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# Adsorption of phenol compounds by nanoporous silica aerogel

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Adsorption kinetic.

**Abstract.** Phenolic compounds are important environmental pollutants, whose separation and removal from water and industrial wastewater, especially in the oil industry, is essential. In the present research, the efficiency of an adsorbent silica aerogel in removing 4-Chlorophenol(4-CP) and 4-Bromophenol(4-BP), as phenolic compounds, from an aqueous solution, is studied, and the effects of various factors, such as contact time, pH and initial concentration, are analyzed. It was observed that the amount of adsorption increases at low pH, and this amount increases by incrementing the concentration of the emissions. Additionally, increasing the amount of adsorbent causes a decrease in halophenols. Results show that 4-BP is much better than 4-CP for adsorption onto the silica aerogel. Langmuir and Freundlich adsorption isotherms have been applied to model the equilibrium adsorption data. The study on the adsorption isotherms of these contaminants shows that adsorption of these emissions follows the Freundlich isotherm. In addition, adsorption kinetics using pseudo-first-order and pseudo-second order equations, elovich, and an intra-particle diffusion model, were analyzed. The results showed that the uptake of these compounds follows the intra-particle diffusion model and pseudo-second order equation.

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## 1. Introduction

Water pollution, caused by chemical substances produced in various industrial units entering surface water or groundwater, is a major threat to the environment [1-3]. Overcoming this threat is a serious challenge [4]. Hence, extensive activities concerning industrial wastewater treatment before entering the environment, in order to remove pollutants, are necessary. Among different pollutants, phenol and its derivatives in the presence of sewage, in many industries, including refineries, petrochemical, wood, steel, coal, rubber, paper, plastics, paint etc. are of great importance.

Thus, the removal and separation of these compounds have been highlighted by many researchers. For the separation of these compounds, there are various methods such as biological filtration [5,6], solvent extraction [7], chemical oxidation [8], photodegradation [9], coagulation [10], ion exchange [11], electrochemical methods [12], and adsorption [13,14]. Among the methods mentioned, adsorption technology has been mostly developed because of lower operating costs, easier operational control and, most importantly, its direct process [15]. Adsorption is a process in which molecules of fluids are collected on the surfaces of an adsorbent. Many adsorbents have been employed for the removal of phenolic compounds from wastewater [1,4,14,16-20]. Due to the constraints, such as difficult access, lack of high-efficiency, high cost of restoring the adsorbent, and so on, there is a growing interest in the high performance and easy use of adsorbents. Hence,

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assessment of other adsorbents to find an appropriate one is necessary. Silica aerogel is a very porous and nanostructured solid that has specific physical and chemical characteristics. Silica aerogel is chosen as an adsorbent due to its high specific surface area and high level of porosity.

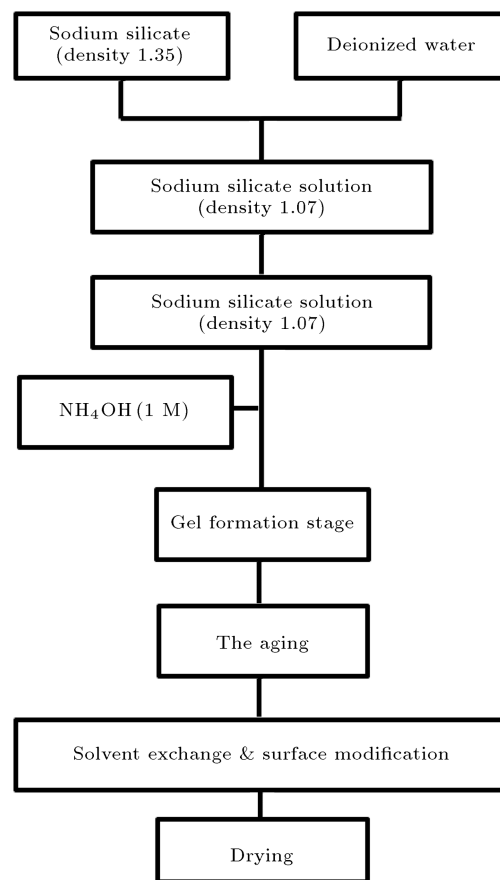
Phenol is an aromatic compound which is derived from benzene and substituted for hydrogen by adding a hydroxyl group to the carbon. Halophenols are a group of organic compounds which are formed through substitution of one or more halogen atoms in the phenolic ring. The solubility of halophenols is low in water and this solubility becomes even less by the increasing number of halogens in their structure. 4-chlorophenol and 4-bromophenol are kinds of halogenated phenol by which the chlorine and bromine are attached to the fourth ring on the benzene as halogens. The presence of these compounds in water causes an unpleasant flavor and makes water unsuitable for consumption. Due to their toxic effects and carcinogenic nature, these materials are considered harmful to the environment. Silica aerogel materials are porous nano structures, which have characteristics such as high porosity, low density, high specific surface area, environmental sustainability and ability of use in a variety of applications. A significant application of these materials is their role as an adsorbent [21-23].

