

Zeolitic material synthesised from fly ash: use as cationic exchanger[†]

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Abstract: The potential use as a 'once through' cation exchanger of a zeolitic material (NaP1 zeolite as the main active component) synthesised from fly ash has been evaluated and compared with a commercial weak acid exchanger, Amberlite IRC-50. The cationic exchange has been tested for different cations present in sewage: NH_4^+ (urban sewage) and Pb^{2+} , Zn^{2+} and Cr^{3+} (waste from electrolytic baths). The NH_4^+ retention capacity was higher in the zeolite (0.7 meq g^{-1}) than in Amberlite IRC-50 (0.21 meq g^{-1}). The retention capacities of metallic cations obtained for NaP1 zeolite ($1.16 \text{ meq Pb}^{2+} \text{ g}^{-1}$, $1.45 \text{ meq Zn}^{2+} \text{ g}^{-1}$ and $1.57 \text{ meq Cr}^{3+} \text{ g}^{-1}$) were also higher than in Amberlite IRC-50 ($0.32 \text{ meq Pb}^{2+} \text{ g}^{-1}$, $0.25 \text{ meq Zn}^{2+} \text{ g}^{-1}$ and $0.35 \text{ meq Cr}^{3+} \text{ g}^{-1}$). When solutions containing all the metallic cations were used, lower retention capacities were obtained for both exchangers.

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INTRODUCTION

Large quantities of fly ash are produced in electric power plants throughout the world every year. Attempts to recycle fly ashes as a soil enhancer have been limited due to the low amount of beneficial nutrients present. Other limiting factors include the high alkalinity and the presence of hazardous leachable trace elements.¹ Some fly ashes have been used widely as cement or pavement materials, and in reclamation, quarry-fill and sludge stabilisation.² Nevertheless, a large proportion of fly ash production is disposed to landfill. Such disposal becomes expensive and may bring about serious environmental pollution problems. The shortage of landfill sites and tighter environmental regulation have led to a need to find new ways of utilising fly ashes.^{3–5}

Several authors have shown that fly ash can be used as raw material for synthesising zeolites.^{4,6–8} Since the main components of fly ash are SiO_2 and Al_2O_3 , this material is a readily available source of Si and Al for zeolite synthesis. Zeolites have uniform pore sizes and large surface areas that make them very useful materials for a wide range of applications such as ion exchange, molecular sieves, adsorbents and catalysts.³

Several papers have reported that various types of zeolites could be obtained by changing the source of fly ash or the activation parameters (mainly temperature, activation agent, concentration of the activating solution and time of activation).^{4,6–8} For potential industrial application, one of the most interesting

zeolitic products is NaP1, due to its high cation exchange capacity (CEC).⁹

Several studies have been undertaken to determine the cation exchange capacities of zeolites^{3,4,10,11} by using high cation concentrations. It has been proved that the use of some zeolites as ion exchangers has several advantages over other methods for environmental applications, exhibiting good selectivities for cations such as ammonium,¹² as in the use of natural clinoptilolite in an industrial process for wastewater treatment.¹³

This paper focuses on the study of a zeolitic material, synthesised from fly ash, and its use as a cation exchanger in a 'once through' process without the need for a subsequent regeneration process after being spent. This would prevent the problem of the low resistance to hydrolysis compared with the higher stability of the natural zeolites such as clinoptilolite.

Cation exchangers were tested for different cations present in waste waters: NH_4^+ (urban sewage) and Pb^{2+} , Zn^{2+} and Cr^{3+} (from electrolytic baths). To compare the CEC of the NaP1 with a commercial exchanger, a synthetic cation exchange resin (Amberlite IRC-50) was selected and its CEC for the above-mentioned cations evaluated. This exchanger was used in the sodium form, and undergoes reactions typical of the salt of a weak acid and strong base with its high exchange capacity deriving from carboxylic acid groups. In its sodium form the resin is highly dissociated and Na^+ is easily exchangeable.¹⁴ On the

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other hand, it is known that in the hydrated form, cations in a zeolite lattice are not firmly held and they can be readily exchanged.

