Journal of
Environmental
Nanotechnology

Research Article

Adsorption of Phenolic Compounds on Mesoporous Aluminophosphate Molecular Sieves from Aqueous Solution

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Received: 08.11.2018 Accepted: 22.12.2018 Published: 30-03-2019
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ABSTRACT

The removal of phenolic compounds through adsorption has been reported on many natural materials and activated carbon, but the adsorption on mesoporous as well as nanoporous $AlPO_4$ has not been reported yet; hence, in the present investigation, an attempt has been to use mesoporous $AlPO_4$ as an adsorbent for the removal of phenolic compounds (phenol and p-cresol). The formation of mesoporous $AlPO_4$ was confirmed by FT-IR analysis. To achieve maximal adsorption, phenolic compounds' adsorption conditions such as contact duration, pH, starting concentration of the solution, temperature and adsorbent dose were tuned. On mesoporous $AlPO_4$, the Langmuir and Freundlich adsorption isotherms were investigated to determine monolayer and multilayer adsorption capacities. The adsorption kinetics of phenolic compounds on mesoporous $AlPO_4$ were studied for determining thermodynamic parameters of adsorption from energy, enthalpy and entropy.

Keywords: Mesoporous $AlPO_4$; Nanoporous; Phenolic compounds' adsorption.

1. INTRODUCTION

Water pollution control is presently one of the major thrust areas of scientific research. Years of increased industrial, textile and domestic activities have resulted in the generation of a large amount of wastewater containing many toxic pollutants. Organic pollutants in nano-size comprise a potential group of chemicals that can be dreadfully hazardous to human health. The most important organic pollutants are phenols and their derivatives (Meena *et al.* 2005; Anjaneyulu, 2005). Chemical pollutants continuously released from various sources raise a number of ecological concerns because their biodegradation is normally very slow, and conventional treatments are either ineffective or not environmentally compatible (Hang-Yan Wang, 2009). The colour of effluent dumped into receiving waterways has become a severe issue in recent years. Physical and chemical techniques such as coagulation, flocculation, biosorption, photodecomposition, and ultrafiltration have been researched in an attempt to alleviate the environmental problem (Galindo *et al.* 2003; Robinson *et al.* 2001). The adsorption process is the method of choice for removing organic compounds from wastewater among these strategies (Dabrowshi, 2001).

Many industries that discharge hazardous wastewaters provide many problems to human health, including diarrhea, liver damage, anaemia and dark urine (Kumar *et al.* 2007). Especially, phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and cause significant taste and odor problems to drinking water (Iffat *et al.* 2004).

2. EXPERIMENTAL

2.1 Materials and Methods

The compounds utilized in this study are analytical-grade compounds that were employed without additional purification. Aluminium hydroxide (97%, Merck), phosphoric acid (88%, Nice), the long-chain alkylbenzene, (SDBS, 25 wt. % in water, Aldrich) were used for the preparation of mesoporous $AlPO_4$. The Phenol and p-cresol shown in Fig. 1 (a) and Fig. 1 (b) were used to study the removal of organic pollutants. The properties of phenol and p-cresol were given in Table 1. The tetrahedral framework of synthesized mesoporous AlPO4 was confirmed by Fourier Transform Infrared (FT-IR) spectroscopy; the measurement of the sample was taken using JASCO-410 FT-IR model spectrophotometer by using KBr pellet technique. A double-beam UV-Vis. Spectrophotometer (Perkin Elmer, Lambada 25) was used to determine the concentration of the samples.

2.2 Synthesis of Mesoporous $AlPO_4$

7.48 g of aluminium hydroxide was added to 17.5 g of sodium dodecylbenzene sulfonate solution with vigorous stirring. The combination was then given 9.8 g of phosphoric acid solution. At room temperature, the

https://doi.org/10.13074/jent.2019.03.191341

mixture was stirred for 6 h. The final gel, having a molar composition of Al_2O_3:P_2O_5:0.5SDBS:300H_2O, was heated at 150 °°C with stirring until the aluminophosphate mesoporous also called nanoporous molecular sieves were completely precipitated. The completed product was rinsed many times with distilled water, filtered and dried for three hours at 120 °C. To eliminate the template, organic impurities and activate the active sites of mesoporous together with nanoporous aluminophosphate molecular sieves, this sample was calcined at 600 °C for 6 h.

