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Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media

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ABSTRACT

Contamination of natural water with organic pollutants is a problem of major concern and the demand for effective adsorbents for the removal of toxic compounds is increasing. Present work deals with the adsorption of 2-chlorpphenol (2-CP) and 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous solutions on a new nano sorbent; amino-modified ordered mesoporous silica (APS-MCM-41) material. It was found that APS-MCM-41 shows significant adsorption for 2-CP and 2,4,6-TCP. This might be due to the acid and alkaline interactions among the amino functional groups and chlorophenols. Batch adsorption studies were carried out to study the effect of various parameters like adsorbent dose, pH, initial concentration and contact time. It was found that adsorption of 2-CP and 2,4,6-TCP depends upon the solution pH. From the sorption studies it was observed that the uptake of 2,4,6-TCP was higher than that of 2-CP. Freundlich and Langmuir adsorption isotherms were used to model the equilibrium adsorption data for 2-CP and 2,4,6-TCP.

1. Introduction

Chlorophenols are a widespread class of water pollutants that are known to cause serious human health problems; hence these chemicals are found in the list of priority pollutants of the Environmental Protection Agency (EPA) [1] and in the European Union (EU) [2]. They are widely used in industry as intermediates in the production of dyes, plastics and pharmaceuticals. Chlorophenol are commonly found in the wastewater of pulp and paper industry, which pollute the groundwater resources [3]. In addition, the chlorination process of tap water leads to the generation of chlorophenols from phenols, which are responsible for the unfavorable smell.

Several methods such as adsorption [4,5], chemical oxidation [6,7], photodegradation [8,9], coagulation flocculation [10], etc. are being used for the removal of chlorophenols from wastewater streams. Adsorption technology, in particular, has been used for the removal of phenolic compounds from wastewaters [11]. Intensive research work has been done on the removal of phenolic compounds using activated carbon as the adsorbent [2,12–15]. The regeneration of activated carbon is normally by means of thermal procedure and there is significant cost and capacity loss associated with this process. Alternative adsorbents studied include naturally occurring materials such as biosorbents [16,17], clays [18], zeolites [11,19] and resins [20,21]. Zeolites, in particular, comprise a regular aluminosilicate cage-like microporous structure with exchangeable counter cations. Although it was believed that the micropores provide adsorptive sites but at the same time, it was found that the surface area of micropores cannot be fully utilized in adsorption. The extent to which a particular adsorbate molecule is adsorbed on these zeolite materials is limited by a number of physical factors which include the size of the adsorbing molecules, the pore diameter of the zeolite and the length of the diffusion path [22].

As an alternative to the microporosity and size selectivity of zeolites, the use of a mesoporous silicate as an adsorbent for the removal of phenolic compounds from aqueous solution seems to be promising. Mesoporous silicates offer a number of potential advantages as adsorbents including larger pore volume and diameter, high surface area and regular channel type structures. It is also possible to manipulate these properties so as to suit those of the adsorbate [23]. MCM-41 is a member of family of silicate mesoporous materials, designated as M41S. Hexagonally ordered mesoporous silicate materials extended as molecular sieves show broad range of (13–100 Å) pore size. These materials are synthesized via a liquid crystal templating mechanism by subsequent removal of the organic template through calcination or acid dissolution. The structures are defined by ordered arrays of templating surfactant molecules and the pore size is adjusted by changing the hydrocarbon chain length of the surfactant. Varying surfactant/Si ratio and synthesis conditions produce solids with uniform hexagonally ordered cylindrical pores (MCM-41), layered materials (MCM-50), and materials with a three-dimensional pore system and cubic symmetry (MCM-48) as well as other structures [24]. These materials

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are potentially useful for catalytic, electronic, optical, magnetic and separation applications [25–29]. Their modification by functionalized molecules can lead to adsorbents with specific properties [30–32]. Removal of harmful organics by mesoporous materials grafted with organic or metal complexes has drawn much attention [33–36].

In this project, MCM-41 was prepared and functionalized with aminopropyl (AP) ligands by post-synthesis treatment. Generally, silanol groups and amino groups are effective for the adsorption of organic compounds due to their high adsorption energy or potential charge association. In addition, presence of free electron pairs on amine group within mesopores of MCM-41 materials should lead to sorptive properties for weak acidic organic compounds in water. The structural order and textural properties of the mesoporous materials were studied by XRD and nitrogen adsorption. The presence of amino functional groups on the surface of mesoporous silica was confirmed by means of FTIR analysis. The objective of this study was to evaluate the effectiveness of mesoporous APS-MCM-41 material for the sorption of 2-CP and 2,4,6-TCP. The effects of various operating parameters such as effect of adsorbent dose, initial concentration, pH of the solution and contact time were thoroughly studied. The Freundlich and Langmuir adsorption isotherms were used to model the equilibrium adsorption data.