Taking into account all these considerations, it was thought that Amberlite IRC-50 in the sodium form could be an appropriate cation exchanger to be compared with the zeolitic material in the same chemical form.

EXPERIMENTAL

Continuous ion exchange was carried out in a glass column of 1 cm inner diameter containing 1 g of zeolitic material or Amberlite IRC-50 as a fixed bed to check the cation retention capacities of both exchangers.

The zeolitic product used for ion-exchange experiments was synthesised from fly ash (Teruel Power Station in Spain) having a very low cation exchange capacity (0.02 meq g^{-1}).⁷ The Synthesis was carried out in a pilot plant experiment using the conventional activation method.¹⁵ XRD analysis showed approximately 40% of NaP1 zeolite and a similar percentage of analcime, and a trace of sodalite. A small residue of mullite from the original fly ash was also detected. This zeolitic product was granulated by pressing and then crushed and sieved to ($-0.5 + 0.2 \text{ mm}$) to minimise the pressure drop in the exchange column.

The CEC of the material gave a value of 1.9 meq g^{-1} (was determined in a stirred bath by Querol *et al.*).¹⁵ Considering the mineralogical composition of the zeolitic material and the CEC calculated for the two main zeolites present,⁷ the contribution to the CEC can be calculated as being about 70% due to NaP1, 30% to analcime and a negligible contribution from the residual mullite. Thus, the zeolitic material is considered to be NaP1 zeolite from the point of view of use as a cation exchange.

The CEC was also determined in the column by flowing ($6 \text{ cm}^3 \text{ h}^{-1}$) a 0.35 M solution of NH_4NO_3 through the zeolitic bed. In this case, the CEC obtained was 1.3 meq g^{-1} . The lower value obtained suggests that the CEC could be reduced during the granulation process.

Amberlite IRC-50 is a commercial resin with a particle size of $-1.2 + 0.3 \text{ mm}$; it contains carboxylic acid groups CEC of 4.5 meq g^{-1} according to the manufacturer. The total exchange capacity is however attainable only under special conditions of high pH values and high ion concentration.

The solution used to evaluate the retention of the NH_4^+ was a synthetic solution containing $30 \text{ mg NH}_4^+ \text{ dm}^{-3}$ prepared from pure NH_4NO_3 . In order to simulate the potential application for the purification of water from a sewage farm in Ebro River (Spain), a solution containing $30 \text{ mg NH}_4^+ \text{ dm}^{-3}$, $126 \text{ mg Ca}^{2+} \text{ dm}^{-3}$ and $32 \text{ mg Mg}^{2+} \text{ dm}^{-3}$ was prepared. These last two cations were selected over others which are present in the water because they could compete with NH_4^+ for exchange.

Cationic solutions were passed through the exchanger bed and effluent solution was recovered in 6 cm^3 fractions for cation analysis. When exchanger saturation was achieved the column was washed with 500 cm^3 of deionised water, and the zeolite column regenerated by a solution of 0.35 M NaNO_3 . The low flow rate used ($6 \text{ cm}^3 \text{ h}^{-1}$) was selected to ensure an adequate contact time.¹⁰ The total amount of NH_4^+ exchanged was recovered and determined by Nessler's reagent.

Similar experiments were performed to determine the retention capacities of Pb^{2+} , Zn^{2+} and Cr^{3+} for both exchangers. In these cases, a higher flow rate was used ($100 \text{ cm}^3 \text{ h}^{-1}$) and the initial concentrations of each type of cation was 20 mg dm^{-3} , with a pH of about 3.5, 5.0 and 4.0 respectively. It had been previously established that $100 \text{ cm}^3 \text{ h}^{-1}$ provided an adequate exchange time for these cations and, consequently, column saturation is faster. The saturated column was again washed with 500 cm^3 of deionised water, and regenerated with NaNO_3 (0.35 M), HNO_3 (10%) or HCl (5%) depending on the exchanger and cation eluted: eg Pb^{2+} with HNO_3 , Zn^{2+} and Cr^{3+} with HCl for the resin and NaNO_3 for NaP1. HNO_3 (10%) was used as an eluent when a solution containing these three cations (20 mg dm^{-3} each) flowed through the column. In this case, the pH of the resulting solution was 3.4. Sequential measurements of pH and metal analysis were made during the saturation process. Concentration of the metallic cations was measured by AAS.

