



Adsorption of phenol and *o*-chlorophenol by mesoporous MCM-41

Priti A. Mangrulkar^a, Sanjay P. Kamble^a, J. Meshram^b, Sadhana S. Rayalu^{a,*}

^a Environmental Materials Unit, National Environmental Engineering Research Institute (CSIR), Nagpur 440 020, India

^b Chemistry Department, RTM, Nagpur University, Nagpur, India

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ABSTRACT

Water pollution by toxic organic compounds is of concern and the demand for effective adsorbents for the removal of toxic compounds is increasing. Present work deals with the adsorption of phenol (PhOH) and *o*-chlorophenol (*o*-CP) on mesoporous MCM-41 material. The effect of surfactant template in MCM-41 on the removal of PhOH and *o*-CP was investigated. The comparison of adsorption of PhOH and *o*-CP on uncalcined MCM-41 (noted as MCM-41) and calcined MCM-41 (noted as C-MCM-41) was investigated. It was found that MCM-41 shows significant adsorption for PhOH and *o*-CP as compared to C-MCM-41, this may be because of the hydrophobicity created by surfactant template in the MCM-41. Batch adsorption studies were carried out to study the effect of various parameters like adsorbent dose, pH, initial concentration and the presence of co-existing ions. It was found that adsorption of PhOH and *o*-CP depends upon the solution pH as well as co-existing ions present in the aqueous solution. The equilibrium adsorption data for PhOH and *o*-CP was analyzed by using Freundlich adsorption isotherm model. From the sorption studies it was observed that the uptake of *o*-CP was higher than PhOH.

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1. Introduction

There is growing public concern over the contamination of groundwater by organic compounds. The removal of organic contaminants from groundwater has become a major focus of research and policy debate or separation of contaminants contained in polluted waters. This is because their presence even at low concentrations can be an obstacle to the use (and/or) reuse of water [1,2]. Phenolic compounds are one of them and of great concern because they are toxic and are known to be carcinogenic when present at elevated levels in the environment. These compounds impart unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. They are common contaminants in wastewaters generated from various industries such as high temperature coal conversion, petroleum refining, resins and plastics. These compounds cause serious environmental problem since biological degradation of phenolics occurs too slowly or does not occur at all [3].

Abbreviations: PhOH, Phenol; *o*-CP, *o*-Chlorophenol; MCM-41, Uncalcined MCM-41; C-MCM-41, Calcined MCM-41; HDTMA, Hexadecyl trimethyl ammonium bromide; TMOS, Tetra methyl ortho silicate; CTAB, *n*-Cetyl trimethyl ammonium bromide; TMAOH, Tetra methyl ammonium hydroxide.

* Corresponding author. Fax: +91 712 2249900.

E-mail address: s.rayalu@neeri.res.in (S.S. Rayalu).

Several methods such as adsorption [4,5], chemical oxidation [6,7], photodegradation [8,9], coagulation flocculation [10], etc. are being used for removal of phenolics from wastewater. Adsorption technology, in particular, has been used for the removal of organic 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 thermal means and there is significant cost and adsorption 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. It was believed that micropores provide adsorptive sites in aqueous solution, but it was found that the total surface area of micropores cannot be totally utilized in adsorption. The extent to which particular adsorbate molecule adsorbs on these zeolite materials is limited by a number of physical factors which includes the size of the adsorbing molecules, the pore diameter of the specific 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 seem 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

Nomenclature

C_0	initial concentration of solute (mg l^{-1})
C_e	equilibrium concentration of solute (mg g^{-1})
K_F	Freundlich constant (mg g^{-1})
q_e	equilibrium adsorbate capacity (mg g^{-1})
V	volume of the aqueous solution (l)
W	mass of adsorbent (g)
$1/n$	heterogeneity factor

possible to manipulate these properties so as to suit those of the adsorbate [23].

MCM-41 is a member of family of silicate mesoporous material, 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 by 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 proposed cubic symmetry (MCM-48) as well as other structures [24]. These materials are potentially useful for catalytic, electronic, optical, and magnetic applications [25]. Their modification by functionalized molecules can lead to adsorbents with specific properties.

Removal of harmful organics by mesoporous materials grafted with organic or metal complexes has drawn much attention recently [26–29]. However, to our knowledge very few articles are published on the possibility of sorption of hydrophobic organic molecules from aqueous solution into the noncalcined mesoporous material.

As-synthesized (using TMOS) MCM-41 materials dried at 90 °C were proposed as sorbents to remove 3-chlorophenol from water. This possibility was recently investigated by Denoyel and Sabio-Rey [30]. Another article reported by Zhao et al. [31] used as-synthesized MCM-41 (using HDTMA and TMOS) materials dried at 70 °C as adsorbent for removal of trichloroethylene and tetrachloroethylene from water. They observed that the MCM-41 without HDTMA (calcined) shows weaker adsorption as compared to uncalcined MCM-41. Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41 was studied by Ghiaci et al. [32]. According to their evaluation using the Langmuir equation, the maximum organics adsorption by as-synthesized MCM-41 was much greater than that of the natural clinoptilolite and ZSM-5 zeolites.

The industrial effluent may sometimes be acidic or alkaline and it may contain different types of co-existing ions which are used for neutralization purpose. To the best of our knowledge effects of pH and presence of co-ions on removal of phenolic from aqueous solution using mesoporous materials has not been reported in the present literature. Hence it is necessary to study the effect of these parameters on adsorption of phenolic compounds on MCM-41. The stability of MCM-41 in aqueous solution and sorption behavior for aqueous organic molecules was also investigated in detail. Retention of templating surfactant molecules within mesopores of MCM-41 materials should lead to sorptive properties for hydrophobic organic compounds in water similar to those exhibited by organo-clays (i.e., organo-cation exchanged clays) [33].

