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Adsorption of phenolic compounds from aqueous solutions using functionalized SBA-15 as a nano-sorbent

M. Anbia *, S. Amirmahmoodi

Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Narmak, Tehran, P.O. Box 16846-13114, Iran

Abstract Amino functional mesoporous silica SBA-15 materials have been prepared as efficient adsorbents for halophenols in wastewater. The organic–inorganic hybrid material was obtained using successive grafting procedures of SBA-15 silica with 3-aminopropyl-trimethoxysilane (NH_2–SBA-15). The comparison of adsorption of halophenols on untreated mesoporous SBA-15 and NH_2–SBA-15 is studied. It is found that NH_2–SBA-15 shows significant adsorption for halophenols. The samples were characterized by X-Ray Diffraction (XRD), nitrogen adsorption-desorption isotherms, Scanning Electron Microscopy (SEM), and Fourier Transform Infrared (FT–IR). Batch adsorption studies have been carried out to study the effect of various parameters, such as contact time, pH, adsorbent dose and initial adsorbate concentration. The equilibrium adsorption data of halophenols onto NH_2–SBA-15 were analyzed using Freundlich and Langmuir adsorption isotherms. From the sorption studies it was observed that the uptake of 4-chlorophenol (CP) was higher than 4-bromophenol (BP) and 4-iodophenol (IP).

1. Introduction

Phenols and phenolic compounds in general are currently produced by industries like petroleum refining, leather and textile, and olive oil production; thus a significant amount of these compounds is present in the corresponding wastewater [1,2]. Such wastewater is of increasing concern and represents a serious potential hazard for human health and aquatic life [3]. The discharge of various industrial effluents containing phenolic pollutants in natural water is an ongoing and serious threat to human health. Phenolic compounds impart an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. Various methods for the removal of phenols from wastewater include coagulation, chemical oxidation, solvent extraction, liquid membrane permeation and adsorption [4].

Adsorption technology in particular has been used for the removal of organic compounds from wastewater [5]. Some research work has been done on the removal of phenolic compounds using activated carbon as the adsorbent [6–10]. The regeneration of activated carbon is normally undertaken 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 [11,12], clays [13], zeolites [14,15] and resins [16,17]. 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 an aqueous solution seem to be promising. Mesoporous silicates offer a number of potential advantages of nanoporous materials (IUPAC classification [18]), as adsorbents including larger pore volume and diameter, high surface area and regular channel type structures. It is also possible to manipulate these properties to suit the adsorbate [19]. The discovery of hexagonally ordered mesoporous silicas [20] has stimulated a renewed interest in adsorbent [21–31] and catalyst designs because of their unique large surface area, well-defined pore size and pore shape.

In 1998, Zhao et al. [32] developed SBA-15 mesostructured silica, which consists of parallel cylindrical pores with axes arranged in a hexagonal unit cell. SBA-15 usually has wider

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* Corresponding author.
   E-mail address: anbia@iust.ac.ir (M. Anbia).

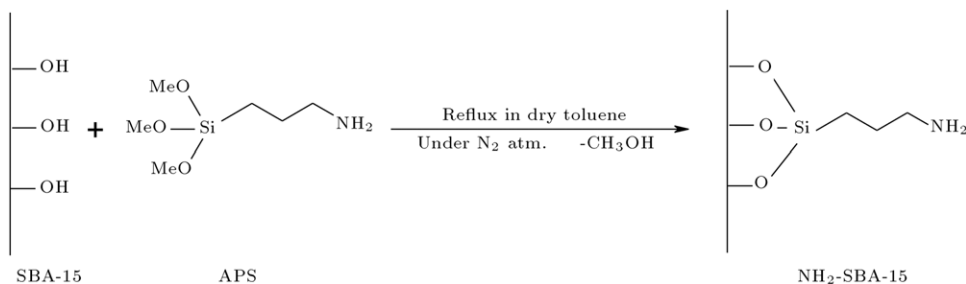Production and hosting by Elsevier

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Figure 1: Schematic illustration of the SBA-15 functionalization.

pores than MCM-41 (SBA-15 pores range from 5 to 30 nm), and higher pore volume. Moreover, in comparison with other mesostructured silica materials, SBA-15 exhibits thicker pore walls (between 3.1 and 6.4 nm), which provide high hydrothermal stability [32,33], and is suitable for use in aqueous media. Using polyprotic acids like H_3PO_4 rather than monoprotic like HCl, in conventional synthesis, during the assembling process of the surfactant, would promote changes in the ionic strength and pH at the interface [34].