RESULTS AND DISCUSSION

NH_4^+ ion exchange

The results obtained for NH_4^+ retention showed that Amberlite IRC-50 has a lower retention capacity (0.21 meq g^{-1}) than NaP1 zeolite (0.7 meq g^{-1}) under the conditions used. It can be seen (Fig 1) that the exchange sites in the resin are rapidly saturated, leading to a sharp increase in NH_4^+ concentration in the eluate. On the other hand, with NaP1 a slow increase in NH_4^+ concentration occurs because, in this case, the ion exchange seems to be influenced by diffusion through channels in the zeolite. This phenomenon could be due to the different cationic sites present in zeolites¹¹ in contrast to the ion exchange resins, where all the positions are equivalent and easily accessible. Moreover, it is important to take into account that in these conditions saturation of NaP1 zeolite was not achieved and it would have been necessary to pass a large amount of NH_4^+ to get complete saturation.

However, it can be readily observed that the exchange capacity in the resin is reduced by 20 times from the total exchange capacity (4.5 meq g^{-1}), while in NaP1 zeolite the capacity is only reduced to half the total exchange capacity (1.3 meq g^{-1}) although saturation has not been achieved. It is well known that as the concentration of cations in solution decreases the

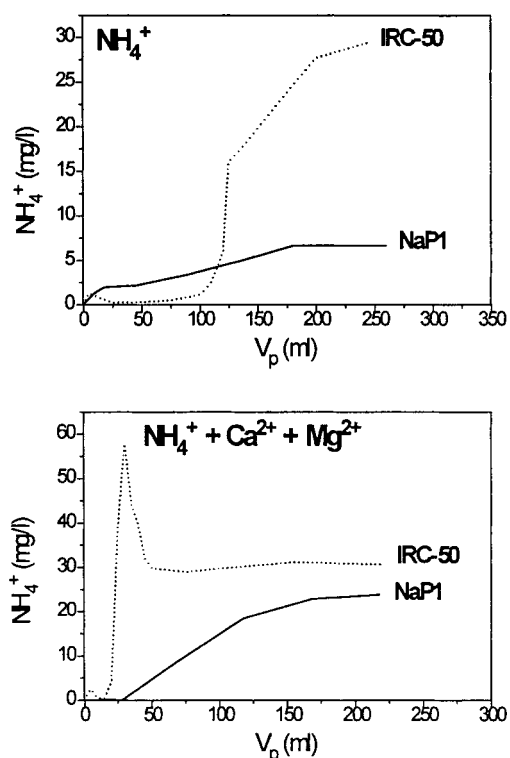


Figure 1. Trends of NH_4^+ saturation vs volume passed (V_p), alone and in presence of Ca^{2+} and Mg^{2+} , for Amberlite IRC-50 and NaP1 zeolite.

selectivity of the exchanger decreases.¹⁰ So, the low initial concentration of NH_4^+ used (30 mg dm^{-3}) has a negative effect on the exchange. This effect is clearer in Amberlite than in NaP1 zeolite probably due to the different physical-chemical characteristics of their cationic exchange sites. Note that not all NH_4^+ is retained from the beginning of the NaP1 zeolite saturation process; a major increase in bed height would be necessary to achieve this.

