

# The Adsorption of Pentachlorophenol from Aqueous Solutions onto Exchanged Al-MCM-41 Materials

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**ABSTRACT:** The ability of a mesoporous molecular sieve to adsorb chlorinated phenols was studied experimentally. Thus, the adsorption isotherms of pentachlorophenol (PCP) from aqueous solutions were measured on (M)Al-MCM-41 (M = Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>) at intervals of 10 K between 303 K and 323 K. The experimental isotherms obtained were of the S-type in terms of the classification of Giles and co-workers. The best fit of the adsorption isotherm data was obtained using the Freundlich model. The adsorption affinity of PCP increased in the order (K)Al-MCM-41 < (Cr)Al-MCM-41 < (Na)Al-MCM-41 < (Cu)Al-MCM-41. At the same temperature, the adsorption of PCP on (Cu)Al-MCM-41 was more pronounced compared to its adsorption on alumina-pillared montmorillonite and mesoporous alumina aluminium phosphates. Analysis of the isosteric curves showed that (Cu)Al-MCM-41 and (Na)Al-MCM-41 presented a heterogeneous profile. In contrast, (K)Al-MCM-41 and (Cr)Al-MCM-41 did not exhibit energetic heterogeneity throughout the entire range of coverage.

## INTRODUCTION

Chlorinated phenols are introduced into the environment as products of chemical manufacture. In particular, they are widely used as wood preservatives, herbicides, insecticides and fungicides. Furthermore, they may be formed in the environment as chemical and biological breakdown products of other chlorinated xenobiotics such as chlorophenoxy herbicides (Bollag *et al.* 1968). Due to their toxicity, tendency to bioaccumulate and persistence in the environment, chlorinated phenols contaminating industrial effluents must be eliminated.

A variety of techniques are available nowadays for treating these contaminants. Among these may be mentioned biodegradation, advanced oxidation processes and adsorption (Shim and Kawamoto 2002; Laurenti *et al.* 2002; Burrows *et al.* 2002; Pandiyan *et al.* 2002; Juang *et al.* 1996). However, biodegradation suffers from optimization problems in addition to the relatively biorefractory character of the materials involved (Yu and Hu 1994), while advanced oxidation processes are considered to be high-cost methods. Physical adsorption has been considered using granular activated carbons (Jung *et al.* 2001), graphitized carbon black (Kira Ly *et al.* 1996), etc.

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In 1992, a novel mesoporous molecular sieve family, M41S, was discovered (Beck *et al.* 1992; Kresge *et al.* 1992) and the adsorptive properties of MCM-41, one member of the M41S family, have been characterized extensively using a variety of gaseous adsorbates. Recently, the adsorption of nitrogen, neopentane, n-hexane, benzene and methanol was reported (Ribeiro Carrott *et al.* 2001). In addition, Cauvel *et al.* (1997) and Zhao *et al.* (1998, 2000) have studied the hydrophobicity of these zeotypes via the adsorption of various adsorbates.

Despite evidence in the literature of an increased interest in the mesoporous molecular sieve family and associated adsorption properties, no studies of the adsorption of chlorinated phenols from aqueous solutions have as yet been published. In the present work, (Na)Al-MCM-41 was modified by ion exchange using  $K^+$ ,  $Cu^{2+}$  and  $Cr^{3+}$  cations. The adsorptive properties of these modified (M)Al-MCM-41 samples were studied by measuring the adsorption isotherms of pentachlorophenol (PCP) from aqueous solutions.

The choice of PCP can be explained as follows: it is a chlorinated aromatic organic chemical of low volatility and is used as a wide-spectrum biocide to kill small organisms; its main use is as a wood preservative to protect wood from decay and insect attack. Although the chlorinated aromatic phenols are generally toxic to living organisms, PCP is more toxic to plants, animals and humans. PCP can affect sensitive organisms even at such low concentrations as 0.1–1.0  $\mu\text{g/l}$  and can lead to alterations in ecosystems. In addition to its high toxicity, PCP is resistant to biodegradation and persistent in the environment (Crosby 1981; Alleman *et al.* 1992).