The objective of this study was to evaluate the effectiveness of mesoporous MCM-41 (using CTAB) materials for sorption of PhOH

and *o*-CP and to quantify aspects of their environmental stability in aqueous solution. The effect of surfactant template in MCM-41 on the uptake of PhOH and *o*-CP was also studied. The effects of various operating parameters such as effect of adsorbent dose, initial concentration, and pH of the solution were studied in detail. The effect of the presence of co-existing ions on removal of PhOH and *o*-CP was also investigated. The sorption properties of MCM-41 were compared with C-MCM-41 to assess quantitatively the role of the organic template. The equilibrium adsorption data was analyzed by using Freundlich adsorption isotherm.

2. Experimental

2.1. Materials

All the reagents used for experimental studies were of reagent grade. Fumed silica (99 wt.%, Aldrich), *n*-cetyl trimethyl ammonium bromide (CTAB) (99 wt.%, Merck), and tetra methyl ammonium hydroxide (TMAOH) (aq. 25 wt.% Loba Chemie) were used as the reagents for the synthesis of MCM-41. Phenol, *o*-chlorophenol, sodium chloride, sodium carbonate, sodium bicarbonate, and sodium sulfate were obtained from Merck India Ltd. The stock solutions of PhOH and *o*-CP were prepared in distilled water.

2.2. Synthesis of MCM-41

9.84 g of CTAB was dissolved in 67 g of deionized water. It was then stirred on a laboratory stirrer for 5 min. Then 6.92 g TMAOH was added drop wise to it with constant stirring. The mixture was allowed to stir for 10 min. Then the desired silica source, viz, fumed silica (6 g) was added to this solution under stirring and vigorous stirring was further continued for 1.5 h. The resulting gel of composition $\text{SiO}_2:0.27 \text{ CTAB}:0.19 \text{ TMAOH}:40 \text{ H}_2\text{O}$ was heated in a sealed stainless steel autoclave at 383 K for hydrothermal crystallization for desired length of period (48 h). The product was recovered by filtration, washed thoroughly with distilled water and then dried at 313 K for 4 h.

The adsorbents used in this study, C-MCM-41 and MCM-41 were characterized with respect to surface area, particle size, XRD and Fourier Transform Infrared (FTIR). The specific surface areas of adsorbent samples were determined using a specific surface area analyzer (ASAP 2000, Micrometrics) with nitrogen gas as the adsorbate and the particle size was determined on Fritsch particle sizer. The stability of MCM-41 in the presence of aqueous solution of PhOH as well as in the presence of water was studied by characterization of material samples using XRD. Powder X-ray diffraction studies were carried on Phillips analytical diffractometer with monochromated $\text{Cu K}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$). The scanning range of 2θ was set between 1° and 10°. The FTIR analysis was carried on Bruker Vertex-70 by Diffuse Reflectance Accessory technique.

2.3. Batch adsorption

In order to study the effect of different controlling parameters like pH, initial concentration and interfering ions on adsorption of PhOH and *o*-CP, batch sorption experiments were conducted using C-MCM-41 and MCM-41 as the adsorbent. For single solute equilibrium adsorption studies, model solutions of PhOH and *o*-chlorophenol were prepared by dissolving pure samples of the solutes in double distilled water. A known quantity of the adsorbent (0.2–4 g l^{-1}) was taken in 100 cm^3 stoppered conical flask and 50 ml of aqueous solution of PhOH and *o*-CP was added to it. The conical flasks were then kept on a rotary shaker at ambient temperature ($303 \pm 2 \text{ K}$) for 24 h to attain equilibrium. At the

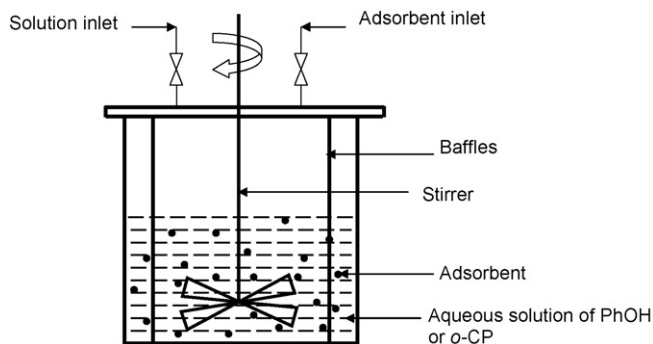


Fig. 1. Experimental setup of the three-neck reactor for kinetic study experiment.

end of the adsorption process the adsorbent was filtered and the residual solution concentration of PhOH and *o*-CP was analyzed by UV-spectrophotometer (Model-UV2100) at wavelength 270 and 274 nm, respectively. In order to reduce measurement errors in all the experiments, the UV absorption intensity of each equilibrium solution sample 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 $\pm 2\%$.

The specific amount of solute (PhOH or *o*-CP) adsorbed was calculated using Eq. (1) as follows:

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

where q_e is the adsorption capacity (mg g^{-1}) in the solid at equilibrium; C_0 and C_e are the initial and equilibrium concentrations of solute (mg l^{-1}), respectively; V is the volume of the aqueous solution (l) and W is the mass (g) of adsorbent used in the experiments.