When NH_4^+ (30 mg dm^{-3}) was passed through the exchangers together with Ca^{2+} and Mg^{2+} , the exchange capacity for NH_4^+ decreased, Amberlite IRC-50 to 0.02 meq g^{-1} and NaP1 zeolite to 0.22 meq g^{-1} . Figure 1 shows that saturation of both exchangers is reached earlier due to the presence of Ca^{2+} and Mg^{2+} in the solution. On the other hand, the results seem to indicate that these cations compete with NH_4^+ , reducing by 10 times the total amount of NH_4^+ retained by Amberlite IRC-50 and by three times in NaP1 zeolite. These effects were confirmed by analysing the amounts of Ca^{2+} and Mg^{2+} retained. Thus, in the case of NaP1 zeolite, $0.52 \text{ meq Ca}^{2+} \text{ g}^{-1}$ and $0.02 \text{ meq Mg}^{2+} \text{ g}^{-1}$ were retained, amounting to a total of 0.76 meq g^{-1} for the three cations. It could be concluded that both the Ca^{2+} and Mg^{2+} cations block the exchange positions in the zeolite and reduce NH_4^+ retention.

Pb^{2+} ion exchange

The results obtained for Pb^{2+} ion exchange were 0.32 meq g^{-1} for Amberlite IRC-50 and 1.16 meq g^{-1}

for NaP1 zeolite. The trends of unretained Pb^{2+} and pH during the saturation process are shown in Fig 2. It can be seen with IRC-50 that there is a slight increase of pH at the beginning of saturation while exchange occurs and then, the pH decreases to the initial value as the level of exchange decreases. On the other hand, while the pH is maintained near 6, all the Pb^{2+} that reaches the resin is retained (formation of hydroxide is not ruled out) and when the pH decreases to 3.5, a fast decrease in Pb^{2+} retention occurs. This observation indicates, as is well known, that higher pH favours the ion exchange process, especially for a weak acid resin like Amberlite IRC-50.

The same study was made for NaP1 zeolite. In Fig 2, a rapid increase of pH (from 3.5 to 8.5) is observed which remains for a longer period of time than found with IRC-50. During this period both hydroxide precipitation and ion exchange could be involved.¹⁶ Nevertheless, it can be seen later that the pH is maintained at about 5 for the remainder of the process, so re-dissolution and exchange of Pb^{2+} would be possible and thus only the exchanged cation remains in the zeolite. It would be expected that the higher pH during the saturation process would favour the retention capacity of NaP1 zeolite.

Finally, it has been shown that the Pb^{2+} retention capacities, estimated from saturation curves, are similar to those obtained from measurements of the eluted solution, so that both exchangers could be regenerated and reused, although this is not proposed, as noted at the beginning of the paper.

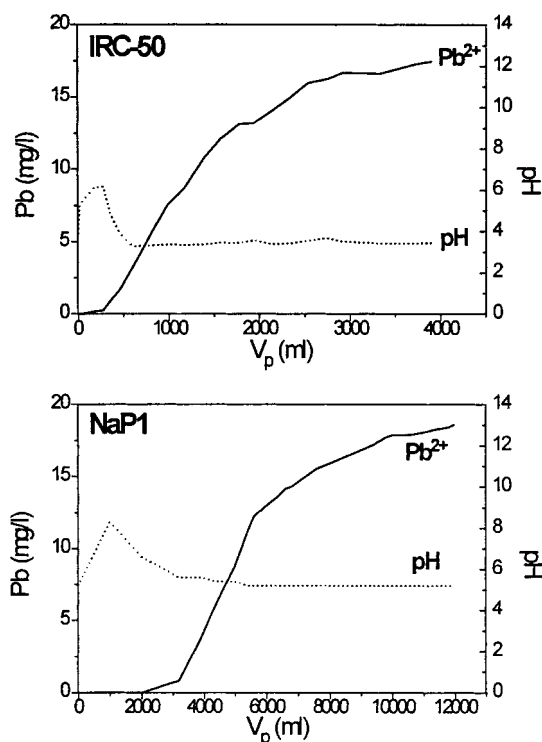


Figure 2. Trends of Pb^{2+} saturation and pH vs volume passed (V_p) for Amberlite IRC-50 and NaP1 zeolite.