2. Experimental

2.1. Materials

All the reagents used for experimental studies were of analytical grade and were purchased from Merck (Darmstadt, Germany). Aqueous solutions were prepared using doubly distilled water. Tetraethoxysilane (TEOS,98%) and cetyltrimethyl ammonium bromide (CTAB), were used to prepare MCM-41, 3-aminopropyl trimethoxy silane (APS) and dry Toluene were used to prepare modified MCM-41. 2-Chlorophenol (2-CP) and 2,4,6-trichlorophenol (2,4,6-TCP) were used as adsorbate.

2.2. Synthesis of MCM-41 mesoporous silica

MCM-41 silica was prepared using low surfactant concentration at room temperature. The source of silicon was TEOS and the structure directing agent was CTAB. MCM-41 was prepared by adding 5.78 g of TEOS (27.7 mmol) into a solution containing 1.01 g of CTAB (2.8 mmol) and 0.34 g of NaOH (8.5 mmol) in 30 ml of de-ionized water [37]. After stirring for 1 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal condition at 110 °C in a Teflon container for 96 h.The molar composition of the initial gel mixture was 1.0:0.1:0.3:60 TEOS/CTAB/NaOH/H_2O. The solid product was obtained by filtration, washed with de-ionized water, ethanol and dichloromethane. The product was then dried in air at 80 °C and calcined.

2.3. Synthesis of amino-modified MCM-41 (APS-MCM-41)

Modification of the prepared MCM-41 was performed as follows: MCM-41 (2.0 g) was suspended in dry toluene (70 ml) and 3-aminopropyl trimethoxysilane (APS) (1.0 g) was added under dry nitrogen atmosphere. The mixture was then refluxed for 12 h. The solid product was filtered, washed with dichloromethane and ethanol, and was dried. It was then soxhlet extracted with a mixture of ethanol and dichloromethane (1:1), in order to remove the silylating reagent residue, and was vacuum dried at 70 °C.

2.4. Characterization

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu Kα radiation. The diffractograms were recorded in the 2θ range of 0.8–10 with a 2θ step size of 0.01° and a step time of 1 s. Adsorption–desorption isotherms of the synthesized samples were measured at 77 K on micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method, while surface area of the sample was measured by Brunaure–Emmet–Teller (BET) method. The Fourier transform infrared spectra for the unmodified and modified samples were measured on a DIGILAB FTS 7000 instrument under attenuated total reflection (ATR) mode using a diamond module.

2.5. Adsorption studies

In order to study the effect of various operating parameters such as pH, initial concentration, adsorbent dose and contact time on the adsorption capacity of 2-CP and 2,4,6-TCP, batch sorption experiments were conducted. For single solute adsorption studies, model solutions of 2-CP and 2,4,6-TCP were prepared by dissolving pure samples of the solutes in double distilled water. A known quantity of the adsorbent (0.1–0.4 g/l) was taken in a 100 ml stoppered conical flask and 10 ml of aqueous solution of 2-CP and 2,4,6-TCP was added to it. The conical flasks were then kept on a rotary shaker at ambient temperature (25 ± 2 °C) for 6 h to attain equilibrium. At the end of the adsorption process, the adsorbent was filtered out and the concentration of 2-CP and 2,4,6-TCP in the residual solution was analyzed by UV-spectrophotometer (MPC-2200, UV 2550) at wavelengths of 274 and 296 nm, respectively [38].

In order to reduce the measurement errors, the UV absorption intensity for each equilibrium solution was measured in triplicates and the average value was used to calculate the equilibrium concentration; based on a standard calibration curve whose correlation coefficient square (r^2) was 0.99. The experimental error was observed to be within ±2%. The specific amount of solute (2-CP and 2,4,6-TCP) adsorbed was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q_e is the adsorption capacity (mg/g) of the adsorbent at equilibrium; C and C_e are the initial and equilibrium concentrations of solute (mg/l), respectively; V is the volume of the aqueous solution (L) and W the mass (g) of adsorbent used in the experiments.

2.6. Adsorption kinetics of chlorophenols

To measure the adsorption kinetics of chlorophenols onto adsorbents, 10 ml of chlorophenol solution with an initial concentration of 50 ppm was introduced into the flask and mixed with 0.002 g of APS-MCM-41. The solution was stirred continuously at 20 °C. Samples were taken from the solution by fast filtration at different time intervals. The concentration of chlorophenols in the residual solution was determined and the amount of adsorption (q_t) was calculated according to Eq. (2).