## EXPERIMENTAL

### Materials and chemicals

The parent (Na)Al-MCM-41 sample was synthesized using a silica source, i.e. Ludox 40 (Fluka), sodium hydroxide (Aldrich), sodium aluminate (Riedel-de Haen, 54%  $Al_2O_3$ , 41%  $Na_2O$ ),  $C_{16}$ TMAOH (Aldrich, 99%) and deionized water according to the following procedures. First, the  $C_{16}$ TMAOH template was dissolved in sodium hydroxide solution with stirring. Secondly, sodium aluminate was added to the above solution followed by Ludox, and the resulting mixture maintained under constant stirring. The final gel had the molar composition  $SiO_2:0.077Al_2O_3:0.5Na_2O:0.125C_{16}TMAOH:127H_2O$ . The gel was transferred into a P.P. bottle and heated at 323 K for 6 days. All chemicals were used as received. The product of the synthesis was recovered by filtration, washed with deionized water, dried at 363 K and finally calcined in air at 823 K (heating rate 2 K/min) for 3 h to remove the template occluded in the solid.

The calcined sample was characterized by X-ray powder diffraction ( $d_{100} = 35 \text{ \AA}$ ) employing a Philips PW 1840 diffractometer using monochromated Cu  $K\alpha$  radiation. The nitrogen adsorption isotherm was measured at 77 K via an ASAP 2010 instrument (Micromeritics, Norcross, GA, USA), using helium and nitrogen of 99.99% purity as supplied by Air Liquide. Before measurement, the sample was outgassed overnight at 573 K under vacuum ( $10^{-4}$  Torr). The nitrogen adsorption isotherm was a typical type IV isotherm according to IUPAC classification. The specific surface area was calculated using the standard BET method ( $S_{BET} = 840 \text{ m}^2/\text{g}$ ).

The lattice parameter  $a_0$  of the hexagonal unit cell can be calculated using the relationship  $a_0 = (2/\sqrt{3})d_{100}$ . The pore diameter may be calculated from this value by subtracting 10  $\text{\AA}$ , i.e. the approximate value for the pore wall thickness usually found in synthesized MCM (Eimer *et al.* 2001). Using these methods, the lattice parameter and diameter calculated for the prepared (Na)Al-MCM-41 were 40.41  $\text{\AA}$  and 30.41  $\text{\AA}$ , respectively. On the other hand, Böhlmann and

Michel (2001) showed that the elemental analysis of calcined (Na)Al-MCM-41 gave an Si/Al ratio comparable to that of the starting gel. Thus, for the determination of the total ion-exchange capacity, the molar composition of the gel, dehydrated without template, was considered. Account should also be taken of the fact that Na/Al = 1 to ensure electroneutrality. The total ion-exchange capacity thereby obtained was 2.12 mequiv/g.

Chemical modification of (Na)Al-MCM-41 was undertaken using ion-exchange methods. These were carried out at room temperature by stirring 5 g (Na)Al-MCM-41 in 100 ml of an aqueous solution containing different concentrations of the appropriate metal nitrate for 24 h. The resulting sample was washed free of nitrate ion and dried overnight at 353 K. The Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup> or Cr<sup>3+</sup> content was determined on the basis of the variations in the concentrations of these cations in solution and in the solid product using a Perkin-Elmer 2380 atomic absorption spectrophotometer. Data concerning the initial concentration of M<sup>n</sup>(NO<sub>3</sub>)<sub>n</sub> and the compositions of the ion-exchanged samples prepared are presented in Table 1. It should be noted that all samples contained a small amount of protons. This protonation phenomenon has also been reported for Na-Ca exchange relative to NaA (Drummond *et al.* 1983), for NaX exchanged with Zn<sup>2+</sup> and Cu<sup>2+</sup> (Khelifa *et al.* 1999a) and NaZSM-5 exchanged with alkalis (Otremba and Zajdel 1993).

The pentachlorophenol was supplied by Aldrich with a purity better than 99%. Aqueous solutions of PCP at various concentrations were prepared from a 500 mg/l stock PCP solution in 0.005 mol/l NaOH. Achard *et al.* (1996) have shown that the solubility of PCP in water is only 86.2 ± 2 mg/l at 319.8 K. Diluting the stock solution allowed working solutions to be prepared. In each case, the pH was adjusted to 6 by adding HCl.

### Adsorption procedure

The kinetics of PCP adsorption by (M)Al-MCM-41 was determined via the batch method. Thus, (M)Al-MCM-41/PCP solution mixtures were stirred for different time intervals in a thermostatic bath at 303 K. Temperature fluctuations in this bath were of the order of ± 0.5 K.