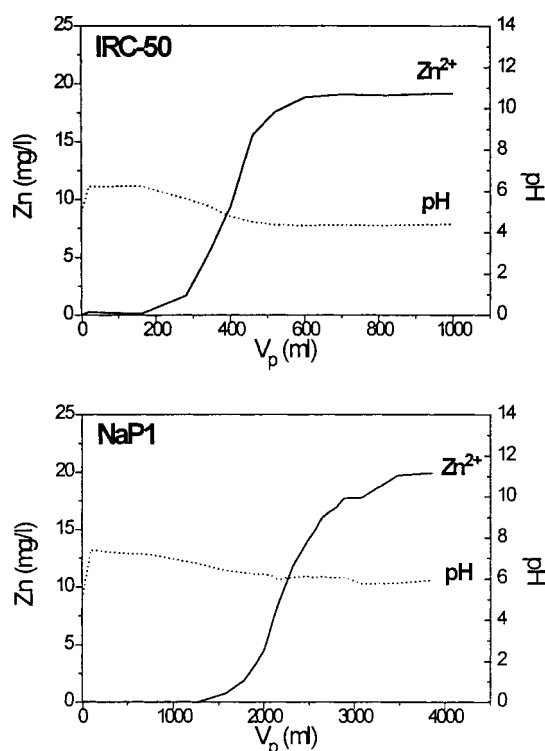


Figure 3. Trends of Zn^{2+} saturation and pH vs volume passed (V_p) for Amberlite IRC-50 and NaP1 zeolite.

Zn^{2+} ion exchange

The results obtained for Zn^{2+} exchange were 0.25 meq g^{-1} for Amberlite IRC-50 and 1.45 meq g^{-1} for NaP1 zeolite. The trends of unretained Zn^{2+} and pH during the saturation process are shown in Fig 3. The behaviour of both exchangers for Zn^{2+} retention is similar to Pb^{2+} , and as in the former case, the Zn^{2+} retention capacities calculated from saturation curves and from the eluted solution were very similar.

Cr^{3+} ion exchange

The retention capacity obtained for Cr^{3+} is different if calculated from eluted solutions or saturation curves. The results were 0.11 meq g^{-1} for Amberlite IRC-50 and 0.01 meq g^{-1} for NaP1 zeolite from the eluted solutions, while 0.35 meq g^{-1} for Amberlite IRC-50 and 1.57 meq g^{-1} for NaP1 zeolite were achieved. In this case, it is clear that Cr^{3+} remains in the exchangers after the regeneration process. This phenomenon has been previously described by other authors.¹⁷

On the other hand, the zeolite saturation process and pH trends are similar to those for the ion exchange resin, but in the latter case exchange is completed in a shorter period of time (Fig 4). It could be said that in spite of the higher valence of this cation its access to the channels is not difficult because it has the smallest size, therefore the retention capacities are similar to the other cations.

The retention capacities obtained for the metallic cations are presented in Table 1 where it can be seen that the capacities change slightly, depending on the exchanged cation. It can be concluded from the results

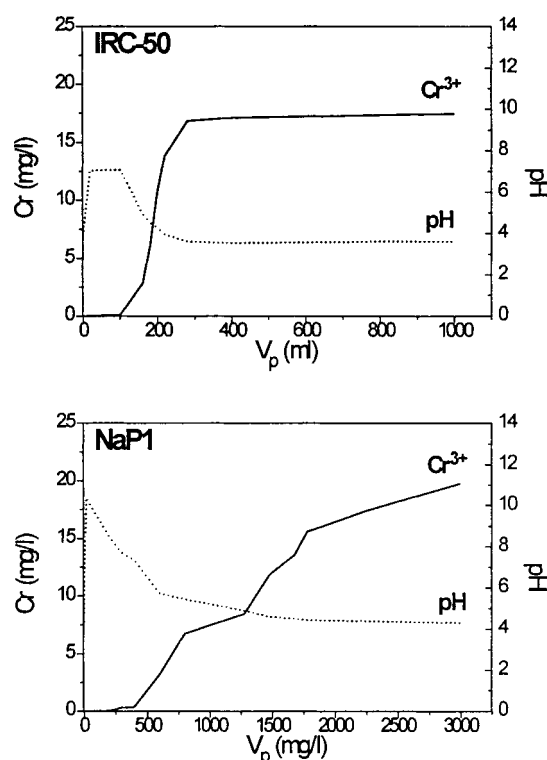


Figure 4. Trends of Cr^{3+} saturation and pH vs volume passed (V_p) for Amberlite IRC-50 and NaP1 zeolite.