In this study, a silica aerogel was synthesized by a water glass precursor and an ambient pressure drying method. After characterization of silica aerogel properties, it was used as an adsorbent to remove 4-CP and 4-BP from an aqueous solution. The effect of several elements such as adsorption time, pH of the solution, initial concentration of contaminant and adsorbent dosage on the adsorption was studied. Adsorption kinetics were analyzed using pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion model equations. Also, Langmuir and Freundlich adsorption isotherm models were used for analysis of the results.

## 2. Materials and methods

4-chlorophenol (4-CP, Sigma Aldrich-USA) and 4-bromophenol (4-BP, Fluka) as contaminants, 4-aminoantipyrine, potassium ferricyanide, ammonium chloride and ammonium hydroxide, all from Merck, were used to analyze the pollutants in water. Sodium hydroxide and hydrochloric acid (Merck chemicals) were used to adjust the pH of the solutions.

Solutions were prepared in distilled water. A stock solution of halophenols was prepared by dissolving 0.1 g of halophenol in 100 ml balloons. The concentration of phenolic components was spectrophotometrically measured by a colorimetric method using a M501 Single Beam Scanning UV/Visible Spectrophotometer.



**Figure 1.** Block flow diagram of the silica aerogel synthesis.

### 2.1. Synthesis of silica aerogel

Synthesis of silica aerogel is generally divided into three stages: Preparation of the gel, the aging process, changing the solvent and surface modification, followed by gel drying.

The schematic diagram in Figure 1 shows the several stages of the synthesis.

A sodium silicate solution with a density of  $1.35 \text{ g/cm}^3$  is diluted with deionized water to reach the desired density of  $1.07 \text{ g/cm}^3$ . Then, ion-exchange resin (Amberlite 120  $\text{H}^+$ , Merck) was used to replace the  $\text{Na}^+$  ions and  $\text{H}^+$  ions. To accomplish the complete exchange process, the sodium silicate solution was mixed with the same volume of resin for 15 minutes under severe mixing conditions. If the mixing process is undertaken slowly, the prepared sol can be changed to solid gel immediately at pH of about 4. Before performing ion exchange, the solution pH was about 11.5 to 13, but, after ion-exchange, due to the release of  $\text{H}^+$  ions, the pH of the solution reached 1-2.

For gel formation, the pH of the resulting solution should be adjusted in a range of 3.8-5, and this is done by adding an ammonium hydroxide (1 M) catalyst. The resulting solution was then transferred to containers with Teflon lids, leaving the cell for gel

formation to complete. It may take a few minutes to several hours, depending on the pH of the cell.

After gel formation, 3 hours were required for completion of the gel aging step in an environment impervious to air. The aging step is necessary to complete the reactions of the gel formation process and also to strengthen the gel structure. It also reduces the risk of gel breaking. The gel was immersed in an alcohol and solvent media for 36 hours to accomplish the aging step in the alcohol and in changing the solvent. The aging step, solvent exchange, and surface modification steps were carried out at 60°C to increase the reaction rate and decrease the reaction time. Because of the volatile solvent used in the reactions, it is not possible to perform the reaction at high temperatures. The optimal time for the reactions was 36 hours.