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where q_t is the amount of adsorption at time t, C_0 is the initial concentration of chlorophenols in the solution, C_t is the concentration of chlorophenols in the solution at time t, V is the volume of the solution, and m is the mass of APS-MCM-41.

3. Results and discussions

3.1. Characterization of APS-MCM-41

The X-ray diffraction (XRD) patterns in the range of 1.0–10.0 2θ of ordered mesoporous material, MCM-41, and the functional-

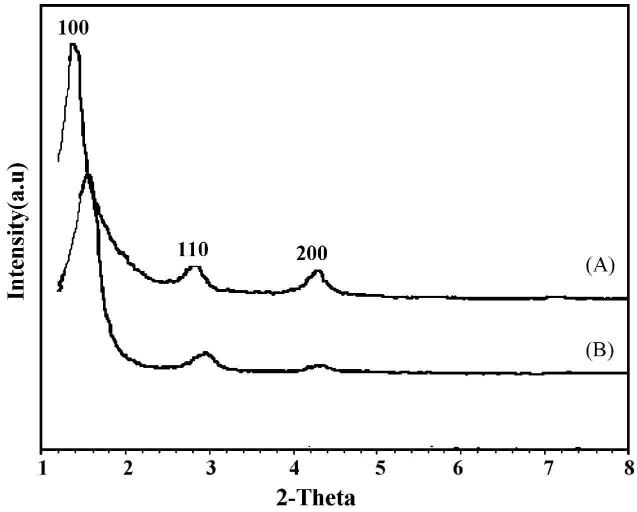

Fig. 1. XRD patterns of MCM-41 (A) and APS-MCM-41 (B).

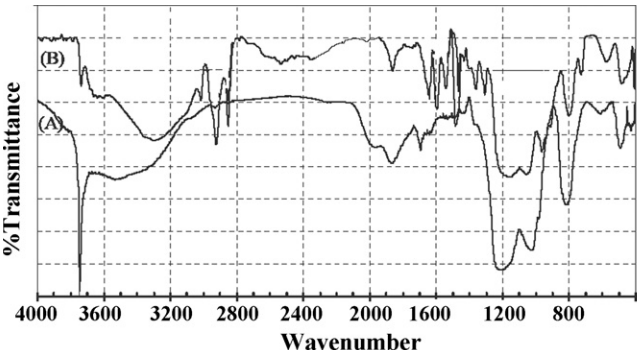

Fig. 2. The FT-IR spectra of MCM-41 (curve A) and APS-MCM-41 (curve B).

ized sample, APS-MCM-41, are shown in Fig. 1. The XRD patterns of the MCM-41 show strong (1 0 0) peak and proportional (1 1 0) and (2 0 0) peak intensities. In the X-ray diffraction pattern of the prepared material, the peak (1 0 0) of the parent MCM-41 was preserved while the other peaks were disappeared. The latter was attributed to the incorporation of organic groups inside the channels of MCM-41. This pattern is confirming the presence of the hexagonal structure of the pores and suggesting that the modification process does not affect the framework integrity of the ordered mesoporous MCM-41 [39–41].

The functional groups contained by the samples were also identified using FT-IR. Fig. 2 shows the FT-IR spectra of the modified sample along with the unmodified mesoporous MCM-41. The O—H stretching bonds of silanol groups were observed at 3200–3800 cm^{-1}. Silanol groups on the silica surface of MCM-41 exist as several types, such as isolated, hydrogen bonded, and geminal types of silanol [42]. The IR absorption bands of these silanol groups correspond to the peaks at 3740, 3200–3600, and 3715 cm^{-1}, respectively. The results showed that the surface silanol group was mainly of the isolated type, IR absorption bands for which were observed at 3746 cm^{-1}. Si—O bond stretching was detected at 976 cm^{-1}. In general, the functionalized silicas with 3-aminopropyl trimethoxysilane show an IR peak for the CH_2 rocking vibration of Si—CH_2R at around 700 cm^{-1}. Broad NH_2 stretching at 3250–3450 cm^{-1}, an N—H deformation peak at 1640–1560 cm^{-1}, C—H stretching of methyl groups at 3000–2840 and 1450 cm^{-1} [43]. The efficiency of the grafting process is demonstrated by a significant decrease in the silanol bands at around 3746 cm^{-1}, with an association increase of new bands characteristic of the immobilized aminopropyl groups.