Table 1. Retention capacities (meq g^{-1}) of metallic cations

Cation	Amberlite IRC-50	NaP1 zeolite
Pb^{2+}	0.32	1.16
Zn^{2+}	0.25	1.45
Cr^{3+}	0.35	1.57

that the affinity order of the cations in Amberlite IRC-50 is $Cr^{3+} \approx Pb^{2+} > Zn^{2+}$, and the order for the NaP1 zeolite is: $Cr^{3+} > Zn^{2+} > Pb^{2+}$.

Pb^{2+} , Zn^{2+} and Cr^{3+} ion exchange

The retention capacities obtained when a mixture of the three cations was passed through the column are shown in Table 2.

As can be observed, the amounts retained by zeolite, calculated from saturation curves, are higher than those obtained by elution. This suggests that total regeneration of zeolite has not been achieved. This phenomenon was previously observed in Cr^{3+} ion

Table 2. Retention capacities (meq g^{-1}) of metallic ions in a mixture of the three cations

Cation	Amberlite IRC-50		NaP1 zeolite	
	Eluted	Retained	Eluted	Retained
Pb^{2+}	0.04	0.07	0.28	0.52
Zn^{2+}	0.00	0.01	0.06	0.42
Cr^{3+}	0.03	0.05	0.00	0.79

exchange with the single ion solution but did not occur for Zn^{2+} and Pb^{2+} . On the other hand, there is a drastic decrease in the retention capacity for each cation compared with the retention obtained individually in the previous experiments. It is possible from observation of XRD (Fig 5) that the zeolite structure is slightly modified during the ion exchange process. It can be seen that there are small shifts in the NaP1 peaks for the sample used for ion exchange (NaP1-Me) compared with the original NaP1. Moreover, in NaP1 the peak at $2\theta = 26^\circ$ is split into two peaks in the NaP1-Me spectrum. It is possible that these structural changes could make the total regeneration of this zeolite difficult and this phenomenon seems to be due to the presence of Cr^{3+} in the framework. On the other hand, it is well known that low pH levels are undesirable in zeolite applications because this affects the chemical structure of zeolite. Thus perhaps the low pH in the mixture could be responsible for these changes. In this case, it is important to note that low pH levels were present in the single ion solution containing only Pb^{2+} and this cation was totally recovered from zeolite on regeneration, while the Pb^{2+} in the mixture were only partially recovered. So, it could be concluded that the inclusion of Cr^{3+} in the zeolite framework leads to a disturbance which prevents the total regeneration of this zeolite.

The trends of cation saturation and pH are shown in Fig 6 for Amberlite IRC-50 and NaP1 zeolite. In Amberlite IRC-50, the initial pH increase is slightly lower than for the individual cases, this corresponding with a strong reduction in metal exchanged. On the