The surfactant removal has also been found as a possible factor for modification, in order to obtain different textural properties. When using non-ionic triblock copolymer surfactants, such as Pluronic® P123 (EO_{20}–$PO_{70}EO_{20}$), the calcination temperature seems to govern the contraction of the hexagonal unit cell and further framework condensation. Thus the retention of the original size and volume of SBA-15 is favored when a two-step calcination method is employed, which prevents the silica matrix from shrinking [34,35].

In this work, SBA-15 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, the presence of free electron pairs on the amine group within mesopores of SBA-15 material should lead to sorptive properties for weak acidic organic compounds in water.

The objective of this study was to evaluate the effectiveness of mesoporous NH_2–SBA-15 material for the sorption of halophenols. The effects of various operating parameters, such as the effect of initial adsorbate concentration, adsorbent dose, contact time and pH of the solution have been studied. The Freundlich and Langmuir adsorption isotherms have been used to model the equilibrium adsorption data.

2. Experimental

All reagents used for experimental studies were of analytical grade and were obtained from Merck, except Pluronic® P123 (EO_{20}–$PO_{70}EO_{20}$) and H_3PO_4 (85%), which were purchased from Aldrich. Aqueous solutions were prepared using double distilled water. Tetraethoxysilane (TEOS, 98%), 3-aminopropyl trimethoxy silane (APS, 98%) and dry toluene (99.9%) were used to prepare adsorbents and 4-chlorophenol (CP), 4-bromophenol (BP) and 4-iodophenol (IP) were used as adsorbates.

2.1. Synthesis of SBA-15 mesoporous silica

Hexagonally ordered SBA-15 mesoporous materials were synthesized employing phosphoric acid as the catalyst. The synthesis procedure was based on the use of P123 ($EO_{20}PO_{70}EO_{20}$) as the directing agent of the silica mesostructure. The template agent was dissolved in an acidic aqueous solution. The molar composition of the initial solution presented here is as follows: 1 SiO_2 : 0.017 P123:1.5 H_3PO_4 : 208 H_2O. Tetraethyl orthosilicate was used as the silica precursor. These solutions were stirred at 35 °C for 24 h in sealed Teflon beakers and then further heated at 100 °C for 24 h. The obtained products were filtered, washed with doubly distilled water and then dried at 90 °C for 12 h in air.

The surfactant removal for a sample consisted of a two-step procedure, based on heating, first at 250 °C for 3 h and then at 550 °C for 4 h. Further details of the experimental conditions employed for material characterization are described elsewhere [34].

2.2. Modification of SBA-15

The grafting modification method was employed in this study (Figure 1). SBA-15 (1.0 g) was suspended in 30 mL of dry toluene, and 4 mL of APS was added under a dry nitrogen atmosphere. The mixture was then refluxed for 10 h. The solid product was recovered by filtration, washed with dichloromethane and ethanol, and dried. It was then soxhlet extracted with a mixture of ethanol and dichloromethane (1:1), in order to remove the silylating reagent residue, and dried at 70 °C under a vacuum, overnight [30,36].

2.3. Characterization

X-ray Diffraction (XRD) was utilized to identify the crystal structure of SBA-15 samples. XRD patterns were recorded with a Philips 1830 powder X-ray diffractometer, using the Cu-Kα radiation source of wavelength 1.5406 Å for 2 h, ranging from 0.8° to 6.0°, with a 2θ step size of 0.01° and a step time of 1 s. Adsorption-desorption isotherms of synthesized samples were obtained at 77 K (−196 °C) on micromeritic model ASAP 2010 sorptometer to determine an average pore diameter. Pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method, while the surface area of the sample was measured by the Brunaure–Emmet–Teller (BET) method in the range of relative pressures between 0.05 and 0.20. Scanning Electron Microscopy (SEM) micrographs were taken on a Philips—XL30 microscope. Fourier Transform Infrared (FTIR) spectra of mesoporous materials, before and after modification, were observed by using FT-IR 8400S SHIMADZU.