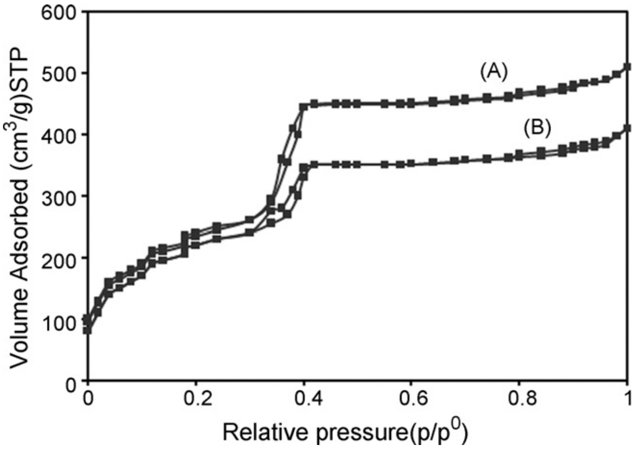

Fig. 3. Nitrogen adsorption–desorption isotherms of MCM-41 (A) and APS-MCM-41 (B).

Fig. 3 shows the nitrogen adsorption–desorption isotherms performed at 77 K for the MCM-41 silica before and after grafting with 3-aminopropyl trimethoxysilane. The textural properties of these materials are summarized in Table 1. Both the surface area and the total pore volume of the modified sample dropped significantly compared with the non-functionalized sample, MCM-41. The decrease in the pore volume of the material after silanization is the direct consequence of the silanization process which fills the mesopores.

3.2. Adsorption studies

3.2.1. Effect of chemical modification

In order to evaluate the efficiency of the prepared adsorbents, the equilibrium adsorption of the chlorophenols was studied as a function of equilibrium concentration. The adsorption isotherms of 2-CP and 2,4,6-TCP on APS-MCM-41 and MCM-41 are shown in Figs. 4 and 6. It is seen that the order of adsorption in terms of the amount adsorbed (mg/g) at different conditions is: APS-MCM-41 > MCM-41.

APS-MCM-41 registers higher adsorption capacity (338.84 and 275.42 mg/g for 2,4,6-TCP and 2-CP, respectively) than the untreated mesoporous MCM-41 (103 and 97 mg/g for 2,4,6-TCP and 2-CP, respectively).

The higher adsorption capacity of APS-MCM-41 can be explained by several facts. This may be because of the hydrophobicity created by propyl amine group. It is also surmised that the presence of a free electron pair causes more interaction between chlorophenols and adsorbent in APS-MCM-41. In other words, chlorophenols are weak acids and there are acid and alkaline interactions among amine groups and chlorophenols.

Table 1
Textural properties determined from nitrogen adsorption–desorption experiments at 77 K and powder XRD measurements.

Sample	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (Å)	d_{100} (Å)	Wall thickness (Å)
MCM-41	1183	1.24	51.1	62.4	21.9
APS-MCM-41	1049	0.91	31.3	55.9	23.2

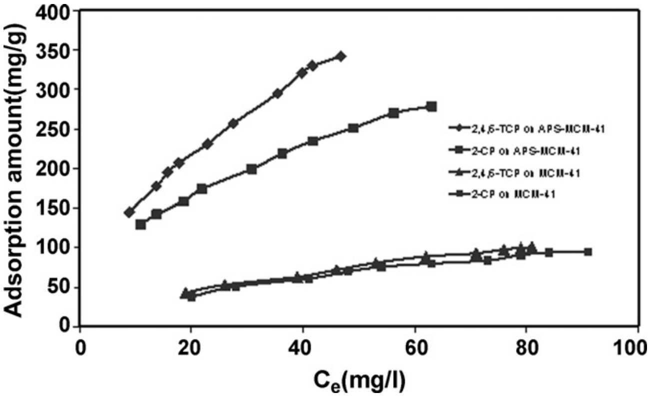

Fig. 4. Adsorption isotherm for 2,4,6-TCP and 2-CP removal on APS-MCM-41 and MCM-41 (contact time = 6 h, agitation speed = 250 rpm, adsorbent dosage = 0.2 g/l, room temperature = 25 ± 2 °C).

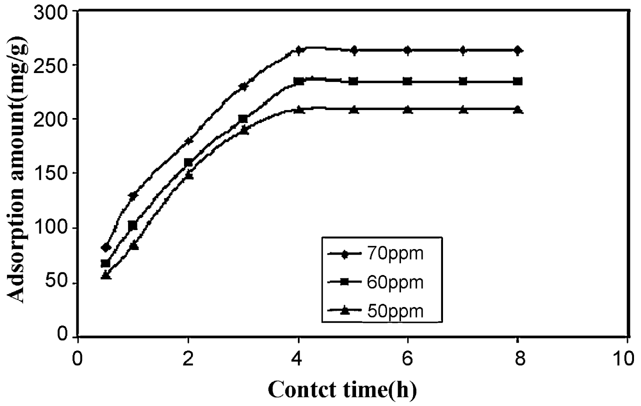

Fig. 5. Effect of initial concentration on removal of 2,4,6-TCP on APS-MCM-41 (adsorbent dosage = 0.2 g/l, contact time = 6 h, room temperature = 25 ± 2 °C).