2.4. Kinetic study

In order to estimate equilibrium adsorption time for the uptake of PhOH and *o*-CP by MCM-41, time-dependent sorption studies were conducted in a three-necked glass vessel having a capacity of 500 ml. A schematic diagram of the three-neck reactor used for kinetic study is shown in Fig. 1. The solution of PhOH and *o*-CP was transferred into the vessel and a known weight (1 g l^{-1}) of the adsorbent was added to it. The suspension was stirred using a four-blade, pitched turbine impeller with the stirring speed 500 rpm. Samples were withdrawn from the vessel at frequent time intervals and analyzed for the concentration of PhOH and *o*-CP by UV-spectrophotometer.

3. Results and discussions

3.1. Stability and characterization of MCM-41

The BET surface area of the mesoporous MCM-41 was found to be $45.1 \text{ m}^2 \text{ g}^{-1}$ which is very low as compared to the C-MCM-41. This may be because in MCM-41, the mesopores are occupied by the surfactant molecules lowering the surface area. The average particle size of MCM-41 was found to be around $30.59 \mu\text{m}$.

Fig. 2(a) and (b) shows the small angle XRD pattern of MCM-41 and C-MCM-41. Three well-resolved peaks are observed in the sample which can be indexed as (100), (110) and (200) associated with the hexagonal symmetry of mesopores. In order to study the stability of the MCM-41 in presence of water and aqueous solution of PhOH, the XRD patterns of the treated MCM-41 were also obtained. Fig. 2(c) and (d) shows the XRD patterns for

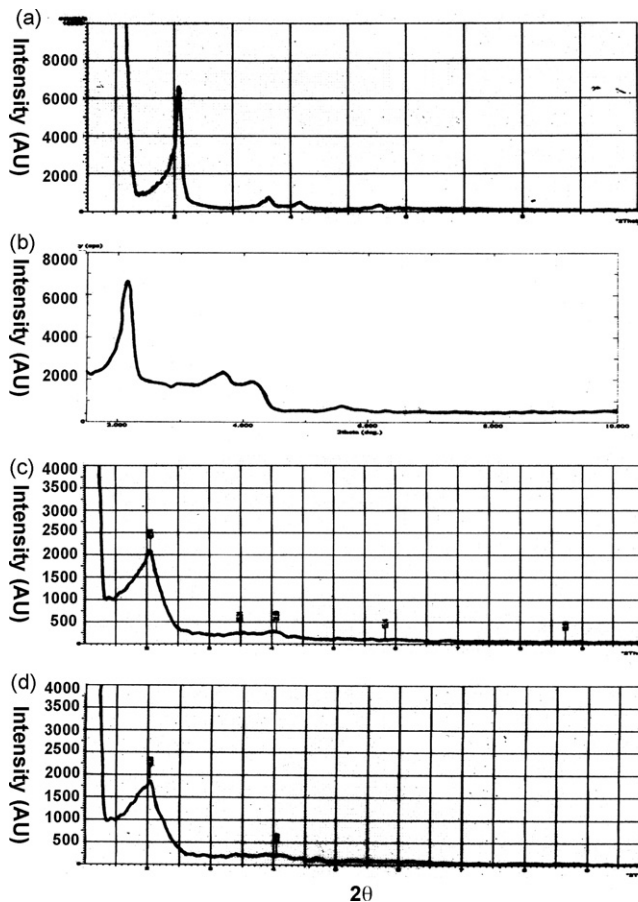


Fig. 2. XRD pattern for (a) MCM-41, (b) C-MCM-41, (c) after the adsorption of PhOH on MCM-41 and (d) after the adsorption of water on MCM-41.

treated samples of MCM-41 in aqueous solution of PhOH and water, respectively. It can be observed from these figures that the structural stability of the sample is retained. The XRD pattern shows the diffraction peaks at (100, 110 and 200) indicating uniform pore channels in a regular hexagonal array.

The FTIR spectrum is as shown in Fig. 3. A broad band in the range of 3700.43 and 3016.30 cm^{-1} is seen which can be attributed to the framework Si-OH group interaction with the defect sites and adsorbed water molecules. The presence of organic surfactant results into various C-H stretching vibrations which can be seen at 2919.75 and 2850.54 cm^{-1} . The characteristic band for ammonium

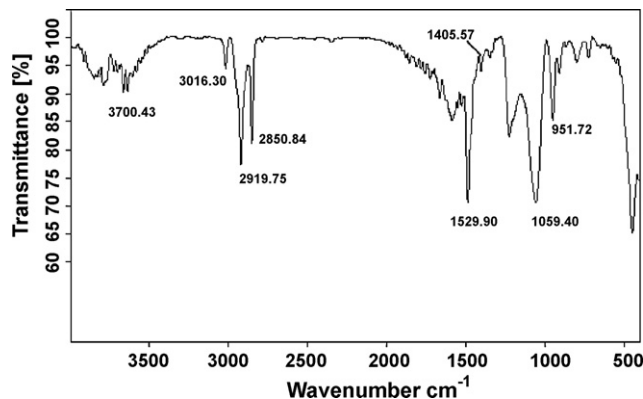


Fig. 3. FTIR spectra of MCM-41.

