e , m mol/g | h, m mol/g | k ₂ , g/m mol min | R ² ₂ |
| Na-Y | | | | | | | |
| 303 | 0.029 | 0.610 | 0.981 | 0.72 | 0.521 | 0.517 | 0.993 |
| 313 | 0.035 | 0.728 | 0.952 | 0.85 | 0.752 | 0.682 | 0.989 |
| 323 | 0.041 | 0.819 | 0.983 | 0.91 | 0.851 | 0.714 | 0.995 |
| PNa ₂ -Y | | | | | | | |
| 303 | 0.032 | 0.852 | 0.937 | 0.98 | 0.901 | 0.782 | 0.991 |
| 313 | 0.047 | 0.938 | 0.975 | 1.02 | 1.237 | 0.915 | 0.993 |
| 323 | 0.061 | 1.351 | 0.981 | 1.15 | 1.582 | 1.210 | 0.998 |

Conclusions

From this study it is concluded that phosphoric acid modified ZSM-5 zeolite can be a better adsorbent than the parent zeolite. The modification can also be extended to other zeolites for enhanced sorption properties. The removal efficiency increases with the increase in temperature and hence sorption process is endothermic in nature. The adsorption isotherm data fit well with Langmuir isotherm while the kinetic data were represented by pseudo-second order kinetic model. This study forecasts that treatment of wastewater, particularly heavy metal ion removal and softening of hardwater, could be better carried out with the modified zeolite. The results of this study clearly envisage that such modified zeolites can very well be recommended for wastewater treatment and control of environmental pollution.

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