3.2.2. *Effect of contact time and concentration*

In order to establish an equilibration time for the maximum uptake and to evaluate the kinetics of the adsorption process, the adsorption of chlorophenols on APS-MCM-41 was studied as a function of contact time. The results are shown in Figs. 5 and 6. It is seen that the rate of uptake of the chlorophenols is rapid at the beginning and 50% of adsorption is completed within 1 h. Figs. 5 and 6 also indicate that the time required for equilibrium is 4 h. Thus, for all equilibrium adsorption studies, the contact period was kept 6 h. The effect of concentration on the equilibration time was also investigated as a function of initial concentration of chlorophenols. It was found that the time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration.

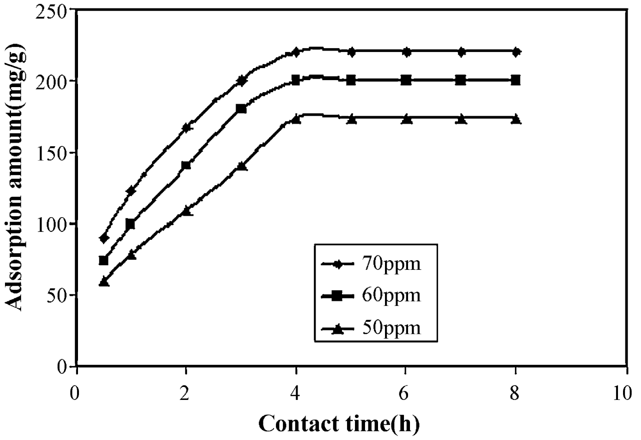

Fig. 6. Effect of initial concentration on removal of 2-CP on APS-MCM-41 (adsorbent dosage = 0.2 g/l, contact time = 6 h, room temperature = 25 ± 2 °C).

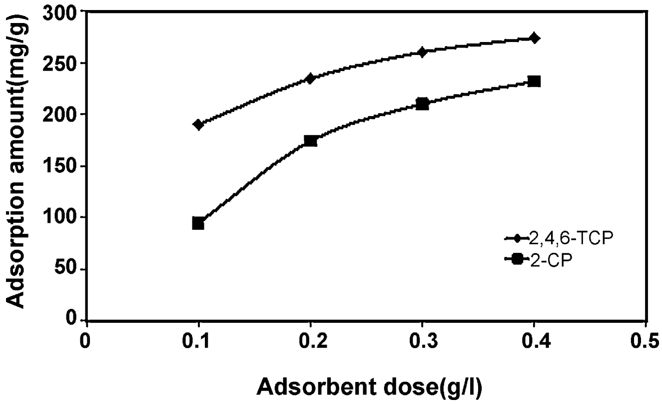

Fig. 7. Effect of adsorbent dose on removal of 2,4,6-TCP and 2-CP on APS- MCM-41 [initial concentration = 50 mg/l, contact time = 6 h, room temperature = 25 ± 1 °C.

3.2.3. *Effect of adsorbent dose*

The effect of adsorbent dose on the uptake of 2-CP and 2,4,6-TCP on APS-MCM-41 was studied. The results are shown in Fig. 7. The present study shows that the APS-MCM-41 is an effective adsorbent for the removal of 2-CP and 2,4,6-TCP from aqueous solution. It can be seen from Fig. 7 that the amount of adsorption for 2-CP and 2,4,6-TCP was increased with the increase in adsorbent dose. This increase in loading capacity is due to the availability of greater amount of active sites of the adsorbent. The adsorption capacity for 2,4,6-TCP is higher than that for 2-CP due to the stronger interactions of the former with APS-MCM-41. It is notable that chlorophenols are weak acids. Therefore, their interactions with adsorbent species depend on their acidity strength. As such, TCP with higher acidity strength in comparison with CP is expected to be adsorbed more efficiently.

3.2.4. *Effect of pH*

The pH of the aqueous medium is an important factor that may influence the uptake of the adsorbate. The chemical characteristics of both the adsorbent and the adsorbate vary with pH. The pH of the solution affects the degree of ionization and speciation of various pollutants which subsequently leads to a change in the reaction kinetics and equilibrium of the adsorption process. The effect of initial pH on the adsorption of 2-CP and 2,4,6-TCP by APS-MCM-41 was studied. NaOH and HCl solutions were used to adjust the pH of the solution. The experimental results for the uptake of 2-CP and 2,4,6-TCP on APS-MCM-41, in the pH range of 1–11, are shown in Fig. 8. It was observed that the relative uptake of 2-CP and 2,4,6-TCP was significantly affected by pH. The adsorption capacity of chlorophenols remains nearly constant at $7 < \text{pH} < 11$, while at acidic region the adsorption capacity for both of 2-CP and 2,4,6-TCP decreases. This observation is due to the interactions of the protons with APS-MCM-41. There are acid-alkaline interactions among adsorbates and APS-MCM-41. Therefore, the amount of adsorption depends on the acidic strength of the species. At low pH values, adsorption capacity decreases due to the presence of protons in solution which compete with the chlorophenols to be adsorbed on APS-MCM-41 species.