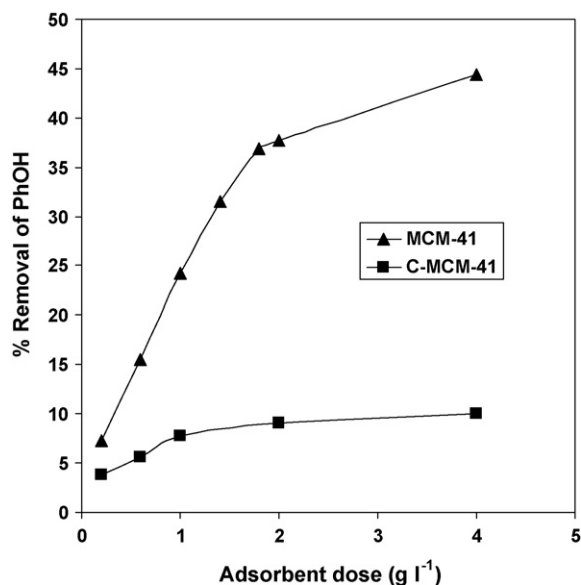


Fig. 4. Comparison of adsorption of PhOH on MCM-41 and C-MCM-41 [initial concentration = 50 mg l⁻¹ pH 7, contact time = 24 h]; (▲) MCM-41, (■) C-MCM-41.

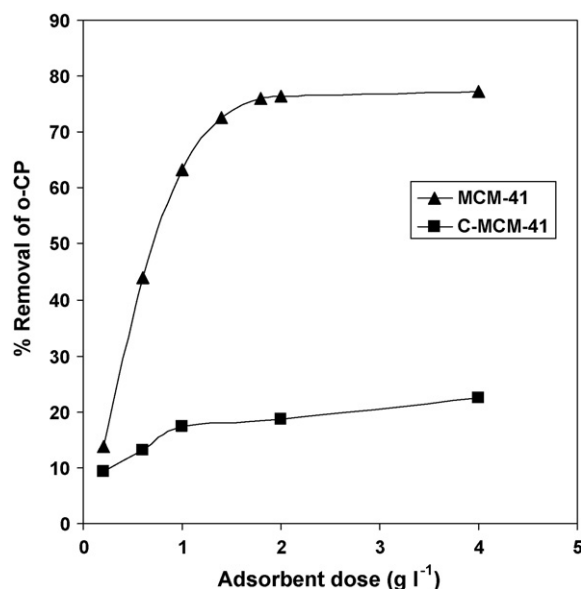


Fig. 5. Comparison of adsorption of o-CP on MCM-41 and C-MCM-41 [initial concentration = 50 mg l⁻¹ pH 7, contact time = 24 h]; (▲) MCM-41, (■) C-MCM-41.

ion can be seen at 1405.57–1529.90 cm⁻¹. The stretching vibrations of Si–O–Si and Si–OH can be seen at 1059.40 and 951.72 cm⁻¹. These values are comparable to those reported by Samanta et al. [34].

3.2. Effect of various parameters on adsorption of PhOH and o-CP by MCM-41

3.2.1. Influence of surfactant template on adsorption of PhOH and o-CP on MCM-41

When the surfactant concentration in aqueous solution is beyond the critical micelle concentration (CMC), then micelles are formed and they act as templates for preparing MCM-41 materials. To create porosity, the templates are often removed. However, in this work, the template (i.e., cationic surfactants) was deliberately kept in order to create hydrophobicity. The existence of cationic template within the framework of MCM-41 materials causes the change in the surface chemistry and porosity of the adsorbent, which in turn affects the sorption behavior of adsorbent.

The adsorption of PhOH and o-CP on MCM-41 and C-MCM-41 was studied in order to understand the influence of surfactant template on adsorption behavior. From Figs. 4 and 5 it was observed that the adsorption of PhOH and o-CP on MCM-41 is significantly high as compared to C-MCM-41. The reason is explained as follows:

The surface chemistry varies between C-MCM-41 and MCM-41. Two different types of adsorption sites exist on the surface of C-MCM-41: low adsorption energy of less polar Si–O–Si (siloxane) groups and high adsorption energy of polar Si–OH (silanol) groups [35]. In addition to this, MCM-41 also possesses high adsorption energy of quaternary alkylammonium groups (Si–C–C–[N⁺–(CH₃)₃]) contributed from cationic template. Apparently, the surfactant template can alter the surface chemistry and population of sorption sites of the materials. Therefore the silanol groups and cationic groups are effective for the adsorption of organic compounds due to their high adsorption energy or potential charge association [36]. These quaternary ammonium cationic species render hydrophobicity to MCM-41 and hence the adsorption of PhOH and o-CP on MCM-41 is high as compared to C-MCM-41. Similar results were obtained in the adsorption of toluene and cumene on MCM-41 by Huang et al. [36].

3.2.2. Effect of adsorbent dose

The effect of adsorbent dose on the uptake of PhOH and o-CP on MCM-41 was studied and is shown in Figs. 6 and 7, respectively. It can be seen from Figs. 6 and 7 that percentage removal of PhOH and o-CP increased with the increase in adsorbent dose while loading capacity (amount of PhOH and o-CP loaded per unit weight of adsorbent) gradually decreased for the same. The maximum adsorption capacity for PhOH and o-CP were found to be 12.46 and 30 mg g⁻¹ at an adsorbent dose of 0.05 and 0.057 g l⁻¹, respectively. This increase in loading capacity is due to the availability of greater amount of active sites of adsorbent. It can also be seen from these figures that the uptake of solute markedly increased up to adsorbent dose of 0.05 g l⁻¹ and thereafter no significant increase was observed. This may be because of the very low equilibrium concentration of solute, i.e. driving force responsible for adsorption