Surface modification in the solution was operated at 60°C for 24 h with respect to predetermined effective parameters. After this step, the obtained gel was dried at 24°C overnight. Further drying was done at 160°C for 1 h through a ramped slow heating to avoid sudden shock heating.

## 2.2. Specifications of silica aerogel

Aerogel density was determined by weighing the volume of the sample. The surface area was measured by

BET analysis using the amount of N<sub>2</sub> gas adsorbed in different partial pressures. Pore size distribution was obtained from BJH results. The hydrophobicity of samples was determined by the contact angle of water with the aerogel surface. Organic and inorganic bonds of the aerogel were evaluated by using FTIR analysis, which gives information about the various chemical bonds of C-H, Si-C, Si-O-Si, Si-OH, and -OH [23,24]. Differential weight loss and phase changes were measured using TG-DTA, considering temperature variations from 30 to 500°C and 10°C/min heating rate. The morphology and pore structure of the silica aerogel were observed by Scanning Electron Microscopy (SEM).

Properties of the synthesized aerogel were characterized with contact angle, SEM, BET, BJH, and TG/DTA tests, and the results are presented in Table 1. The SEM image for samples synthesized is shown in Figure 2. As is clear from this figure, the synthesized samples have nano-porous structures.

TEM images of hydrophobic silica aerogels were obtained using Philips EM208 operating at an acceleration voltage of 90 kV. As shown in Figure 3, the diameters of the pores in the sample were mainly distributed from 5 to 60 nm, which are confirmed by BJH results. The TEM image indicated that the

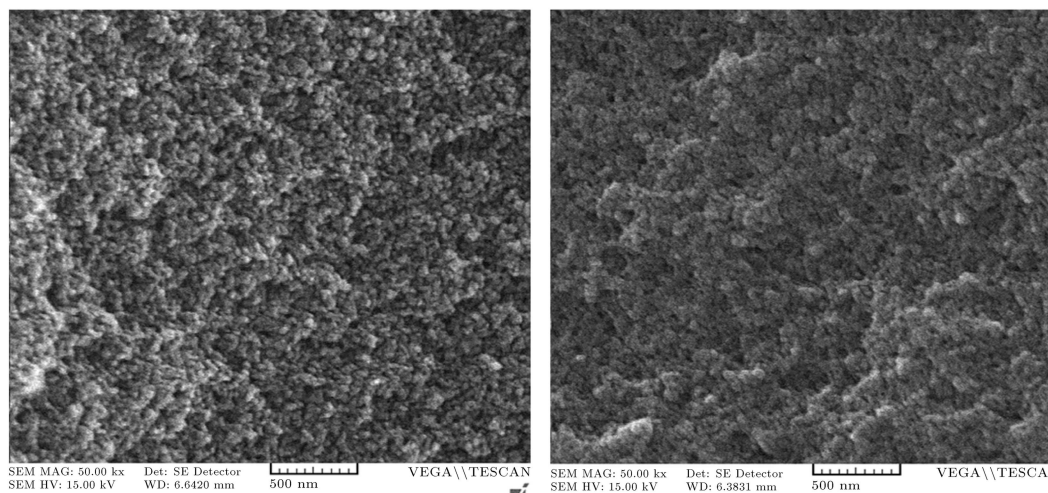
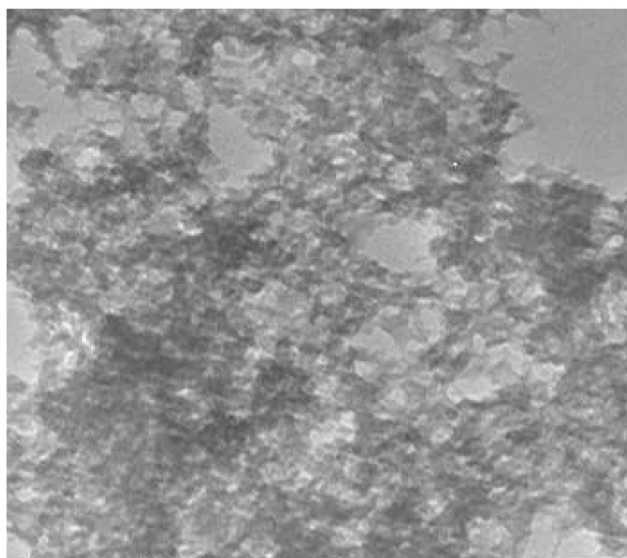