For each experiment involving measurement of the kinetics of adsorption or equilibrium adsorption, 0.2 g (M)Al-MCM-41 (M = Na, K, Cu and Cr) was mixed with 25 ml PCP solution at the desired concentration in distilled water. After equilibration, 5 ml of the supernatant was then removed for analysis by UV-vis spectrophotometry, the amount of PCP adsorbed being determined from the difference between the initial and final PCP concentrations. Such concentrations were measured using a Shimadzu-120-01 UV-vis spectrophotometer at a wavelength of 320 nm (Hu *et al.* 1994; Mollah and Robinson 1996).

TABLE 1. Characteristics of (M)Al-MCM-41 Materials Studied

Adsorbent	[M] (mol/l) (M <sup>n+</sup> = K <sup>+</sup> , Cu <sup>2+</sup> or Cr <sup>3+</sup> )	Na (wt%)	M (wt%)	H (wt%)
(Na)Al-MCM-41	–	100	–	–
(K)Al-MCM-41	5 × 10 <sup>-2</sup>	46	47	7
(Cu)Al-MCM-41	2 × 10 <sup>-2</sup>	44	52	4
(Cr)Al-MCM-41	2 × 10 <sup>-2</sup>	39	55	6

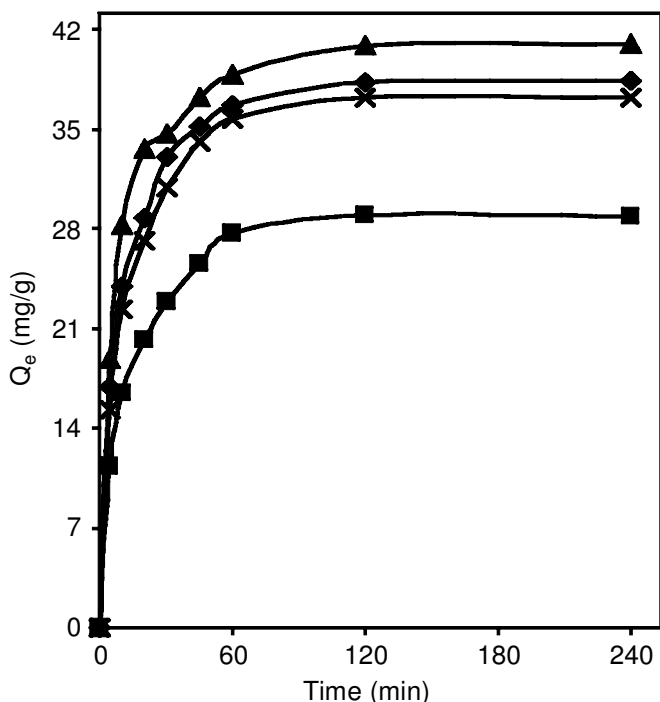
## RESULTS AND DISCUSSION

### Adsorption isotherms and kinetics

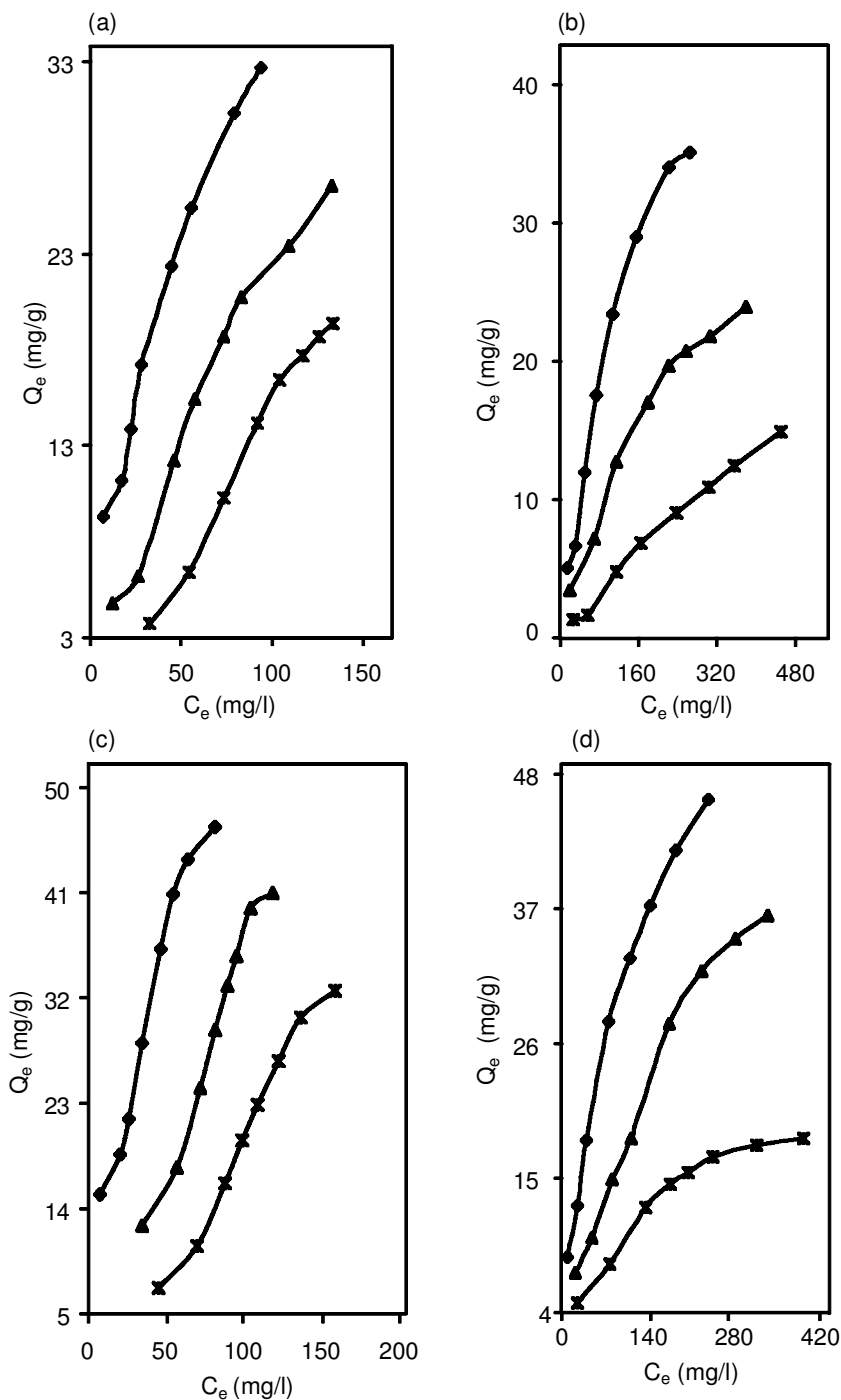
Kinetic curves relating to the adsorption of PCP by (Na)Al-MCM-41, (K)Al-MCM-41, (Cu)Al-MCM-41 and (Cr)Al-MCM-41 are presented in Figure 1. It will be noted that the adsorption capacity exhibited a marked increase at low contact times after which it varied only slightly. No changes in PCP concentrations were observed