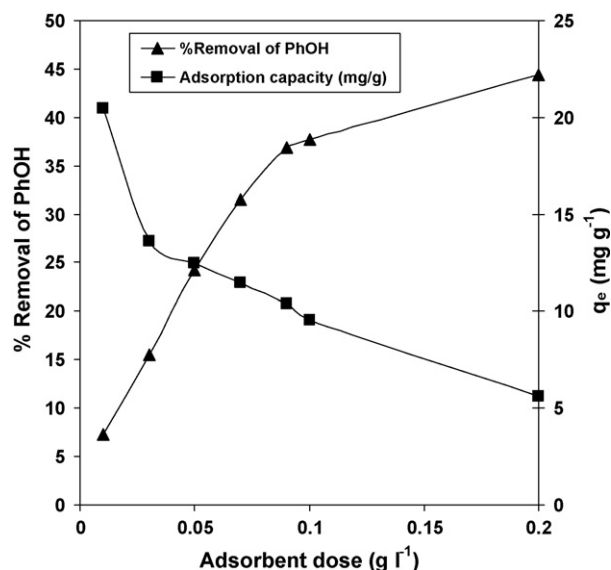


Fig. 6. Effect of adsorbent dose for adsorption of PhOH on MCM-41 [initial concentration = 50 mg l⁻¹ pH 7, contact time = 24 h]; (▲) % removal of PhOH, (■) adsorption capacity (mg g⁻¹).

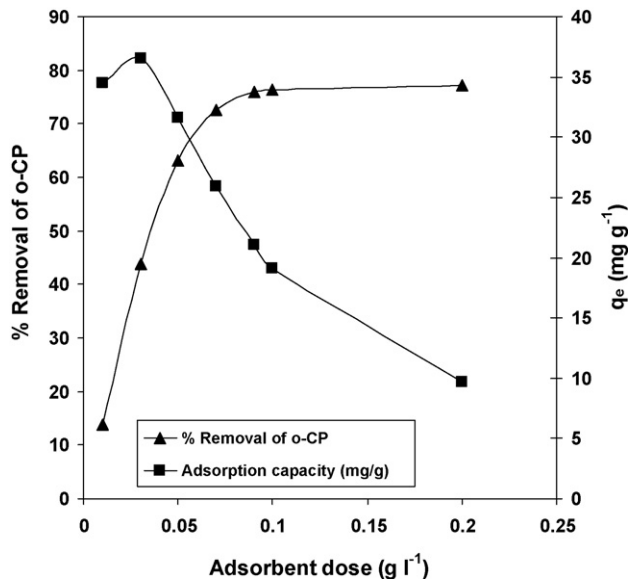


Fig. 7. Effect of adsorbent dose for adsorption of *o*-CP on MCM-41 [initial concentration = 50 mg l⁻¹, pH 7, contact time = 24 h]: (▲) % removal of *o*-CP, (■) adsorption capacity (mg g⁻¹).

becomes negligible. Similar behavior has also been reported previously for other adsorbents by Kamble et al. [11]. The adsorption capacity of *o*-chlorophenol is higher as compared to phenol and could be attributed to (i) anions and high pH have more pronounced effect on adsorption of phenol as compared to *o*-chlorophenol due to higher ionization which leads to formation of phenolate ions and (ii) more hydrophobic nature of *o*-chlorophenol than phenol.

3.2.3. Effect of pH

The pH of 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 reaction kinetics and equilibrium characteristics of the adsorption process. The effect of initial pH on adsorption of PhOH and *o*-CP by MCM-41 was studied. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic range, pH was varied using HCl. The experimental result for the uptake of the PhOH and *o*-CP on MCM-41 in the pH range of 3–11 are shown in Fig. 8. It was observed that the relative uptake of PhOH and *o*-CP was significantly affected by pH. The adsorption capacity of *o*-CP remains nearly constant at 11 > pH > 7, while at acidic pH adsorption capacity decreases. In case of PhOH adsorption capacity remains constant between pH 7 and 9, while at 7 < pH < 9 adsorption capacity decreases. In case of PhOH at alkaline pH > 9 the adsorption capacity decreases, this may be because of the formation of phenolate ions. While at acidic pH the adsorption capacity of both PhOH and *o*-CP decreases due to the interaction of the protons with silanol groups of MCM-41 via hydrogen bonding.

3.2.4. Effect of initial concentration

Effect of initial concentration on the uptake of PhOH and *o*-CP was studied at different initial PhOH and *o*-CP concentrations ($C_0 = 50, 75$ and 100 mg l⁻¹) by keeping other parameters constant. The effect of initial concentrations on uptake of PhOH and *o*-CP is shown in Fig. 9. It was observed that the uptake of PhOH and *o*-CP increased with increase in concentration. It was also observed that the adsorption of *o*-CP is high as compared to PhOH. This may be