Figure 2. SEM result of aerogel synthesized (Tescan company model TS5136MM).

Table 1. Characteristics of the synthesized aerogel.

Parameter	Value	Equipment
Density	0.11 gr/cm <sup>3</sup>	Microbalance scale, (10 <sup>-5</sup> g precision, Mettler)
Contact angle	143°, Super hydrophobic	Data physics - OCA 15 plus
Surface area	600-850 m <sup>2</sup> /gr	Belsorb, Japan
Total volume of pores	2.36-2.6 cm <sup>3</sup> /gr	Belsorb, Japan
Average pore size	16.5 nm	Belsorb, Japan
Thermal stability	Up to 400°C	Pyris diamond, from Perkin Elmer Co
Porosity	> 95%	(1 - (ρ <sub>aerogel</sub> - ρ <sub>silica</sub> )) * 100



50 nm 56000x 2012/2/29 10:40  
90Kv Philips EM208

**Figure 3.** TEM image for hydrophobic silica aerogel (Philips EM208).

prepared materials were nanoporous and formed from nanoparticles with few nanometers.

### 2.3. Colorimetric method for estimating the concentration of phenolic compounds

This method is based on photometric tests that show that phenolic compounds react with 4-aminoantipyrine at pH of 10 in the presence of free potassium cyanide. For each 100 ml of a solution that contains phenolic compounds, 2 ml of buffer solution, 2 ml of 4-aminoantipyrine solution (20 g/L) and, finally, 2 ml of potassium ferricyanide (80 g/L) were added to balance the pH to 10. After that, a buffer solution containing 16.9 g ammonium chloride was mixed with 143 ml ammonium hydroxide and the solution was brought to 250 cc by adding distilled water. After 30 minutes, an antipyrine red color formed and the absorbance was measured at a wavelength of 510 nm [25,26].

### 2.4. Adsorption studies

Adsorption of phenolic compounds was undertaken onto the synthesized adsorbents. Due to the low density of silica aerogel, a continuous system with reflux was used at ambient temperature. Solutions of various levels of phenolic compounds were prepared and were placed in contact with 0.05 g of adsorbent. After the adsorption process and reaching equilibrium, the concentration of the adsorbate was determined by a UV-spectrophotometer. In order to increase the accuracy of measurement, the UV absorption intensity of each sample was measured three times and the equilibrium concentration was taken as the average of three numbers, based on a standard calibration curve whose correlation coefficient square was 0.99. The

adsorption capacity was calculated using Eq. (1):

$$q_e = (C_0 - C_e) \frac{V}{m}, \quad (1)$$

where  $q_e$  is the adsorption capacity (mg/g) of the adsorbent at equilibrium;  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the adsorbate in solution (mg/L), respectively,  $V$  is the volume of solution (L), and  $m$  is the mass of adsorbent (g).

### 2.5. Adsorption kinetic studies of phenolic compounds

To study the kinetics of phenolic pollutants adsorbed on the adsorbent, 0.05 g of the adsorbent is placed in contact with 1100 ml of phenolic solution, and the amount of adsorption at different times was calculated using Eq. (2):

$$q_t = (C_0 - C_t) \frac{V}{m}, \quad (2)$$

where  $q_t$  is the amount of adsorption at time  $t$  (mg/g),  $C_0$  is the initial concentration (mg/L),  $C_t$  is the concentration at time  $t$  (mg/L),  $V$  is the volume of the solution (L), and  $m$  is the mass of adsorbent (g).