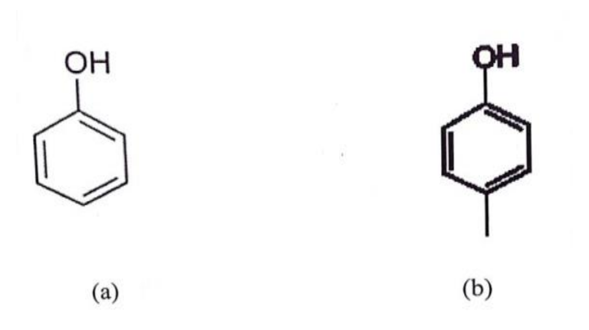

Fig. 1: Structure of (a) phenol and (b) p-cresol

2.3 Preparation of Stock Solution

Stock solution (1000 mg/L) of phenol and p-cresol were prepared by dissolving in double-distilled water. Experimental solutions of desired concentrations were then obtained by successive dilutions with distilled water.

2.4 Adsorption Experiment

The mesoporous $AlPO_4$ was activated by heating in an electric Bunsen at 500 °C for 4 h to remove physically adsorbed species present in the pores and surfaces. Then 0.5 g of mesoporous $AlPO_4$ was added with 50 ml of phenol and p-cresol solutions separately. The solution was agitated (Kemi agitator) at 150 rpm. The solutions' concentrations were measured spectro-photometrically. The maximum absorbances were found using Scanning Spectro-photometry at the respective wavelength. The maximum wavelength (λ_{max}) used were 269 nm and 285 nm for phenol and p-cresol, respectively.

To find out the maximum removal of phenol and p-cresol over mesoporous $AlPO_4$, the conditions like contact time, pH, dye concentration, temperature and adsorbent dosage were optimized. The effect of contact time was studied up to adsorption equilibrium. The effect of pH was studied in 2 to 11 range. The adsorption of phenol and p-cresol over mesoporous $AlPO_4$ were studied in the concentration range of 10-50 mg/L. The temperature effect of adsorption of phenol and p-cresol was studied in the range of 30-70 °C. The mesoporous $AlPO_4$ dosage effect was studied in 0.5-2.5 g range.

The adsorption capacity (mg phenol/g adsorbent) of mesoporous $AlPO_4$ was calculated by using the equation,

$$q = (C_0-C_e)\ V/W$$

The removal percentage (%) was calculated by using the equation,

$$\text{Removal in percentage} = (C_0-C_e) \times 100/\ C_0$$

where,
q is the amount of adsorbate adsorbed on mesoporous $AlPO_4$ (mg g^{-1}),
C_0 and C_e are the initial and final concentrations of adsorbate in solution (mg L^{-1}), respectively.
V is the volume of solution (L), and W is the adsorbent weight (g).

Amino-antipyrine method for detection of phenol concentration:

3 ml of phenol solution was taken in a 10 ml volumetric flask. To this 1 ml of ammonia buffer solution (pH = 10), 2 ml of 2%, 4-aminoantipyrine solution and 6 ml of 4% potassium ferricyanide solution were added in the mentioned order and diluted up to 100 ml with distilled water. The solution was checked for complex formation using UV-Vis. spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Characterization of Mesoporous $AlPO_4$

The $AlPO_4$ was by following the reported literature. To verify the framework of the prepared mesoporous $AlPO_4$, FT-IR study has been carried out.

The FT-IR spectrum of the calcined sample was shown in Fig. 2. The asymmetric stretching of tetrahedral $AlPO_4$ was observed near 1106 cm^{-1}, corresponding symmetric stretching was observed around 674 cm^{-1} and bending mode was positioned near 466 cm^{-1}. The broad peak at 3423 cm^{-1} was due to –OH groups and water molecules present in these molecular sieves. This tetrahedral framework vibration proved the formation of $AlPO_4$ sieves.