after 2 h. Hence, it was considered that a shaking time of 4 h would be of sufficient length to achieve sorption equilibrium. This time was used for all the equilibrium adsorption experiments reported here. The results concerning the bioadsorption of PCP from aqueous solution by activated sludge biomass showed that in that case equilibrium was attained within less than 2 h (Jianlong *et al.* 2000).

The equilibrium adsorption of PCP on (M)Al-MCM-41 was studied via a batch process at 303 K, 313 K and 323 K. The corresponding adsorption isotherms are depicted in Figure 2 as plots of the amount adsorbed per g adsorbent (mg/g) ( $Q_e$ ) as a function of the quantity of PCP remaining in the equilibrium solution (mg/l) ( $C_e$ ). At 303 K and a  $C_e$  value of 15 mg/l, (Cu)Al-MCM-41 adsorbed an amount of PCP approximately equal to that adsorbed at 293 K by alumina-pillared montmorillonite ( $Q_e = 15.3$  mg/g), but much more than the amount adsorbed at 293 K by mesoporous alumina aluminium phosphates ( $Q_e = 4$  mg/g) (Danis *et al.* 1998).

Over the temperature range studied, the adsorption isotherms indicated that the quantity of PCP adsorbed decreased with increasing temperature. Tse and Lo (2002) studied the effect of



**Figure 1.** Adsorption kinetics of PCP on (M)Al-MCM-41. Experimental data: ◆, (Na)Al-MCM-41; ■, (K)Al-MCM-41; ▲, (Cu)Al-MCM-41; ✕, (Cr)Al-MCM-41.