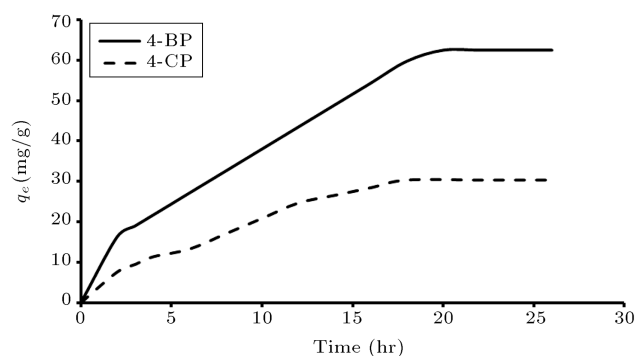
## 3. Results and discussion

### 3.1. Effect of contact time

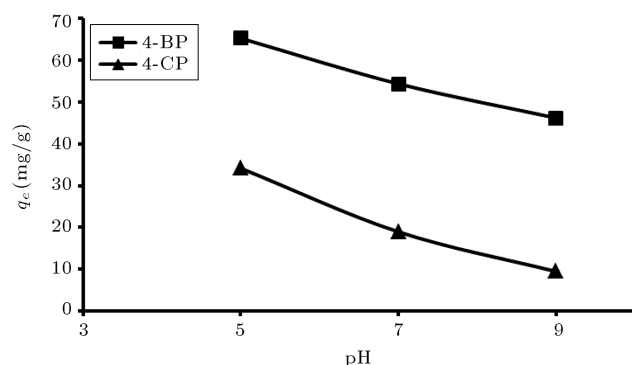
The effect of contact time on the adsorption of halophenol versus equilibrium was studied. Adsorption results are shown in Figure 4. As can be seen, the early adsorption process is fast. Rapid adsorption is due to the interfacial bonding of species on the surface of the adsorbent. According to Figure 4, after 18 hours, any specific change in the adsorption capacity was not observed and the slope remained relatively constant. However, to ensure, equilibrium time was considered for 20 hours.

### 3.2. Effect of pH

In this study, the effect of pH on the adsorption capacity was studied. pH was adjusted from 5 to 9 (5,



**Figure 4.** Effect of contact time on removal of 4-CP and 4-BP on silica aerogel adsorbent; initial concentration= 50 mg/L, adsorbent dosage= 0.05 g, and pH=5.

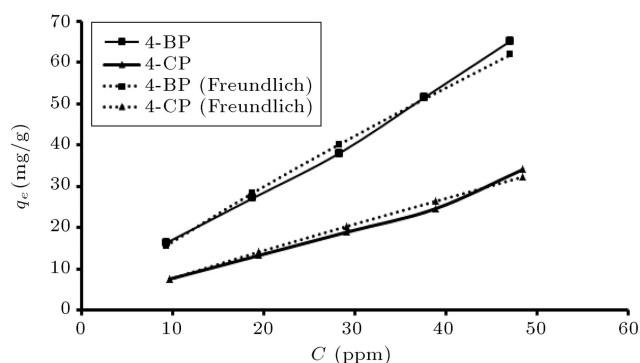


**Figure 5.** Effect of pH on removal of 4-CP and 4-BP on silica aerogel; initial concentration= 50 mg/L, adsorbent dosage= 0.05 g.

7, 9) by adding HCl 0.1 N and NaOH 0.1 M. The results are shown in Figure 5. According to the results, it can be seen that halophenols adsorption by silica aerogel is higher at acidic pH. This is probably due to the protonation of the adsorbent surface at low pH, which led to the higher adsorption of halophenolic ions. These ions are negatively charged and are directly adsorbed by the electrostatic on the adsorbent surface. Also non-ionized molecules of pollutants may be adsorbed by physical force. At high pH value, the presence of  $\text{OH}^-$  ions can compete with halophenol molecules to reach the adsorption sites. Excessive adsorption of  $\text{OH}^-$  ions can fill the adsorbent surface with positive charges, which converts it to a negatively charged surface. Therefore, desorption of halophenol ions is occurred and pollutant adsorption is reduced.