3.3. *Adsorption modeling*

Equilibrium studies were carried out to determine the adsorption capacity and equilibrium constant for 2-CP and 2,4,6-TCP on

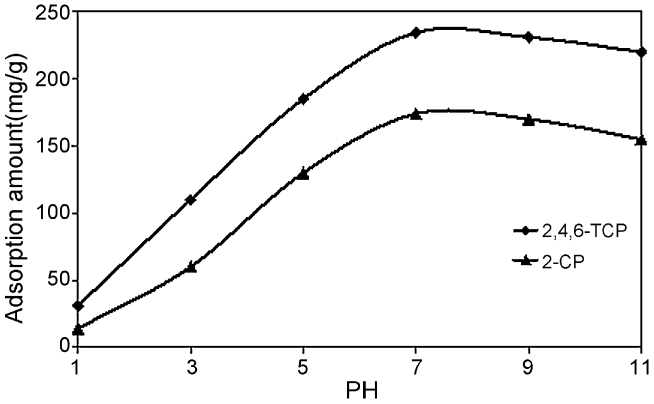

Fig. 8. Effect of pH on removal of 2-CP and 2,4,6-TCP on APS-MCM-41 [initial concentration = 50 mg/l, adsorbent dose 0.2 g/l, contact time = 6 h].

APS-MCM-41. The distribution of solute between the liquid and solid phases is a measure of the distribution coefficient in the adsorption process and can be expressed by the Freundlich and Langmuir equations.

Adsorption equilibrium data, expressed by the mass of adsorbate adsorbed per unit weight of adsorbent, and liquid phase equilibrium concentration of adsorbate, are usually represented by adsorption isotherms, which is of importance in the design of adsorption systems. Two important isotherms, i.e. Freundlich (Eq. (3)) and Langmuir (Eq. (4)) isotherms, are selected in this study.

$$\mathrm{Ln}q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \qquad (3)$$

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right) C_e \qquad (4)$$

where q_e (mg/g) is the amount of chlorophenols adsorbed per gram of APS- MCM-41 at equilibrium; C_e (mg/l) the equilibrium concentration of chlorophenols in solution; K_f, a Freundlich isotherm constant for the system and the slope $1/n$, ranging between 0 and 1, indicative of the degree of nonlinearity between solution concentration and adsorption. q_m(mg/g) the maximum monolayer adsorption capacity; b(l/mg) the constant related to the free energy of adsorption. The isotherm data has linearized using the Freundlich and Langmuir equations. The data of these isotherms which are not shown Figures for the sake of briefness are provided in Table 2. It is clear that the adsorption isotherms can be fitted well using two isotherm models (evidenced from the correlation coefficients, >0.990). The value of Langmuier and Freundlich for 2-CP and 2,4,6-TCP are shown in Table 2. The values of constants for 2,4,6-TCP are higher than those for 2-CP, which indicate the higher adsorption capacity towards 2,4,6-TCP. As it was explained earlier, chlorophenols are weak acids and there are acid-alkaline interactions among chlorophenols and APS-MCM-41 species. Therefore the amount of adsorption depends on the acidic strength of the chlorophenols. TCP with greater K_a has higher interactions with APS-MCM-41, and is adsorbed more than CP. Meanwhile, the adsorption capacities of APS-MCM-41 for the adsorption of chlorophenols were comparable to those of some other adsorbent materials reported in literature at the same conditions [44,45]. This fact would prove the potential of the produced adsorbents to be used in a commercial scale.

Table 2
Longmuir and Freundlich constants for adsorption of 2-CP and 2,4,6-TCP on APS-MCM-41.

Analyte	Langmuir			Freundlich		
	q_m (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n (l/mg)	R^2
2-CP	400	0.033	0.992	38.19	1.09	0.9983
2,4,6-TCP	500	0.040	0.992	46.95	1.95	0.9963

4. Conclusions

The present study shows that the APS-MCM-41 is an effective adsorbent for the removal of 2-CP and 2,4,6-TCP from aqueous solution. This may be due to the hydrophobicity created by propyl amine group, and acid and alkaline interactions among amine group and chlorophenols. The sorption of 2,4,6-TCP on APS-MCM-41 was more as compared with that of 2-CP. This could be attributed to greater acidity of 2,4,6-TCP as compared with 2-CP which leads to stronger interactions between the specie and sorbent. The value of adsorption capacities of APS-MCM-41 were comparable to the adsorption capacities of other adsorbent materials for the adsorption of chlorophenols at the same conditions. It was observed that the adsorptions of 2-CP and 2,4,6-TCP were highly dependent on the pH of the aqueous solution. Adsorption isotherms were well predicted by Freundlich equilibrium adsorption model.