3.2 Adsorption Studies

The effect of removal of phenol and p-cresol over mesoporous $AlPO_4$ through adsorption at different conditions such as contact time, concentration, pH, temperature and adsorbent dosage was optimized for maximum adsorption.

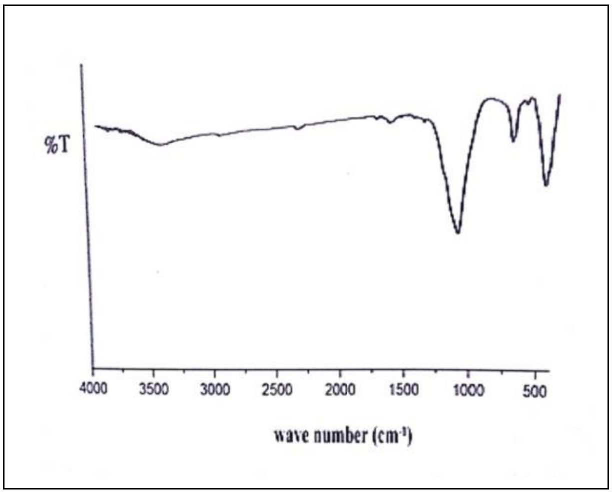

Fig. 2: FT-IR spectrum of calcined mesoporous $AlPO_4$

3.2.1 Effect of contact time

The effect of contact time has been carried out at room temperature for the adsorption of phenol and p-cresol on mesoporous $AlPO_4$ up to 40 min (Fig. 3). Adsorption equilibrium was observed at 30 min for both (phenol and p-cresol); further increase in contact time was not effective in increasing the adsorption. Initially a large number of vacant sites were available for the adsorption; hence, the adsorption rate was very high for phenol. The removal of p-cresol from the aqueous solution on the mesoporous $AlPO_4$ was far less than that of phenol, showing the different affinities of the phenolic species on the active sites of mesoporous $AlPO_4$.

3.2.2 Effect of pH

The removal of hazardous pollutants, phenol and p-cresol, is influenced by the pH factor. The effect of pH was studied in the range from 2 to 11 (Fig. 4). The pH of the solution was adjusted by using 0.1 N NaOH and/or 0.1 N HCl. The adsorption of phenol and p-cresol increased gradually with the increase of pH and reached a maximum at pH 7. Further increase in pH decreased the adsorption. At pH 7, the adsorption was found to be maximum, whereas below and above 7, the adsorption was not favorable. The lower adsorption at low pH might be due to the protonation of phenolic compounds, due to which, there might be the formation of a positive charge on both the adsorbent and adsorbate system, resulting in the net reduction of phenolic compounds' adsorption. With the increase in pH from 5 to 7, the molecular form of phenolic species persisted in medium, and surface protonation was minimum, leading to the enhancement of adsorption.

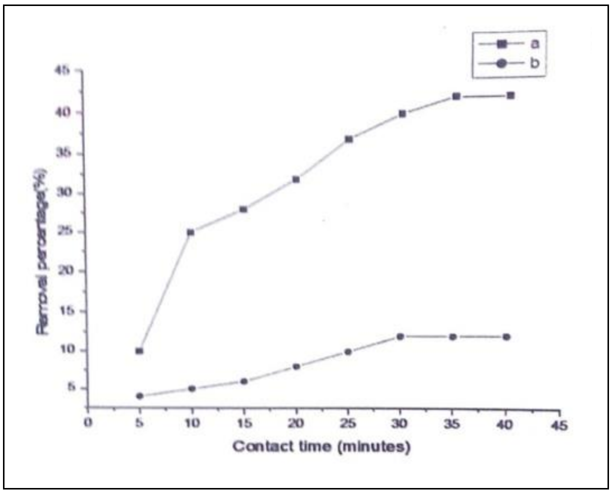

Fig. 3: Effect of contact time for adsorption of (a) Phenol and (b) p-cresol over mesoporous $AlPO_4$ (Conc.: 10 mg/L, Temperature: 30 °C, Adsorbent dosage: 0.5 g)