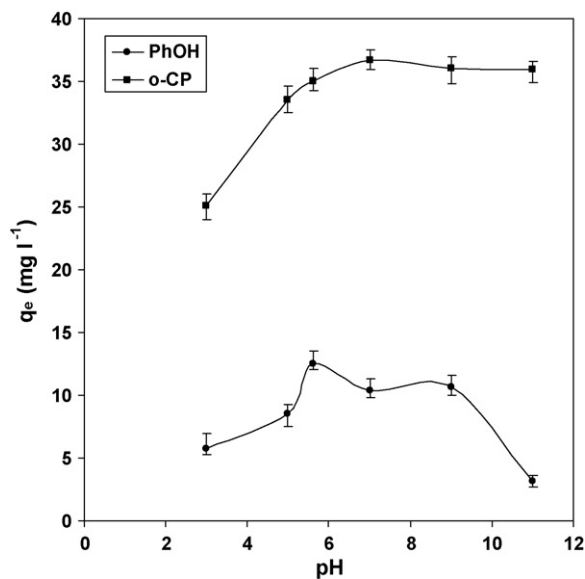


Fig. 8. Effect of pH on adsorption of PhOH and *o*-CP on MCM-41 [initial concentration = 50 mg l⁻¹, contact time = 24 h]: (●) PhOH, (■) *o*-CP.

attributed to higher hydrophobicity of *o*-CP as compared to PhOH and hence adsorption of *o*-CP on MCM-41 is high.

3.2.5. Effect of the presence of anions

Industrial effluents contain apart from pollutants different salts at different levels of concentration. The anion and cation parts of the salt have different effects on the adsorption of substrate. The effect of the presence of various anions such as chloride, sulfate, bicarbonate and carbonate was studied using 0.1 M salt solution and initial concentration of 50 mg l⁻¹ of aqueous solution of solutes. In case of PhOH the percentage removal in the presence of sodium chloride, sodium sulfate, sodium bicarbonate and sodium carbonate was 11.95%, 15.27%, 11.95% and 21.42%, respectively, whereas in the absence of anions the percentage removal was 24.17% (Fig. 10). Similarly, in case of *o*-CP the percentage removal in the presence of sodium chloride, sodium sulfate, sodium bicarbonate and

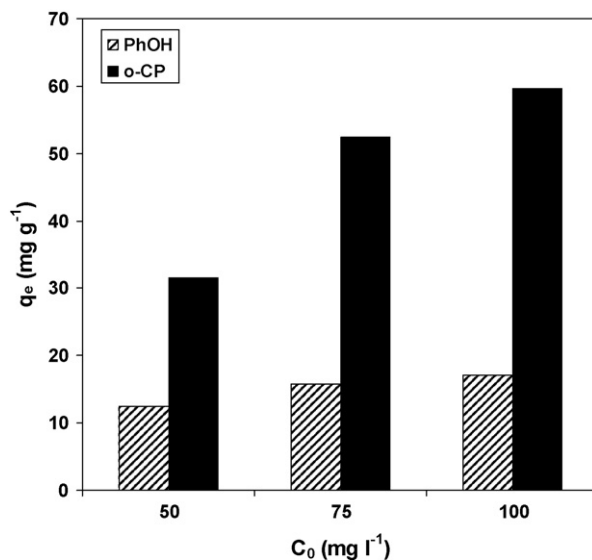


Fig. 9. Effect of initial concentration on adsorption of PhOH and *o*-CP on MCM-41 [initial concentration = 50 mg l⁻¹, optimum dose = 1 g l⁻¹, contact time = 24 h]: (▨) PhOH, (■) *o*-CP.

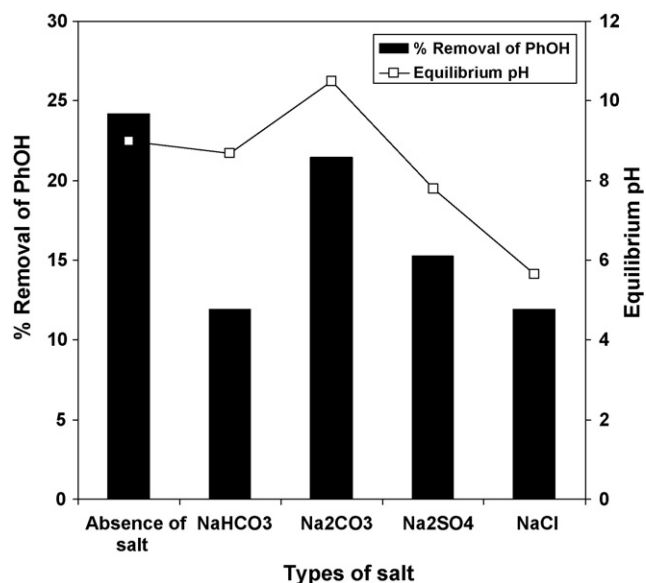


Fig. 10. Effect of the presence of anions on adsorption of PhOH on MCM-41 [initial concentration = 50 mg l⁻¹, optimum dose = 1 g l⁻¹, contact time = 24 h, pH 7]: (■) % removal of PhOH, (□) equilibrium pH.

sodium carbonate was found to be 49.90%, 46.93%, 59.27% and 44.85%, respectively, whereas in the absence of anions the percentage removal was 63.19% (Fig. 11). The effect of the salts on the adsorption of PhOH and *o*-CP clearly indicates that the salts have a substantial detrimental effect on adsorption. The adsorption capacity in the presence of these ions might also block the active sites of the adsorbent surface thus deactivating the adsorbent towards the organic molecules. The effect of interference of ions on the percentage removal of PhOH is high as compared to *o*-CP. This may be attributed to (i) anions and pH have more pronounced effect on adsorption of PhOH due to higher ionization which leads to formation of phenolate ions and (ii) less hydrophobicity of PhOH as compared to *o*-CP.