2.4. Adsorption studies

The adsorption of halophenols on prepared adsorbents was studied at ambient temperature (25±2 °C) employing the batch method. A known quantity of the adsorbent (0.1–0.4 g L^{-1}) was taken in a 100 ml stoppered conical flask and a 10 ml aqueous solution of CP, BP and IP was added to it, separately. The glass tubes were tightly stoppered to avoid vaporization losses
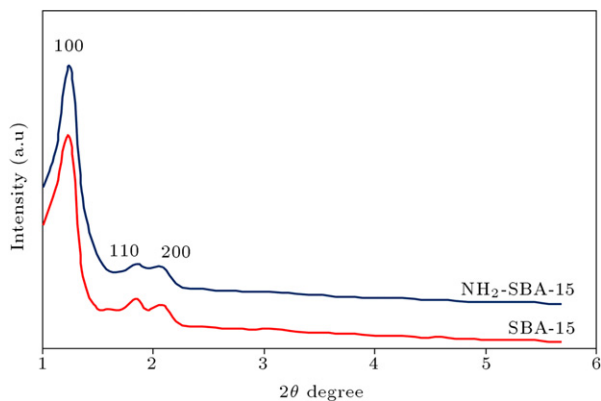
Figure 2: XRD patterns of SBA-15 and NH$_2$–SBA-15.

Figure 3: The FT–IR spectra of SBA-15 (A) and NH$_2$–SBA-15 (B).

of halophenols from the aqueous solutions. After equilibrium, the concentration of the adsorbate in the residual solution was analyzed by a UV-spectrophotometer (MPC-2200, UV 2550) at λ_{max} of 279 nm for 4-chlorophenol (CP), 280 nm for 4-bromophenol (BP), and 282.0 nm for 4-iodophenol (IP), respectively. In order to reduce measurement errors, the UV absorption intensity for each equilibrium solution was measured in triplicate, 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 ± 5%. The specific amount of solute CP, BP and IP adsorbed was calculated using Eq. (1):

$$q_e = (C_o - C_f)\frac{V}{m}, \tag{1}$$

where q_e is the adsorption capacity (mg g^{-1}) of the adsorbent at equilibrium; C_o and C_f are the initial and final concentrations of the adsorbate in solution (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

### 2.5. Adsorption kinetics of phenolic compounds

To measure the adsorption kinetics of the phenolic compound onto the adsorbent, 25 mL of phenolic compound solution with an initial concentration of 250 mg L^{-1}, was introduced into the flask and mixed with 0.01 g of NH$_2$–SBA-15. The solution was stirred continuously at 298 K. Samples were taken from the solution by fast filtration at different time intervals. The concentration of CP, BP and IP in the residual solution was determined and the amount of adsorption (q_t) was calculated according to Eq. (2):

$$q_t = (C_o - C_t)\frac{V}{m}, \tag{2}$$

where q_t is the amount of adsorption at time t, C_o is the initial concentration of phenolic compound in the solution, C_t is the concentration of phenolic compound in the solution at time t, V is the volume of the solution, and m is the mass of NH$_2$-SBA-15.