3.2.3 Effect of concentration

The phenol and p-cresol adsorption on mesoporous $AlPO_4$ were studied in the concentration range of 10 - 50 mg/L at room temperature and shown in Fig. 5. The adsorption capacity of the mesoporous $AlPO_4$ was found to be maximum at 10 mg/L and further increase in concentration decreased the adsorption of phenol and p-cresol on the adsorbent. The initial concentration provided an important driving force to overcome all mass transfer resistance of the phenolic compound between the aqueous and solid phases. The phenolic compounds interact with active sites present in the surface and the pores of mesoporous as well as nanoporous aluminophosphate molecular sieves, facilitating phenol and p-cresol adsorption. At higher concentrations, phenolic compounds were bound to each other through hydrogen bond and hence the adsorption percentage decreased. Moreover, at higher concentrations, the surface area and active sites were saturated. Hence, adsorption decreased with the increase in concentration.

3.2.4 Effect of temperature

The effect of temperature for the removal of phenol and p-cresol on mesoporous $AlPO_4$ was studied in the temperature range of 303 to 343 K (30 to 70 °C) and shown in Fig. 6. The adsorption increased with the increase of temperature from 30 °C to 70 °C indicating that the adsorption process was endothermic. This may due to an increase in interaction between adsorbate and adsorbent.

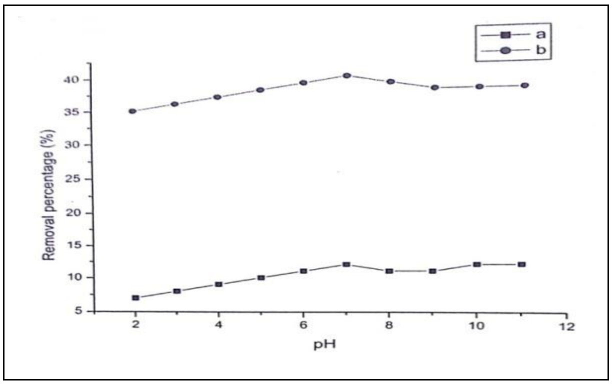

Fig. 4: Effect of pH on adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30 min, Concentration: 10 mg/L, Temperature: 30 °C, Adsorbent dosage: 0.5 g)

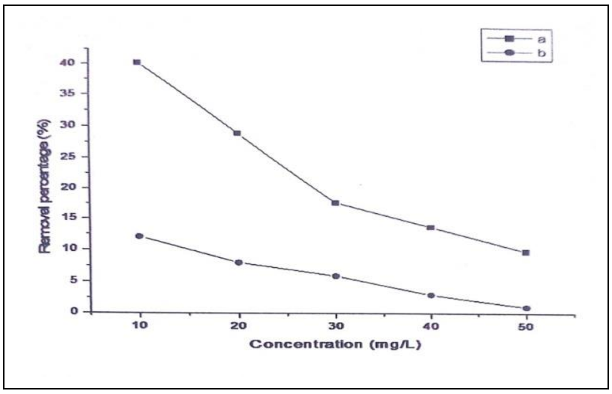

Fig. 5: Effect of Concentration on adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30 mins, Temperature: 30 °C, Adsorbent dosage: 0.5 g, pH: 7)

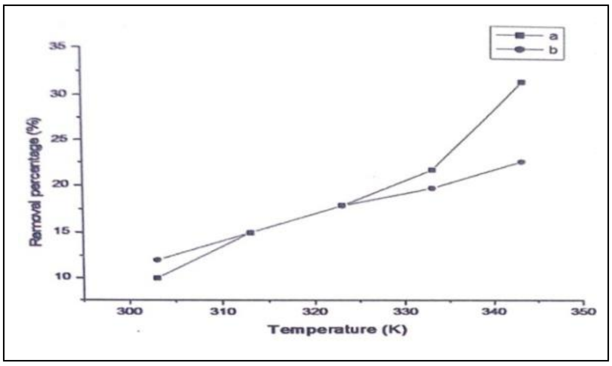

Fig. 6: Effect of Temperature on adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30 mins, Concentration: 500 mg/ L, Adsorbent dosage: 0.5 g, pH: 7)

3.2.5 Effect of adsorbent dosage

The effect of adsorbent dosage (0.5-2.5 g) on adsorption of phenol and p-cresol was studied (Fig. 7). The percentage removal of the phenol and p-cresol was found to increase with the increase in adsorbent dosage, since the increase in dosage increased the surface area and active sites. Hence, adsorption increased with the increase of mesoporous $AlPO_4$.