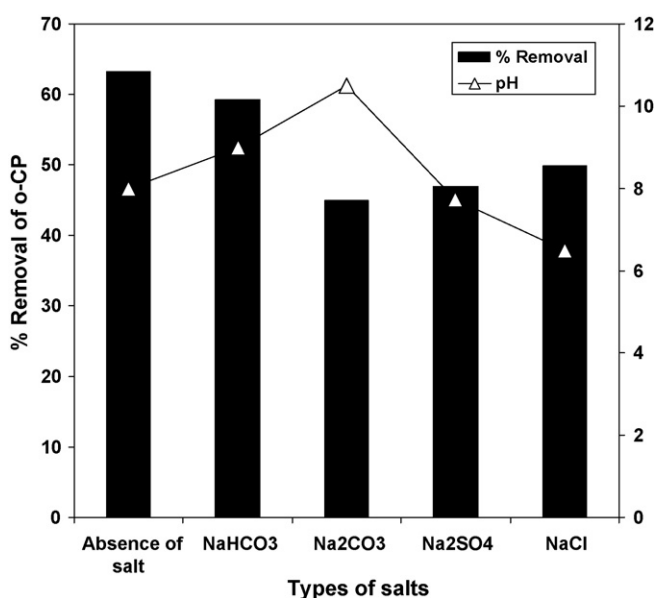


Fig. 11. Effect of the presence of anions on adsorption of *o*-CP on MCM-41 [initial concentration = 50 mg l⁻¹, optimum dose = 1 g l⁻¹, contact time = 24 h, pH 7]: (■) % removal of *o*-CP, (△) equilibrium pH.

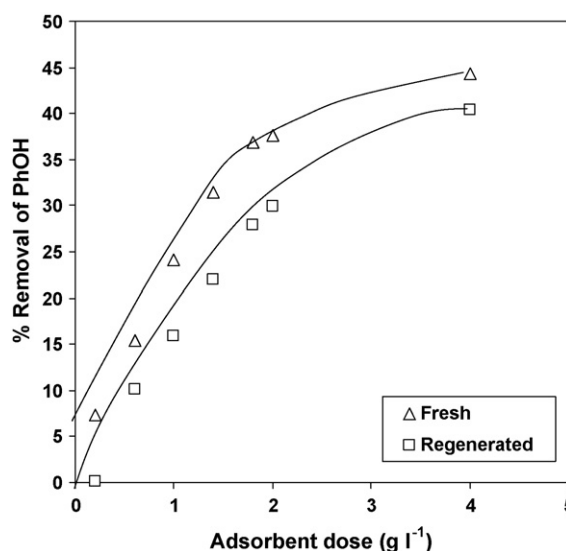


Fig. 12. Regenerated use of MCM-41 adsorbent for removal of PhOH [initial concentration = 50 mg l⁻¹, contact time = 24 h, pH 7]: (△) fresh adsorbent, (□) regenerated adsorbent.

3.2.6. Regeneration of the adsorbent

The regeneration of adsorbent is one of the important factors which affect the overall cost of the adsorption process. The regeneration of adsorbent material was carried out by using 0.1 M NaOH solution. From Figs. 12 and 13 it was found that the regenerated adsorbent shows slightly less percentage removal for PhOH and *o*-CP, respectively, from aqueous solution than the fresh adsorbent. This may be due to the loss of some of the surfactant molecules from the silica surface.

4. Equilibrium modeling

Equilibrium studies were carried out to determine the adsorption capacity and equilibrium constant for PhOH/*o*-CP on MCM-41. The distribution of solute between the liquid phase and the solid phase is a measure of the distribution coefficient in the adsorption

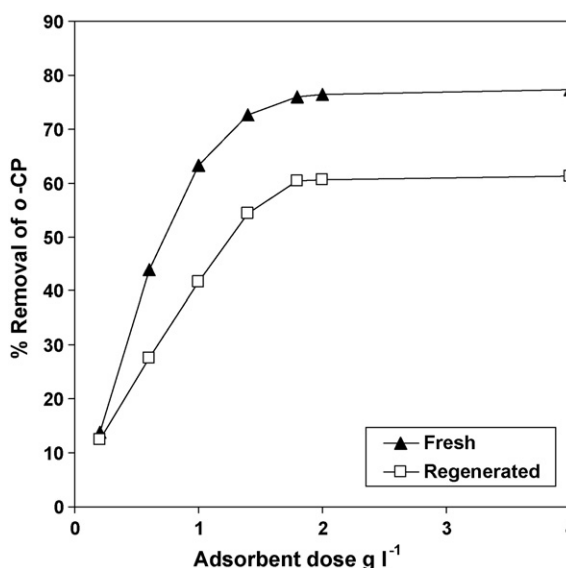


Fig. 13. Regenerated use of MCM-41 adsorbent for removal of *o*-CP [initial concentration = 50 mg l⁻¹, contact time = 24 h, pH 7]: (▲) fresh adsorbent, (□) regenerated adsorbent.

Table 1
Freundlich adsorption constants for phenol and *o*-chlorophenol onto MCM-41 and C-MCM-41

	MCM-41	C-MCM-41
Phenol		
K_F (mg g^{-1})	0.712	1.22×10^{-12}
n	0.95	0.036
r^2	0.94	0.97
<i>o</i> -Chlorophenol		
K_F (mg g^{-1})	2.01	6.57×10^{-10}
n	1.64	0.074
r^2	0.91	0.99

process and can be expressed by the Freundlich and Langmuir equations.