3. Results and discussions

The X-ray Diffraction (XRD) patterns in the range of (1.0–6.0) 2θ of ordered mesoporous material, SBA-15, and the functionalized sample, NH$_2$–SBA-15, are shown in Figure 2. The XRD patterns of the SBA-15 show a strong (100) peak and proportional (110) and (200) peak intensities. In the X-ray diffraction pattern of the prepared material, the peak (100) of the parent SBA-15 was preserved, while the intensities of the
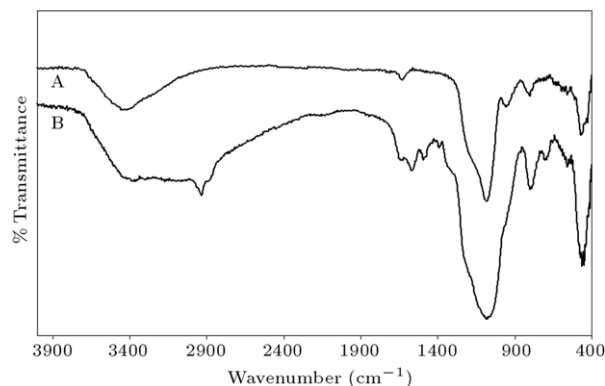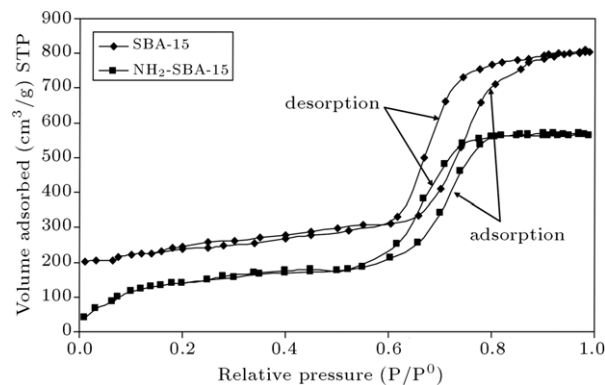
Figure 4: Nitrogen adsorption desorption isotherms of SBA-15 and NH$_2$–SBA-15.

other peaks were sharply decreased. The latter is attributed to the incorporation of organic groups inside the channels of SBA-15. This pattern confirms the presence of the 2D hexagonal structure of the pores and suggests that the modification process does not affect the framework integrity of the ordered mesoporous SBA-15 [20,36–38].

Figure 3 shows the infrared spectra of SBA-15 before and after modification. There are several bands appearing in the amino-functionalized SBA-15. Actually, it is difficult to determine the functional group −NH$_2$ attached to the surface mesoporous material by observing the peak around 3460 cm^{-1}, because the band of −NH$_2$ overlaps with that of the O–H stretching vibration. The presence of peaks at 2937 and 1560 cm^{-1} corresponds to C–H stretching and N–H (primary amine) bending vibration, respectively [36,39]. The large reduction in the absorbance of the O–H stretch band on the NH$_2$-functionalized sample surface also confirms the replacement of −OH groups with the −Si(CH$_2$)$_3$NH$_2$ groups [40].

The nitrogen adsorption–desorption isotherms, performed at 77 K for the SBA-15 silica, before and after grafting with 3-aminopropyl trimethoxysilane, are shown in Figure 4. Both mesoporous materials yield a type IV isotherm. The type IV isotherm (IUPAC classification) is typical for mesoporous systems [18]. The isotherm of SBA-15 is reversible and in good agreement with that previously reported [33]. The textural properties of SBA-15 silica, before and after grafting with 3-aminopropyl trimethoxysilane, are summarized in Table 1. The surface areas of SBA-15 and NH$_2$–SBA-15 samples were 812 and 620 m^2 g^{-1}, and their average pore sizes were 63 and 58 Å, respectively. Both the surface area and the total pore volume of
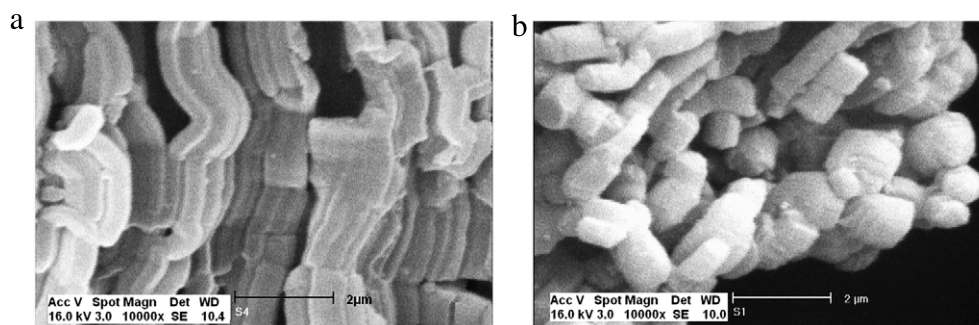
Figure 5: SEM image of (a) SBA-15 and (b) NH$_2$–SBA-15 support materials (magnification: 10 kx).