**Figure 2.** Adsorption isotherms of PCP on (a) (Na)Al-MCM-41, (b) (K)Al-MCM-41, (c) (Cu)Al-MCM-41 and (d) (Cr)Al-MCM-41. Data points in each section of the figure correspond to the following temperatures:  $\blacklozenge$ , 303 K;  $\blacktriangle$ , 313 K;  $\times$ , 323 K.

temperature on the desorption kinetics of PCP from soil and showed that PCP exhibited a preference for the aqueous phase rather than the soil matrix when the temperature was raised.

Adsorption isotherms for solutes of low solubility have been classified by Giles *et al.* (1960) into four principal classes. Using this classification, the experimental isotherms obtained in the present study were of type S. It should be noted that adsorption isotherms for PCP, TCP and DCP on alumina-pillared montmorillonite and mesoporous alumina aluminium phosphates (Danis *et al.* 1998), and of PCP and DCP on sediments (Lawrence *et al.* 2000) all showed S-type characteristics. The initial part of the S curve indicates little interaction between PCP and the solid at low concentrations. However, as the concentration in the liquid phase increased, adsorption occurred more readily (Calvet 1989). This behaviour was explained in terms of a synergistic effect, with the adsorbed molecules facilitating the adsorption of additional molecules as a result of attractive adsorbate–adsorbate interactions. This was particularly the case when the solute molecule possessed a fairly large hydrophobic component, as with pentachlorophenol which exhibited moderate intermolecular attraction leading to vertical packing in the adsorbed layer and met strong competition for sites from solvent molecules.

Various studies carried out on the organic micropollution of water have generally shown that the lower the solubility of the solute, the greater will be its adsorption capability. Thus, the affinity of the granular activated carbons towards chlorophenols follows the sequence: PCP > 2,4,6-TCP > 2,4-DCP > CP, i.e. in line with the decreasing solubility of these compounds in water (Jung *et al.* 2001).

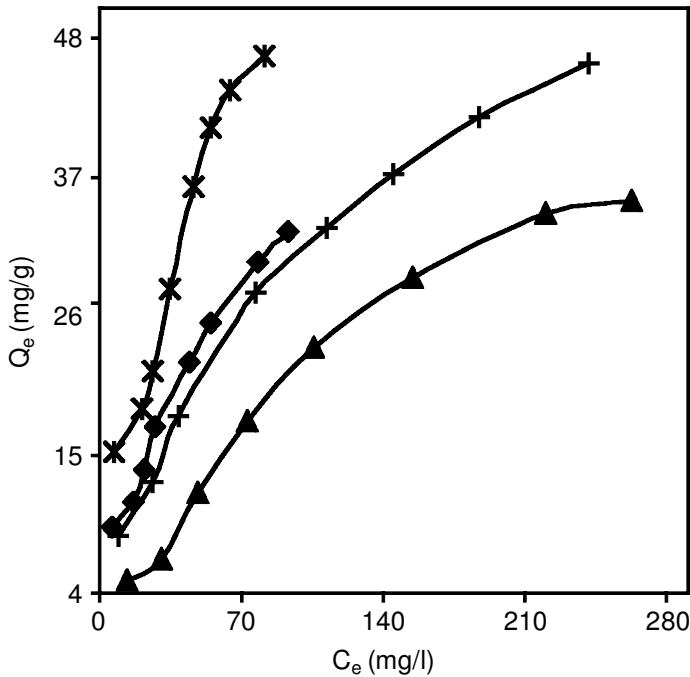
### Adsorption affinity

Figure 3 presents the adsorption affinity of PCP on (M)Al-MCM-41 as measured at 303 K, with the value exhibited by (Cu)Al-MCM-41 corresponding to the highest adsorption affinity. On the other hand, the lowest adsorption capacity towards PCP appears to be associated with (K)Al-MCM-41. Indeed, the affinity sequence may be written as: (Cu)Al-MCM-41 > (Na)Al-MCM-41 > (Cr)Al-MCM-41 > (K)Al-MCM-41.

In the discussion of adsorption isotherm determination given above, mention was made of the fact that the adsorption of molecules is facilitated by attractive adsorbate–adsorbate interactions. Previous work has shown that such attractive adsorbate–adsorbate interactions become more pronounced in CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> adsorption on Cu(x)X (Khelifa *et al.* 1999b,c, 2001a). Thus, the introduction of Cu<sup>2+</sup> ions via ion exchange with NaX weakened the adsorbate–adsorbent interactions in favour of adsorbate–adsorbate interactions. A similar behaviour could explain the high affinity of (Cu)Al-MCM-41 towards PCP adsorption as being due to the predominance of attractive adsorbate–adsorbate interactions relative to adsorbate–(Cu)Al-MCM-41 interactions.