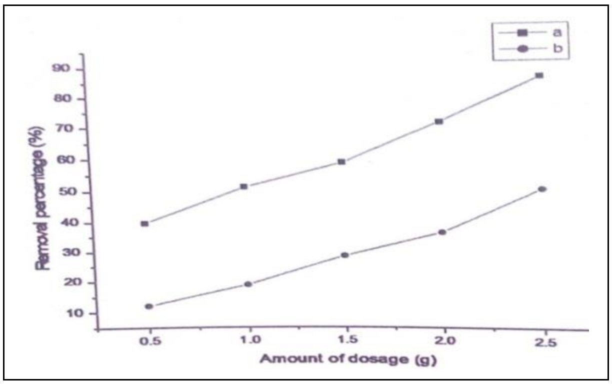

Fig. 7: Effect of Adsorbent dosage on adsorption of phenol and p-cresol on mesoporous $AlPO_4$ (Contact time: 30 mins, Concentration: 500 mg/L, Temperature: 30 °C, pH: 7)

4. Adsorption Isotherms

Langmuir and Freundlich isotherms govern the distribution of phenol and p-cresol between the adsorbent and solution.

4.1 Langmuir adsorption isotherm

For the adsorption of phenol and p-cresol, adsorption isotherm data at various concentrations were measured and fitted with the Langmuir adsorption isotherm equation (Fig. 8). This research was carried out as a model to better understand phenol monolayer adsorption and p-cresol multilayer adsorption on mesoporous $AlPO_4$.

The Langmuir equation is represented as,

$$C_e/Q_e = (1/Q_{max} K_L) + (C_e/Q_{max})$$

where,
Q_e is the equilibrium concentration of adsorbate on the adsorbent (mg g^{-1})
C_e is the equilibrium concentration of adsorbate in the solution (mg L^{-1})
Q_{max} is the monolayer capacity of adsorbent (mg g^{-1}) and
K_L is the Langmuir adsorption constant

Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent, and $1/K_L$ value gives half maximum adsorption. A plot of C_e/Q_e vs. C_e was a straight line with a slope of $1/Q_{max}$ and an intercept of $1/Q_{max}$ K_L. The R^2 values for the adsorption of phenol and p-cresol on mesoporous $AlPO_4$ were presented in Table 1.

The correlation coefficient (R^2) values were very close to 1 ($R^2 = 0.992$) for phenol, indicating that the adsorption of phenol on mesoporous $AlPO_4$ followed the Langmuir adsorption isotherm. The maximum monolayer adsorption capacity of mesoporous $AlPO_4$ for phenol was 0.5226 mg/g. The correlation coefficient (R^2) value was not close to 1 ($R^2 = 0.86$) for p-cresol and hence the adsorption of p-cresol was not following the Langmuir adsorption isotherm. This may occur due to the steric effect of the methyl group present in the p-cresol. This result clearly indicated that the mesoporous $AlPO_4$ has more affinity with phenol molecule than p-cresol.

4.2 Freundlich Adsorption Isotherm

The adsorption of phenol was studied at various concentrations and the adsorption measurements were then used to validate the adsorption isotherms using the Freundlich equation (Table 1).

The Freundlich equation is represented as,

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

where,

K_F is the Freundlich constant and n is the number of layers.

The plot of ln Q_e vs. ln C_e gave a straight line (Fig. 9) with an intercept of ln K_F and a slope of 1/n. The correlation coefficient for adsorption of phenol and p-cresol was not close to 1 (0.620 for phenol and 0.045 for p-cresol). This result revealed that both adsorption processes were not following the Freundlich isotherm model.