Table 1: Textural properties determined from nitrogen adsorption desorption experiments at 77 K.

Adsorbent	d Spacing (nm)	A_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})
SBA-15	6.3	812	1.1
NH$_2$–SBA-15	5.8	620	0.8

the modified sample dropped significantly, compared with the non-functionalized sample, SBA-15. The decrease in the pore volume of the material after silanization is a direct consequence of the silanization process, which fills the mesopores.

Figure 5 shows the SEM image of SBA-15 and NH$_2$–SBA-15. Generally, the image for both materials reveals that they consist of many rope-like domains, with relatively uniform sizes of 1.5–2 μm, which are aggregated into wheat-like macrostructures.

3.1. Effect of contact time and concentration

Generally, adsorption on the porous adsorbents takes place with two mechanisms: physical adsorption due to the adsorbent porosity, and chemical adsorption resulted from interaction between the adsorbent surface and the adsorbed species. The proper porosity size of the mesoporous compounds is the key factor in the high adsorption capacity for the BP, CP and IP species. Moreover, chemically active sites of the surface of the adsorbents cause further improvement in the adsorption capacity. In this section, the effect of the surface factor on the adsorption capacity is considered. In order to establish equilibration time for maximum uptake and to know the kinetics of the adsorption process, the adsorption of halophenols on amino-modified ordered mesoporous silica adsorbent was studied as a function of contact time, and results are shown in Figure 6(a). It is seen that the rate of uptake of all halophenols is rapid at the beginning, and 50% adsorption is completed within 2 h. Figure 6(a) also indicates that the time required for equilibrium adsorption is 4 h. Thus for all equilibrium adsorption studies, the equilibration period was kept at 6 h. The effect of concentration on the equilibration time was also investigated as a function of initial halophenol concentrations, and the results are shown in Figure 7. It was found that the time of equilibrium, as well as the time required to achieve a definite fraction of equilibrium adsorption, is independent of initial concentration.

3.2. Effect of chemical modification

In order to evaluate the efficiency of the prepared adsorbents, the equilibrium adsorption of halophenols was studied
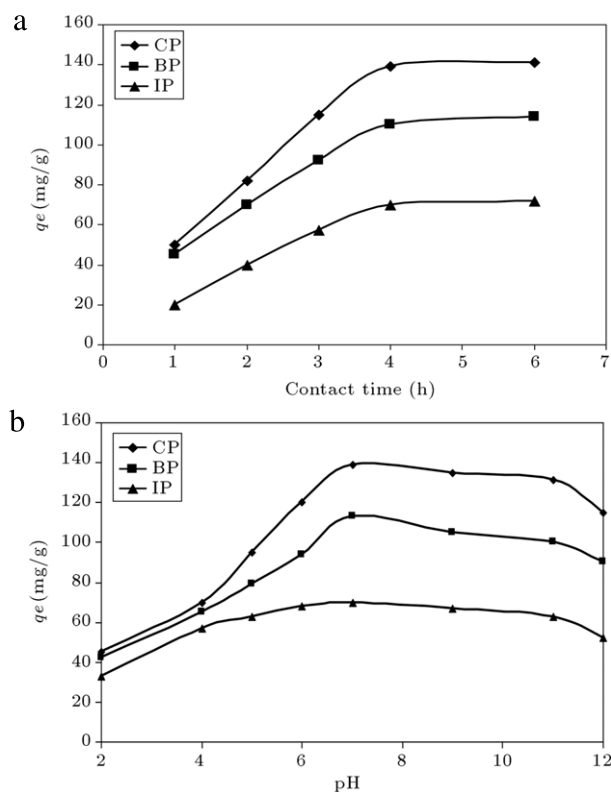
Figure 6: Effect of contact time on uptake of halophenols on NH$_2$–SBA-15 adsorbent (a) and effect of pH on removal of CP, BP and IP on NH$_2$–SBA-15 (b) (initial concentration = 50 mg L^{-1}, agitation speed = 300 rpm, adsorbent dosage = 0.2 g L^{-1} and ambient temperature = 25 ± 2 °C).
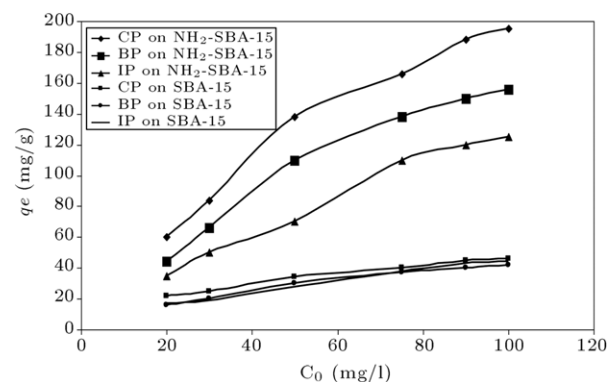
Figure 7: Effect of initial concentration on uptake of halophenols on NH$_2$–SBA-15 and SBA-15 (contact time = 4 h, agitation speed = 300 rpm, adsorbent dosage = 0.2 g L^{-1}, ambient temperature = 25 ± 2 °C).