The Freundlich model is an empirical equation based on sorption on a heterogeneous surface. It is given as [37]:

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

The Freundlich equation can be linearized by taking logarithms and constants can be determined. The above equation can be linearized as follows:

$$\log(q_e) = \log K_F + 1/n \log(C_e) \quad (3)$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, which can be calculated by using above equation. To determine the equilibrium isotherms, adsorbent dose were varied, while the initial concentration of PhOH and *o*-CP was kept constant (Figs. 4 and 5). The value of K_F and n for PhOH and *o*-CP were shown in Table 1. The value of Freundlich constants (K_F) for *o*-CP is high as compared to PhOH, which indicates the higher adsorption capacity for *o*-CP due to its hydrophobicity.

5. Kinetics studies

The kinetics studies provide the equilibrium time required for a sorption reaction as it describes the rate of solute uptake at the solid–solution interface. The sorption of PhOH and *o*-CP by MCM-41 exhibited a biphasic uptake as illustrated in Figs. 14 and 15. The adsorbent exhibited a rapid uptake within the first 20 min itself,

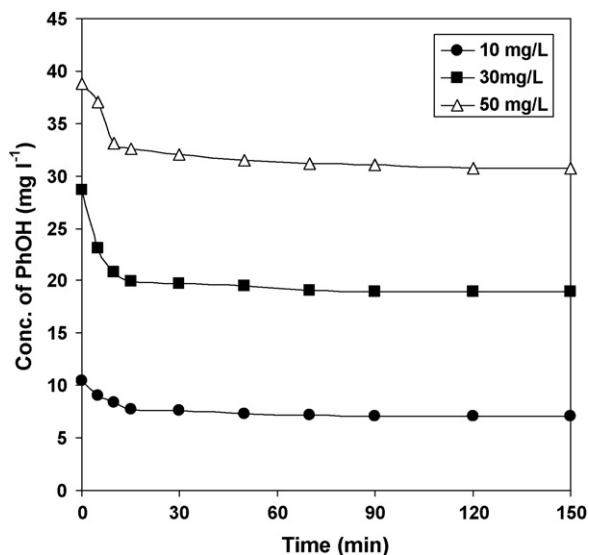


Fig. 14. Kinetics of adsorption for PhOH [contact time = 24 h, Adsorbent dose = 1 g l^{-1} , pH 7]: (●) initial concentration of PhOH = 10 mg l^{-1} , (■) initial concentration of PhOH = 30 mg l^{-1} , (△) initial concentration of PhOH = 50 mg l^{-1} .

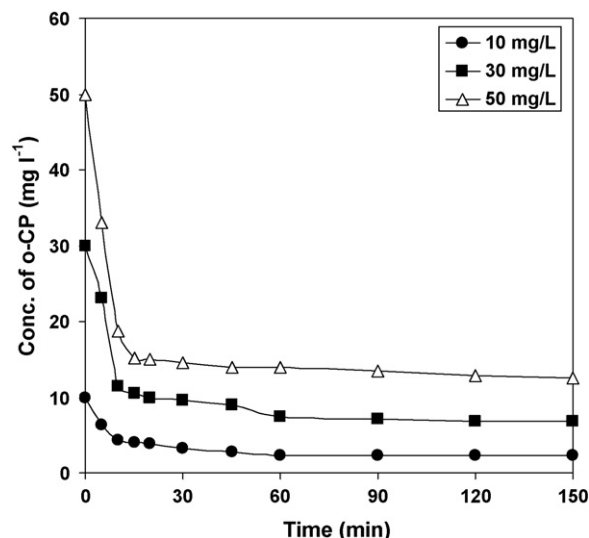


Fig. 15. Kinetics of adsorption for *o*-CP [contact time = 24 h, adsorbent dose = 1 g l^{-1} , pH 7]: (●) initial concentration of *o*-CP = 10 mg l^{-1} , (■) initial concentration of *o*-CP = 30 mg l^{-1} , (△) initial concentration of *o*-CP = 50 mg l^{-1} .

for the initial concentration of PhOH and *o*-CP. This rapid removal was followed by a slow phase which got stabilized thereafter, with no significant removal after 90 min indicating the attainment of equilibrium. The initial rapid uptake indicates surface bound sorption and the slow second phase due to the long-range diffusion of solute ions onto interior pores of the adsorbent [38]. It is generally believed that, when the rate of sorption is rapid, the rate-limiting step is probably a transport process taking place in the liquid phase, such as diffusion in the bulk of the liquid, at the film adjacent to the solid particle, in liquid-filled pores, etc. When the rate of sorption is slow, it is likely that processes taking place at the solid phase are rate determining [39]. Altogether, this slow phase, which denotes the rate limiting could be due to diffusion or other surface reactions.

6. Conclusions

The present study shows that the MCM-41 is an effective adsorbent for the removal of PhOH and *o*-CP from aqueous solution. It was found that MCM-41 shows significant adsorption for PhOH and *o*-CP as compared to C-MCM-41, this may be because of the hydrophobicity created by surfactant template in the MCM-41. It was found that pH and the presence of co-existing ions play an important role in the removal of PhOH and *o*-CP from wastewater. It was observed that the adsorption of PhOH and *o*-CP was highly dependent on pH of the aqueous solution. It was found that co-existing ions have strong negative effect on removal of PhOH as compared to *o*-CP. The sorption of *o*-CP was more as compared to PhOH on MCM-41. This could be attributed to greater hydrophobicity of *o*-CP as compared to PhOH. This was also supported by Freundlich equilibrium adsorption model.

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