The molecular diameter of PCP is ca. 10 Å (Jung *et al.* 2001), whereas the average pore diameter of (Na)Al-MCM-41 is 30.41 Å, i.e. three-times that of the PCP diameter. Thus, it would be relatively easy for the PCP molecule to diffuse into the pores available within (M)Al-MCM-41. In other words, the adsorption process cannot be explained by physical properties such as pore diameter, but more probably by chemical interaction. This interaction would be of an electrostatic attraction type between the negatively charged phenolic compound and positively charged adsorption sites (Jianlong *et al.* 2000). Such sites would be occupied by the exchanged cations and/or Na<sup>+</sup> ions.

However, the development of adsorption affinity cannot be explained by the cationic charge carried by the cation introduced, since (Cr)Al-MCM-41 adsorbed less than (Na)Al-MCM-41. Moreover, the exchange percentages for the compounds were approximately equal, between 47%



**Figure 3.** Adsorption affinities of PCP on (M)Al-MCM-41 at 303 K. Experimental data:  $\blacklozenge$ , (Na)Al-MCM-41;  $\blacktriangle$ , (K)Al-MCM-41;  $\ast$ , (Cu)Al-MCM-41;  $\ast$ , (Cr)Al-MCM-41.

and 55% (Table 1). From these considerations, it would appear that the amount of PCP adsorbed by each sample depended on two distinct but complementary phenomena: interactions of an electrostatic attraction type and that of an adsorbate–adsorbate type.

### Interpretation of adsorption isotherms

The accuracy of the fit of a given model with experimental data may be expressed in terms of the regression coefficient and the average relative error. Results from various samples were eliminated if the average relative error was greater than 10% and/or the regression coefficient was less than 0.96.

The average relative error,  $E_{rm}$ , was determined from the relationship:

$$E_{rm} (\%) = \frac{100}{N_{exp}} \sum_0^{N_{exp}} \frac{|Q_e - Q_{cal}|}{Q_e} \quad (1)$$

where  $Q_e$  is the experimental amount of adsorbate,  $Q_{cal}$  that calculated via the model and  $N_{exp}$  is the number of experimental data points.

Attempts to use the Langmuir equation to represent the experimental isotherms failed to give a satisfactory correlation. The poor ability of this model to represent the experimental data could have been due to the fact that the Langmuir isotherm does not take into account adsorbate–adsorbate interactions.

The Freundlich model has been widely adopted for the characterization of the adsorption of organic pollutants from water and was consequently used in this work to fit the adsorption data. The Freundlich equation may be written in the form:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

where  $Q_e$  is the amount adsorbed at equilibrium,  $C_e$  the concentration at equilibrium,  $K_F$  is a constant taken as an indicator of adsorption capacity and  $1/n$  is a constant indicative of the adsorption intensity. The linearized form of equation (2) is:

$$\ln Q_e = \ln K_F + 1/n \ln C_e \quad (3)$$

Thus, linearization of this model requires construction of the curve  $\ln Q_e = f(\ln C_e)$ , the values of  $K_F$  and  $1/n$  being calculated by the method of least squares. Determination of the linearization parameters, as summarized in Table 2, allowed the calculation of the theoretical isotherms and their comparison with the experimental data.

As seen from Table 2, the Freundlich equation provided a satisfactory description of PCP adsorption onto (Na)Al-MCM-41, (K)Al-MCM-41, (Cu)Al-MCM-41 and (Cr)Al-MCM-41. The Freundlich adsorption isotherm has also been applied to describe the sorption of PCP onto activated sludge biomass (Jianlong *et al.* 2000) and onto peat/bentonite mixtures (Viraraghavan and Slough 1999). A relatively low regression coefficient was obtained for adsorption onto (Cu)Al-MCM-41 at 303 K. A poor correlation with this model was also observed for  $\text{CO}_2$  adsorption on NaX, Zn(x)X and Cu(x)X at low temperatures (Khelifa *et al.* 2001b).