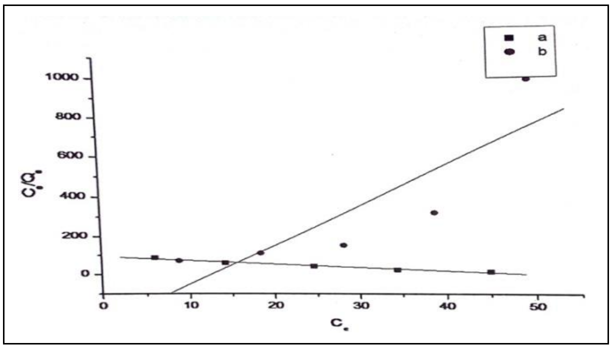

Fig. 8: Linear forms of Langmuir adsorption isotherm plots of phenol and p-cresol on mesoporous $AlPO_4$

Table 1. Langmuir and Freundlich adsorption isotherm parameters

S. No.	Langmuir isotherm			Freundlich isotherm		
	Parameters	Phenol	p-cresol	Parameters	Phenol	p-cresol
1.	Q_{max}	0.5226	0.0492	1/n	0.1151	0.284
2.	K_L	-7.226	-0.0808	K_F	-.0146	-0.662
3.	R^2	0.99	0.86	R^2	0.620	0.045

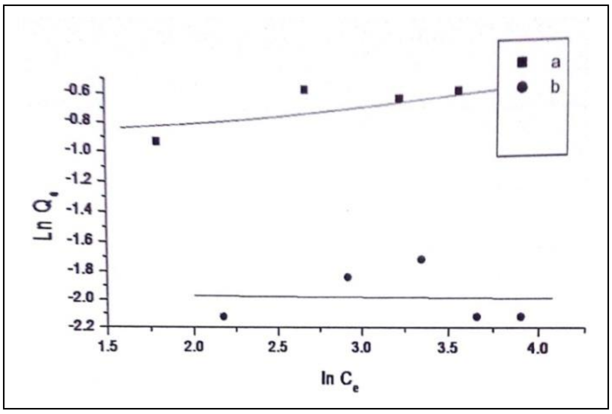

Fig. 9: Linear forms of Freundlich adsorption isotherm plots of phenol and p-cresol on mesoporous $AlPO_4$

5. ADSORPTION KINETICS

The adsorption kinetics of phenol and p-cresol adsorption on mesoporous $AlPO_4$ was studied as a model study to find out the rate constant of the adsorption. The adsorption of phenol was studied at a regular time interval at room temperature. The experimental values were introduced in the pseudo-second order kinetics equation for calculating the rate constant.

The equation for adsorption kinetics is,

$$t/Q_t = (1/k)\, Q^2_e + (1/\, Q_e)\, t$$

where,

K is the rate constant, Q_e and Q_t are the amounts of adsorbate adsorbed per unit mass of the adsorbent at equilibrium and t is the time. The plot of t/Q_t vs. t has given a straight line. Linear plots of the t/Q_t vs. t were shown in Fig. 10 for phenol and p-cresol adsorption on mesoporous $AlPO_4$. The linear regression coefficients were close to 1 (Table 2), indicating that the adsorption of phenol (R^2=0.96) and p-cresol (R^2=0.907) on mesoporous $AlPO_4$ fitted with the pseudo-second-order kinetics.

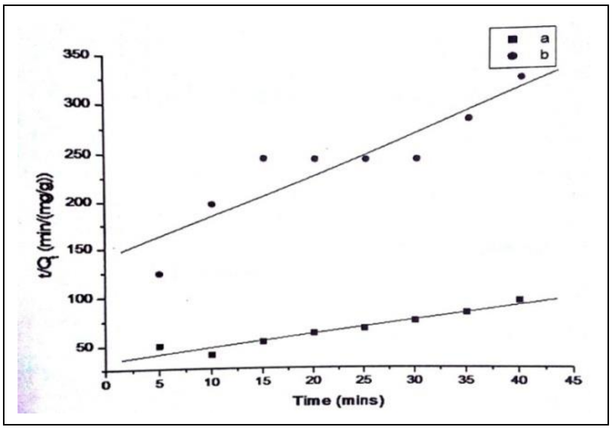

Fig. 10: Linear forms of Pseudo-second order kinetics plots of phenol and p-cresol on mesoporous $AlPO_4$