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References

[1] EPA method 604, Phenols in Federal Register, Environmental Protection Agency, Part VIII, 40 CFR Part 136, 58, Friday October 26, 1984.
[2] EU Directive 2455/2001/EC, Priority substances in the field of water policy (Official Journal L 331 of 15.12.2001) http://europa.eu/scadplus/leg/en/lvb/l28180.htm.
[3] G.W. Patton, L.L. McConnell, M.T. Zaranski, T.F. Bidleman, Laboratory evaluation of polyurethane foam-granular adsorbent sandwich cartridges for collecting chlorophenols from air, Anal. Chem. 64 (1992) 2858.
[4] F.A. Banat, B. Al-Bashir, S. Al-Ashes, O. Hayajnesh, Adsorption thermodynamics and kinetic investigation of aromatic amphoteric compounds onto different polymeric adsorbents, Environ. Pollut. 107 (2000) 391–398.
[5] S. Dutta, J.K. Basu, R.N. Ghar, Studies on adsorption of p-nitrophenol on charred saw-dust, Sep. Purif. Technol. 21 (2001) 227–235.
[6] J. Wu, K. Rudy, J. Spark, Oxidation of aqueous phenol by ozone and peroxidase, Adv. Environ. Res. 4 (2000) 339–346.
[7] X. Hu, F.L.Y. Lam, L.M. Cheung, K.F. Chania, X.S. Zhao, G.Q. Lu, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Catal Today 68 (2001) 129–133.
[8] C. Wu, X. Lui, D. Wei, I. Fan, L. Wang, Present status of management of nasopharyngeal carcinoma, Water Res. 35 (2001) 3927–3933.
[9] W. Han, W. Zhu, P. Zhang, Y. Zhang, L. Li, Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light, Catal. Today 90 (2004) 319–324.
[10] T.A. Ozbelge, O.H. Ozbeze, S.Z. Baskaya, Heavy metal adsorption onto agro-based waste materials, Chem. Eng. Process 41 (2002) 719–730.
[11] S.P. Kamble, P.A. Mangrulkar, A.K. Bansiwal, S.S. Rayalu, Adsorption of phenol and o-chlorophenol on surface altered fly ash based molecular sieves, Chem. Eng. J. 138 (2008) 73–83.
[12] N. Tancredi, N. Medero, F. Moller, J. Piriz, C. Plada, T. Cordero, Phenol adsorption onto powdered and granular activated carbon, prepared from Eucalyptus wood, J. Colloid Interf. Sci. 279 (2004) 357–363.
[13] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Preparation and characterization of activated carbons from Terminalia Arjuna nut with zinc chloride activation for the removal of phenol from wastewater, Ind. Eng. Chem. Res. 44 (2005) 4128–4138.
[14] A. Namane, A. Mekarzia, K. Benrachedi, N. Belhaneche-Bensemra, A. Hellal, Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnC_{l2} and $H\,_3PO_4$, J. Hazard. Mater. B 119 (2005) 189–194.
[15] W. Tanthapanichakoon, P. Ariyadejwanich, P. Japthong, K. Nakagawa, S.R. Mukai, H. Tamon, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents, Water Res. 39 (2005) 1347–1353.
[16] B. Xing, W.B. McGill, M.J. Dudas, Mechanism of slow desorption of organic compounds from sediments: a study using model sorbents, Environ. Sci. Technol. 28 (1994) 466–473.
[17] Z. Aksu, A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, J. Yener, Waste Manage. 21 (2001) 695–702.