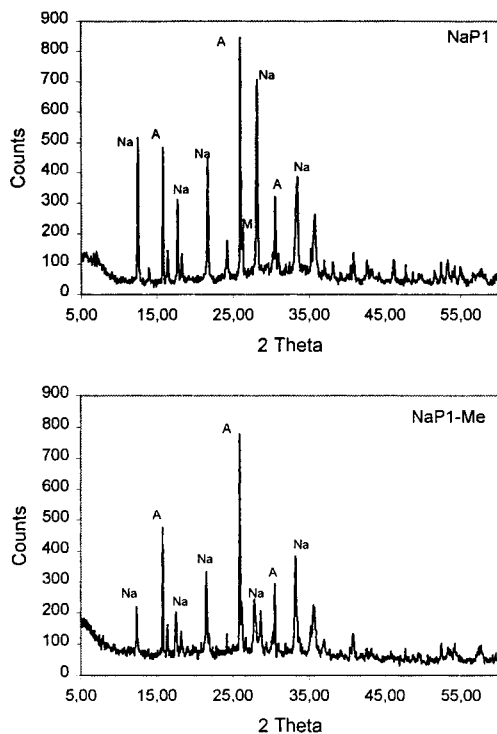


Figure 5. XRD patterns of the zeolitic material before ion exchange experiments (NaP1) and after the exchange with the cation mixture (NaP1-Me). Na, NaP1 zeolite; A, analcime; M, mullite.

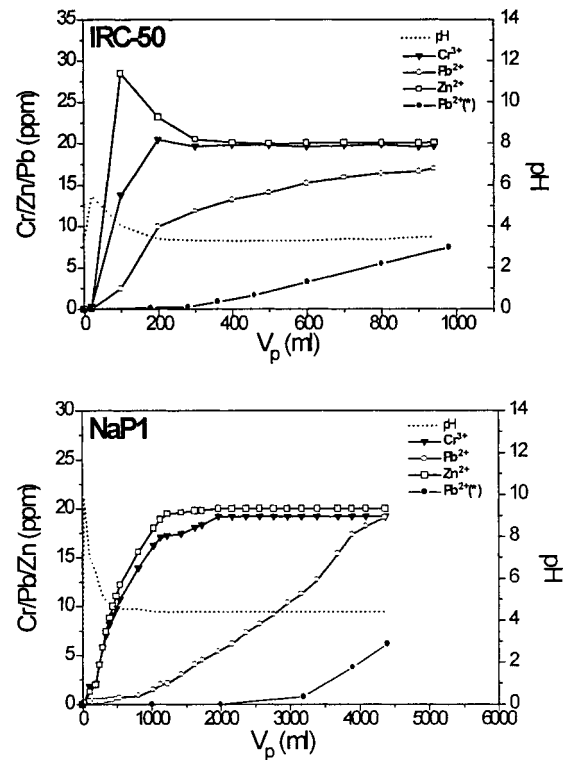


Figure 6. Trends of Pb^{2+} , Zn^{2+} , Cr^{3+} saturation and pH vs volume passed (V_p) for Amberlite IRC-50 and NaP1 zeolite.

other hand, an anomalous behaviour in Zn^{2+} retention can be observed, where its concentration exceeds the initial concentration (20 mg dm^{-3}) for a period of time. This phenomenon can be explained by an initial fast retention of Zn^{2+} followed by liberation of the metal retained in the resin. In conclusion, it can be said that the lower value of the pH for the cation solution seems to be the cause of the decrease in the total retention capacity of the resin. Although the Pb^{2+} retention process does not appear to be complete it is sufficient to compare the trend of Pb^{2+} in the mixture and that for the individual solution [Pb^{2+} (*)], with a clear decrease in the retention capacity.

NaP1 zeolite shows similar behaviour to that for the resin. The Zn^{2+} and Cr^{3+} saturation curves are very similar to each other while Pb^{2+} seems to reach the total saturation slowly. As in the resin, a drastic decrease in metal retention capacity of this zeolite is observed and the trend of Pb^{2+} retention is less than that for the individual solution of Pb^{2+} (*). As observed in Fig 6, both ion exchangers showed a higher retention of Pb^{2+} compared with the other cations.

In general, the synthesised zeolite NaP1 showed a larger capacity for ion exchange than IRC-50 resin in the operating conditions. The explanation could be that the pH increases in all the experiments when the solution passes through zeolitic material favours cation exchange, while the pH decreases in the resin would tend to form very weakly ionised $COOH$ (pK_a about 6–8), which is not available for cation exchange.

All these considerations suggest that the zeolitic

material studied, with NaP1 as main component, could be a good product for environmental applications such as water treatment, soil remediation, etc, but only by considering the material as a 'once though' exchanger.

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