Table 2. Pseudo-second-order kinetics parameters

S. No.	Kinetic parameters	Phenol	p-cresol
1.	K	0.0611	0.0768
2.	Q	0.6972	0.2197
3.	R	0.9616	0.9079

6. ADSORPTION THERMODYNAMICS

The thermodynamic parameters, namely free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have an important role in determining spontaneity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$K_D = q_e/C_e$$

$$\Delta G^o = -RT \ln K_D$$

$$\ln K_D = (\Delta S^o/R) - \Delta H^o/ RT)$$

From the above equations,

$$\Delta G = \Delta H - T\Delta S$$

where,

K_D is the distribution coefficient of the adsorbate, q_e, and C_e are the equilibrium concentrations of adsorbate on mesoporous $AlPO_4$ (mg g^{-1}) and in the solution (mg L^{-1}), respectively. R is the universal gas constant (8.314 J/mol-K) and T is the temperature (K). ΔH^o and ΔS^o parameters can be calculated from the slope and intercept of the ln K_D vs. 1/T plot, respectively (Fig. 11). ΔG^o was calculated using the equation for different temperatures. Results were summarized in Table 4. ΔG^o values at the temperatures of 303, 313, 323, 323, 333 and 343 K were negative, indicating that the process was a feasible adsorption process and spontaneous.

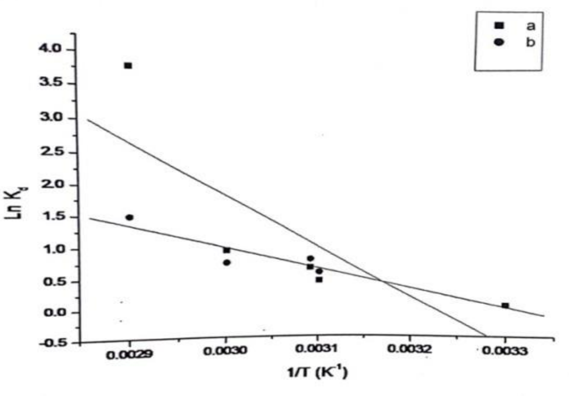

Fig. 11: Linear forms of Adsorption thermodynamic plots of phenol and p-cresol on mesoporous $AlPO_4$

The enthalpy (ΔH^o) values greater than 40 KJ/mol for phenol (68.64 kJ/mol) indicated that the adsorption of phenol over mesoporous $AlPO_4$ was chemisorption and less than 40 kJ/mol for p-cresol (27.92 kJ/mol) indicated that the adsorption of p-cresol over mesoporous $AlPO_4$ was physisorption. The positive value of enthalpy indicated that the adsorption process was endothermic. Moreover, the positive value of ΔS^o indicated that the degrees of freedom increased at the solid-liquid interface during the adsorption.

Table 3. Thermodynamic parameters for adsorption of phenol and p-cresol

S. No.	Thermodynamic parameters	Phenol	p-cresol
1.	ΔH^o (KJ/mol)	68.64	27.92
2.	ΔS^o (KJ/mol/K)	0.21	0.092
3.	ΔG^o (KJ/mol) T=303 K T=313 K T=323 K T=333 K T=343 K	 -1.677 -0.533 -2.743 -1.623 -3.373	 0.044 -0.876 -1.796 -2.716 -3.631

7. CONCLUSION

A mesoporous aluminophosphate molecular sieve has been successfully manufactured. It may be used to extract phenol and p-cresol from aqueous solutions. After 30 minutes, the adsorption equilibrium was reached. The monolayer adsorption capacity of phenol was found to be 0.5226 mg/g. The findings of the adsorption isotherm demonstrated that phenol adsorption on mesoporous aluminophosphate molecular sieves followed the Langmuir isotherm. The Freundlich adsorption isotherm was not applicable to phenol adsorption. Due to the presence of methyl groups, p-cresol was not following both the adsorption isotherms. The methyl group prevented the creation of mono-/multi-layers. Thermodynamic investigations have revealed that the adsorption process was endothermic and spontaneous. The mesoporous $AlPO_4$ was found to be a good adsorbent for the elimination of phenol in this investigation.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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