[18] F.A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, Environ. Pollut. 101 (2000) 391–398.
[19] A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite, J. Hazard. Mater. 144 (2007) 307–315.
[20] K. Abburi, Adsorption of phenol and p-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin, J. Hazard. Mater. B 105 (2003) 143–156.
[21] B.C. Pan, X. Zhang, W.M. Zhang, J.Z. Zheng, B.J. Pan, J.L. Chen, Q.X. Zhang, Adsorption of phenolic compounds from aqueous solution onto a macroporous polymer and its aminated derivative: isotherm analysis, J. Hazard. Mater. B 121 (2005) 233–324.
[22] B.P. Kelleher, A.M. Doyle, T.F. O'Dwyer, B.K. Hodnett, Preparation and use of a mesoporous silicate material for the removal of tetramethyl ammonium hydroxide (TMAH) from aqueous solution, J. Chem. Technol. Biotechnol. 76 (2001) 1216–1222.
[23] X.S. Zhao, G.O. Lu, X. Hu, Natural sesquiterpenoids, Micropor. Mesopor. Mater. 41 (2000) 37–47.
[24] A.C. Voegtlin, C. Matijasic, J. Patarin, C. Sauerland, Y. Grillet, L. Huve, Room-temperature synthesis of silicate mesoporous MCM-41-type materials: influence of the synthesis pH on the porosity of the materials obtained, Micropor. Mesopor. Mater. 10 (1997) 137–147.
[25] M. Anbia, M.k. Rofouei, S.W. Husain, Mesoporous lanthanum tungstate as a novel sorbent for removal of heavy metal ions from aqueous media, Asian J. Chem. 19 (2007) 3862–3868.
[26] M. Anbia, M.k. Rofouei, S.W. Husain, Development of new adsorbents: II. Sorption of toxicmetals on mesoporous lanthanum silicate, Oriental J. Chem. 21 (2005) 199–206.
[27] M. Hudson, S.W. Husain, M. Anbia, Sorption of radionuclides on mesoporous Sn(IV) silicate: a new sorbent, J. Ir. Chem. Soc. 2 (2005) 54–59.
[28] M. Anbia, M.k. Rofouei, S.W. Husain, Synthesis of mesoporous lanthanum phosphate and its use as a novel sorbent, Chin. J. Chem. 24 (2006) 1026–1030.
[29] M. Anbia, N. Mohammadi, A nanoporous adsorbent for removal of furfural from aqueous solutions, Desalination 248, in press.
[30] M. Anbia, K. Mohammadi, Removal of copperphthalocyanine from aqueous solution by cationic templated MCM-41 and MCM-48 nanoporous adsorbents, Chin. J. Chem. 26, in press.
[31] M. Anbia, K. Mohammadi, Novel and efficient nanoporous adsorbent for dichromate ion and furfural removal from aqueous solutions, Asian J. Chem. 21, in press.
[32] M. Anbia, S.E. Moradi, Adsorption of naphthalene-derived compounds from water by chemically oxidized mesoporous carbon, Chem. Eng. J., doi:10.1016/j.cej.2008.09.032, in press.
[33] A. Fukuoka, K. Fujishima, M. Chiba, A. Yamagishi, S. Inagaki, Y. Fukushima, H.J. Hashizume, Adsorption of some aromatic compounds by a synthetic mesoporous silicate, Environ. Sci. Health A 39 (2004) 2615–2625.
[34] K. Inumaru, J. Kiyoto, S. Yamanaka, Molecular selective adsorption of nonylphenol in aqueous solution by organo-functionalized mesoporous silica, Chem. Commun. (2000) 903–904.
[35] X.S. Zhao, G.Q. Lu, A.J. Whittaker, G.J. Millar, H.Y. Zhu, Comprehensive study of surface chemistry of MCM-41 using 29Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA, J. Phys. Chem. B 101 (1997) 6525–6531.
[36] D. Das, J.F. Lee, S. Cheng, Synthesis, characterization, and catalytic activity of sulfonic acid-functionalized periodic mesoporous organosilicas, J. Catal. 223 (2004) 152–160.
[37] H. Chen, Y. Wang, Preparation of MCM-41 with high thermal stability and complementary textural porosity, Ceram. Int. 28 (2002) 541–547.
[38] http://webbook.nist.gov/cgi/cbook.
[39] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature 359 (1992) 710–712.
[40] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc. 114 (27) (1992) 10834–10843.
[41] D.J. Macquarrie, Direct preparation of organically modified MCM-type materials. Preparation and characterization of aminopropyl-MCM and 2-cyanoethyl-MCM, Chem. Commun. 16 (1996) 1961–1962.
[42] B. Lee, Y. Kim, H. Lee, J. Yi, Synthesis of functionalized porous silicas via templating method as heavy metal ion adsorbents: the introduction of surface hydrophilicity onto the surface of adsorbents, Micropor. Mesopor. Mater. 50 (1) (2001) 77–90.
[43] J. Blitz, P. Murthy, R.S. Shreedhara, D.E. Leyden, The role of amine structure on catalytic activity for silylation reactions with Cab-O-Sil, J. Colloid Interface Sci. 126 (2) (1988) 387–392.
[44] Su-Hsia Lin, Ruey-Shin Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review, J. Environ. Manage. 3 (2008) 1–14.
[45] Md Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, J. Adv. Colloid Interface Sci. 143 (2008) 48–67.