Table 2: Langmuir and Freundlich constants for adsorption of CP, BP and IP on NH_2–SBA-15 and SBA-15.

Adsorbate	Adsorbents	Langmuir		R_2	Freundlich	n(L mg^{-1})	R_2
		q_m (mg g^{-1})	B (L mg^{-1})		K_f(mg g^{-1})		
CP	NH_2–SBA-15	210	0.069	0.9910	35.51	1.18	0.9980
	SBA-15	57.5	0.071	0.984	23.4	1.23	0.994
BP	NH_2–SBA-15	169	0.056	0.990	30.02	1.10	0.996
	SBA-15	32	0.069	0.983	19.8	1.14	0.992
IP	NH_2–SBA-15	112	0.049	0.988	27.37	1.03	0.997
	SBA-15	19	0.055	0.981	15.3	1.10	0.993

as a function of equilibrium concentration. The diagrams of the adsorption of CP, BP and IP on NH_2–SBA-15 and SBA-15 are illustrated in Figure 6. It is seen that the order of adsorption, in terms of the amount adsorbed (mg g^{-1}) under different conditions, is: NH_2–SBA-15 > SBA-15. NH_2–SBA-15 showed higher adsorption capacities (141, 114.6 and 72.1 mg g^{-1} for CP, BP and IP, respectively) than the untreated mesoporous SBA-15 (34.1, 30.3 and 28.2 mg g^{-1} for CP, BP and IP, respectively). The higher adsorption capacity of NH_2–SBA-15 could be explained by two facts: 1) because of the hydrophobicity created by propyl amine group, and 2) the presence of a free electron pair causing more interaction between halophenols and NH_2–SBA-15. In other words, halophenols are weak acids and there are acid and alkaline interactions among amine groups and halophenols.

3.3. 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 adsorbent and adsorbate vary with pH. 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 characteristics of the adsorption process. The effect of initial pH on the adsorption of CP, BP and IP by NH_2–SBA-15 was studied. In the alkaline range, the pH is varied using an aqueous solution of NaOH, whereas in the acidic range pH is varied using an HCl solution. The experimental results of the uptake of the CP, BP and IP on NH_2–SBA-15, in the pH range of 2–12, are shown in Figure 6(b). It is observed that the relative uptake of CP, BP and IP is significantly affected by pH. The adsorption capacity of halophenols remained nearly constant at $7 < pH < 11$, while at acidic pH, the adsorption capacity decreased. In the case of IP, the adsorption capacity remained constant between pH 5 and 11. This is due to the interaction of protons with NH_2–SBA-15. There is acid-alkaline interaction among adsorbents and NH_2–SBA-15, therefore, the amount of adsorption depends on the acidic strength of the species. At low pH values, the adsorption capacity decreased due to the presence of protons in the solution, which compete with the halophenols to be adsorbed on NH_2–SBA-15.

3.4. Equilibrium modeling

Equilibrium studies were carried out to determine the adsorption capacity and equilibrium constant for halophenols on NH_2–SBA-15. The distribution of solute between 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 were selected in this study [41].