### 3.3. Effect of initial concentration

The initial concentration of the solution is an important factor affecting the adsorption capacity. Figure 6 shows that by increasing initial concentration, the equilibrium adsorption capacity increases for both pollutants. This is because the initial concentration of halophenols is the major driving force in overcoming the resistance of the mass transfer pollutants from the aqueous phase



**Figure 6.** Effect of initial concentration on removal of 4-CP and 4-BP on silica aerogel; pH=5, adsorbent dosage= 0.05 g. Results compared with Freundlich model are obtained in Table 2.

on the surface of the solid adsorbent. Thus, access of halophenols to the active sites of the adsorbent is improved by increasing the initial concentration. The adsorption curve slopes of the initial concentration at 50 ppm show that the adsorbent is still not saturated at this concentration. Therefore, with increasing initial concentration, the capacity of the adsorbent will be greater. This proves the existence of a great number of adsorption sites on the adsorbent.

### 3.4. Adsorption isotherm

Many models describing experimental adsorption isotherm data have been published in the literature [27]. Langmuir and Freundlich isotherm models are widely used for the design of phenolic compound adsorption systems. In this study, two equilibrium isotherm models were applied at constant temperature to describe the equilibrium between halophenol molecules adsorbed on the adsorbent and solute. The Langmuir isotherm adsorption phenomena occur on a homogeneous adsorbent, whereas the Freundlich adsorption isotherm shows a heterogeneous distribution on the adsorbent.

#### 3.4.1. Langmuir isotherm

The Langmuir isotherm is mathematically expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $q_e$  is the adsorption capacity of the adsorbent at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L), and  $q_m$  (mg/g) and  $K_L$  (L/mg) are Langmuir isotherm constants, respectively, depending on the theoretical maximum capacity of a single layer and adsorption rate [28].

The linear form of the equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

By plotting changes in  $C_e/q_e$  against  $C_e$ , constants  $K_L$  and  $q_m$  can be obtained from the slope and intercept diagrams.

#### 3.4.2. Freundlich isotherm

The Freundlich isotherm is a non-linear form as follows [29]:

$$q_e = k_F C_e^{\frac{1}{n}} \quad (5)$$

where,  $k_F$  and  $n$ , respectively, are Freundlich constants that indicate adsorption capacity and adsorption intensity. Constants  $k_F$  and  $n$  are obtained from the linear regression analysis of Eq. (5):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (6)$$

When the value of  $1/n$  is in the range of 0.1-1.0, favorable adsorption occurs [30].

**Table 2.** Langmuir and Freundlich constants for adsorption of 4-CP and 4-BP on silica aerogel.

Adsorbate	Langmuir		$R^2$	Freundlich		$R^2$
	$K_L$ (L mg <sup>-1</sup> )	$q_m$ (mg g <sup>-1</sup> )		$k_F$ (mg g <sup>-1</sup> )	$n$	
4-BP	0.0063	270.2703	0.5923	2.3729	1.1809	0.9919
4-CP	0.0032	238.0952	0.3014	0.9368	1.1046	0.9901

The isotherm data is linearized using the Langmuir and Freundlich equations. The data of these isotherms are presented in Table 2. According to the result, the adsorption behavior of halophenol on silica aerogel was in close agreement with the Freundlich equation.

### 3.5. Adsorption kinetics

A kinetic study of the adsorption process is crucial, because its information is very valuable and provides mechanisms for the adsorption process. The natural adsorption process is controlled by 3 diffusion stages:

1. Mass transfer in the liquid film surrounding the adsorbent;
2. Transfer of the film adjacent to the surface of the adsorbent;
3. Transfer into the active sites of the adsorbent.

This will be followed by binding species on the adsorption site.

The slowest step among the above-mentioned diffusion stages is determining the rate of adsorption. This is often the second stage, which leads to adsorption, or the third stage, which results in diffusion of the intra-particle. In the present work, the kinetic data have been analyzed using pseudo-first-order, pseudo-second-order, elovich and intra-particle diffusion models.