The data listed in Table 2 also show that the Freundlich parameter,  $K_F$ , was appreciable for the (Cu)Al-MCM-41, (Na)Al-MCM-41 and (Cr)Al-MCM-41 adsorbents, in general agreement with

**TABLE 2.** Linearization Parameters of Freundlich Model

Adsorbent (M)Al-MCM-41	Temp. (K)	Regression coefficient	Average relative error (%)	$K_F$ (l/g)	1/n
(Na)Al-MCM-41	303	0.963	6.3	2.936	0.528
(Na)Al-MCM-41	313	0.970	6.4	0.624	0.778
(Na)Al-MCM-41	323	0.990	4.8	0.051	1.229
(K)Al-MCM-41	303	0.972	9.1	0.723	0.718
(K)Al-MCM-41	313	0.984	7.1	0.456	0.683
(K)Al-MCM-41	323	0.974	8.9	0.058	0.916
(Cu)Al-MCM-41	303	0.958	9.6	4.208	0.545
(Cu)Al-MCM-41	313	0.975	5.5	0.274	1.056
(Cu)Al-MCM-41	323	0.983	4.9	0.047	1.304
(Cr)Al-MCM-41	303	0.990	4.3	2.408	0.546
(Cr)Al-MCM-41	313	0.984	6.3	0.933	0.637
(Cr)Al-MCM-41	323	0.975	6.4	0.883	0.525



strong adsorption, at least at 303 K. On the other hand, the Freundlich parameter (an indicator of the adsorption capacity) decreased with increasing temperature. Similar behaviour was also observed with the experimental isotherms. At 303 K, the  $K_F$  values decreased in the following order: (Cu)Al-MCM-41 > (Na)Al-MCM-41 > (Cr)Al-MCM-41 > (K)Al-MCM-41. The exponential coefficient,  $1/n$ , remained relatively constant with temperature for (Cr)Al-MCM-41 and (K)Al-MCM-41 samples, in contrast to the situation with (Cu)Al-MCM-41 and (Na)Al-MCM-41 for which the parameter increased with increasing temperature. Since the coefficient  $n$  characterizes the intensity of adsorption, its variation — particularly for (Cu)Al-MCM-41 — must be a consequence of the range of adsorption sites distributed within this sample, i.e. sites occupied by  $\text{Cu}^{2+}$  ions and unexchanged  $\text{Na}^+$  cations. In other words, it would appear that both these two types of ions participated in PCP adsorption.

### Isosteric heat

The isosteric heats of adsorption,  $Q_{st}$ , were obtained via an application of the Clausius–Clapeyron equation:

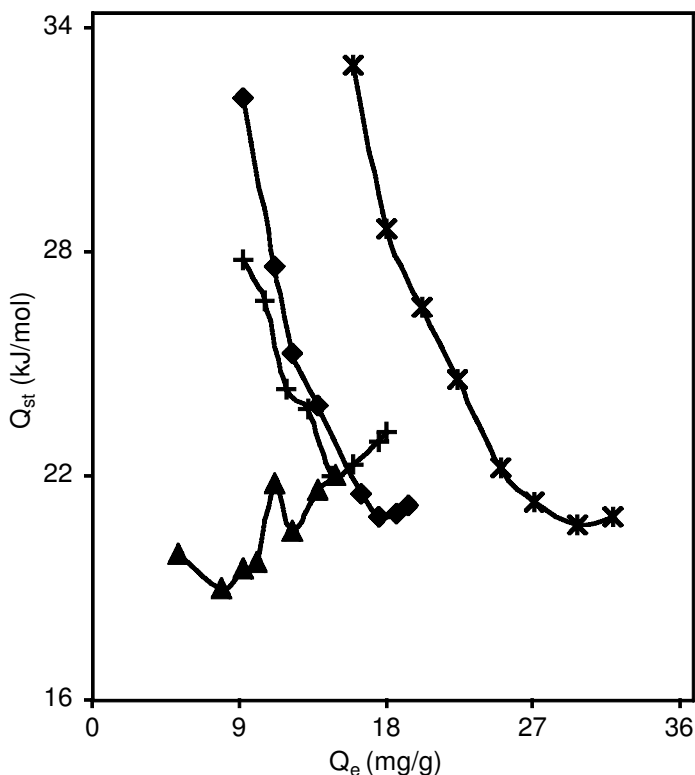
$$\left( \frac{\partial \ln C_e}{\partial T} \right)_{Q_e} = - \frac{\Delta H_{ads}}{RT^2} \quad (4)$$

If  $Q_{st}$  ( $= -\Delta H_{ads}$ ) is independent of temperature for a given amount of PCP adsorbed, plots of  $\ln C_e$  versus  $1/T$  should yield straight lines. To within experimental error, this was the case in the present study. The value of  $Q_{st}$  was then determined from the slope of the linear plot.