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e, \tag{3}$$

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

where q_e (mg g^{-1}) is the amount of halophenols adsorbed per gram of NH_2–SBA-15 at equilibrium; C_e (mg L^{-1}) is the equilibrium concentration of halophenols in solution K_f is 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^{-1}) is the maximum monolayer adsorption capacity, and b (L mg^{-1}) is 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 are presented 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 values of Langmuir and Freundlich constants for the adsorption of halophenols onto NH_2–SBA-15 and SBA-15 are shown in Table 2. As can be seen from the table, the values for CP adsorption are higher than those for BP and IP. This indicates the higher adsorption capacity towards CP. As explained earlier, halophenols are weak acids and there is acid-alkaline interaction among halophenols and NH_2–SBA-15. Therefore, the amount of adsorption depends on the acidic strength of the halophenols; CP with higher K_f has greater interaction with NH_2–SBA-15, and is adsorbed more than BP and IP.

3.5. Comparison with other adsorbents

The value of q_e is important to identify which sorbent has the highest adsorption capacity, and is useful in scale-up considerations. Table 3 shows a comparison of the adsorbent capacity of various adsorbents for some halophenols.

4. Conclusions

1. Based on the present study, NH_2–SBA-15 is an effective adsorbent for the removal of halophenols from aqueous solutions. It was found that NH_2–SBA-15 had a significant adsorption capacity for CP, BP and IP, compared to untreated SBA-15, and that is attributed to the hydrophobicity resulted by the amine group and acid-alkaline interaction among halophenols and this group of NH_2–SBA-15.
2. The sorption of CP on NH_2–SBA-15 was fairly compared to those of BP and IP. This could be related to the greater acidity of CP, due to the greater electronegativity of the chlorine atom in comparison to the bromine or iodine atom, which leads to stronger interaction between the species and

Table 3: Comparison of adsorption capacity halophenols onto some adsorbents.

Adsorbate	Adsorbent	q_e (mg g^{-1})	Reference
4-chlorophenol (CP)	coconut shell charcoal (CSC)	54.65	[42]
4-bromophenol (BP)	Fertilizer industry waste	40.7	[43]
4-chlorophenol (CP)	NH$_2$–SBA-15	141	Present study
4-bromophenol (BP)	NH$_2$–SBA-15	114.6	Present study
4-Iodophenol (IP)	NH$_2$–SBA-15	72.1	Present study

sorbent. It was observed that the adsorption of halophenols was highly dependent on the pH of the aqueous solutions.
3. Adsorption isotherms were well predicted by the Freundlich equilibrium adsorption model.

Acknowledgment

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Mansoor Anbia obtained his M.S. degree from Tarbiat Moallem University in Tehran, doing a case study on "Synthesis, Properties and Applications of Lanthanum Silicates as Mineral Ion-Exchangers". He then did post M.S. research on "Measuring 222Rn Content of Mineral Water Employing Alpha-Spectroscopy and the Liquid Scintillation Method" at the same University, where he also obtained his Ph.D. in 2007 under the supervision of Professor Vaghef Hossein. His thesis was entitled "Case Study on Synthesis, Properties and Analytical Applications of Novel Mesoporous Compounds of Lanthanum Silicate, Lanthanum Phosphate, Lanthanum Tantalate and Titanium Phosphate". Dr. Anbia has been honored with several national and international scientific awards. He is currently Associate Professor at Iran University of Science and Technology and is also the President of the Chemistry and Chemical Engineering Research Center of Iran. His research interests include Inorganic Ion-Exchangers, Mesoporous Adsorbents, Nano Structure New Materials, Chromatography (HTPLC, HPLC & GSC), Removal of Organic and Inorganic Pollutants from Industrial Effluents, Purification Methods for the Recovery of Different Chemical Compounds from Industrial Waste, and Application of New Materials for use in Different Industrial Plants.

Shahram Amirmahmoodi obtained his B.S. degree from Isfahan Technical University in 2006 and was then admitted to the Iran University of Science and Technology for MS studies after successfully passing the national entrance examination under the supervision of Dr. Mansoor Anbia, and graduated in 2010. His M.S. degree topic focused on The Removal of Various Pollutants from Effluents and Wastewater by Nano-Porous Material Adsorbents.