The isosteric adsorption heats as a function of the amount adsorbed are presented in Figure 4. It shows that the overall enthalpy change,  $\Delta H_{ads}$ , for PCP–(M)Al-MCM-41 systems was negative, indicating that the adsorption of PCP onto (M)Al-MCM-41 was exothermic with the product being stable energetically as a consequence of the strong binding of PCP to the adsorbent. The negative enthalpy also indicated that increasing temperature favoured the retention of PCP in the aqueous phase, a similar conclusion to that reached in the study of the desorption of PCP from soil where the adsorption energy was found to be 14.7 kJ/mol (Tse and Lo 2002). The relative higher enthalpy obtained for PCP–(M)Al-MCM-41 systems could be explained by the energetic state of the surface of the (M)Al-MCM-41 samples.

Conformity to the Freundlich model suggests that the energy of adsorption decreased with increasing surface saturation (Kithome *et al.* 1998). The curves corresponding to (Na)Al-MCM-41 and (Cu)Al-MCM-41 exhibited a continuous decrease in the isosteric heat with increasing adsorbate loading. This indicates a higher degree of heterogeneity for the adsorption centres contained in (Na)Al-MCM-41. However, for (Cu)Al-MCM-41 the situation was different. The fact that the highest affinity exhibited by (Cu)Al-MCM-41 was explained above as being due to the predominance of attractive adsorbate–adsorbate interactions relative to adsorbate–(Cu)Al-MCM-41 interactions, suggests that the  $\text{Cu}^{2+}$  ions were not the main specific adsorption sites.

FT-IR spectroscopic studies by Ziolek *et al.* (2001) on (Cu)Al-MCM-41 after NO adsorption emphasized the presence both of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  cations, the  $\text{Cu}^{2+}$  cations being introduced by ion exchange. In other words, the copper ion content of the material was partially reduced to  $\text{Cu}^+$  under these circumstances. IR studies have also shown that insertion of the  $\text{Cu}^{2+}$  ion into a zeolite led to the formation of Cu–O–Cu bridges upon dehydration (Naccache and Bentaarit 1984).



**Figure 4.** Isosteric heats of PCP adsorption on (M)Al-MCM-41. Experimental data: ◆, (Na)Al-MCM-41; ▲, (K)Al-MCM-41; ✱, (Cu)Al-MCM-41; ✚, (Cr)Al-MCM-41.

The presence of such an inactive species in the zeolite lattice would lead to weak interactions between Cu–O–Cu species and the adsorbate, thereby accentuating adsorbate–adsorbate interactions. The same behaviour has been found in gas–CuX systems (Khelifa *et al.* 1999c).

The heterogeneous energetic character of Cu(Al)-MCM-41 with respect to PCP adsorption could be due mainly to the contribution of the unreduced fraction of Cu<sup>2+</sup> ions and unexchanged Na<sup>+</sup> ions. This conclusion may be correlated with the magnitude of the intensity factor, *n*.

The isosteric heats for (K)Al-MCM-41 and (Cr)Al-MCM-41 remained relatively constant over the entire coverage range. Thus, the surfaces of these samples were reasonably homogeneous, with this homogeneity being probably the origin of their weak affinity relative to PCP adsorption.

## CONCLUSIONS

The adsorption isotherms of PCP from aqueous solutions onto (M)Al-MCM-41 (M = Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>) were determined. The experimental isotherms obtained were of the S type according to the classification of Giles *et al.* and were described adequately by the Freundlich model. From considerations of the adsorption affinity and isosteric heat, it was shown that the adsorptive properties of (M)Al-MCM-41 materials relative to PCP were influenced by the nature of the

exchanged cations. Thus, (Cu)Al-MCM-41 exhibited the greatest affinity followed by (Na)Al-MCM-41. This higher adsorption capacity could be the consequence of the heterogeneous energetic states of their surfaces. On the other hand, the energetically homogeneous nature of (K)Al-MCM-41 and (Cr)Al-MCM-41 was probably the reason for their weak affinity relative to PCP adsorption.

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