#### 3.5.1. Pseudo-first-order

The kinetics of the first degree is one of the most widely used in aqueous solutions to describe the kinetics of adsorption of a substance to dissolve relations. The first order equation of Lagergren is generally stated as follows [29]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (7)$$

where  $q_e$  and  $q_t$  are the amounts of phenolic components adsorbed (mg/g) at equilibrium and at time  $t$  (hr), respectively, and  $k_1$  is the rate constant of pseudo-first-order sorption (hr<sup>-1</sup>). The integrated form of Eq. (7) is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t. \quad (8)$$

A plot of  $\ln(q_e - q_t)$  against  $t$  should give a linear relationship with slope  $k_1$  and intercept of  $\ln q_e$ .

#### 3.5.2. Pseudo-second-order

The pseudo-second-order kinetic rate equation is expressed as follows [30]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (9)$$

where  $k_2$  is the rate constant of pseudo-second-order sorption (g/mg.hr). The integrated form of Eq. (9) is:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t. \quad (10)$$

Eq. (10) can be rearranged to obtain Eq. (11), which has a linear form:

$$\frac{1}{q_t} = \left( \frac{1}{k_2 q_e^2} \right) \frac{1}{t} + \frac{1}{q_e}. \quad (11)$$

The plot of  $1/q$  against  $1/t$  of Eq. (11) should give a linear relationship. The  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot.

#### 3.5.3. Elovich model

The applicability of the elovich equation for the adsorption process is also examined. The elovich equation is generally expressed as [33]:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}. \quad (12)$$

To simplify the elovich equation, Chien and Clayton (1980) [33] assumed that  $\alpha\beta t$ , and, by applying boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , Eq. (12) becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t, \quad (13)$$

where,  $\alpha$  is the initial sorption rate (mg/g.hr), and  $\beta$  (g/mg) is the extent of surface coverage which depends on the activation energy adsorption.

Thus, a plot of  $q_t$  vs  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta)\ln(\alpha\beta)$ , if the sorption process fits the elovich equation

#### 3.5.4. Intra-particle diffusion model

The adsorbent structure and its interaction with the adsorbate affect the mass transfer rate, so that the motion of the solute is a function of the concentration gradient [34]. If the adsorption process of the adsorbate on the adsorbent is the determining step of the adsorption rate, the adsorption data can be described by [35]:

$$q_t = k_i t^{0.5} + C, \quad (14)$$

**Table 3.** Kinetic parameters for adsorption of 4-CP and 4-BP on silica aerogel.

Kinetic model	Parameters	4-Bromophenol	4-Chlorophenol
Pseudo-first-order	$R^2$	0.8804	0.9441
	$k_1$ ( $\text{hr}^{-1}$ )	0.1430	0.1606
	$q_e$ (mg/g)	75.3995	36.4121
Pseudo-second-order	$R^2$	0.9481	0.9722
	$k_2$ ( $\text{g}/(\text{mg}\cdot\text{hr})$ )	0.0016	0.0026
	$q_e$ (mg/g)	75.1880	40.8163
Elovich	$R^2$	0.9497	0.9588
	$\alpha$ (mg/g.hr)	16.1812	8.4656
	$\beta$ (g/mg)	0.0473	0.0962
Intra-particle diffusion	$R^2$	0.9804	0.9763
	$k_i$ ( $\text{mg}/\text{g}\cdot\text{hr}^{0.5}$ )	13.802	7.5403
	$C$ (mg/g)	3.6046	2.6614

**Table 4.** Comparison of adsorption capacity for various adsorbents in order to eliminate halophenols.

Adsorbent	Adsorbate	$q_e$ (mg/g)	Reference
TMP-smectite	4-CP	40	[36]
Dodecylammonium bentonite (DDAB)	p-CP	4.5	[37]
Carbonaceous	4-BP	40.7	[38]
Standard activated charcoal	4-BP	90	[38]
Silica Aerogel	4-CP	34	Current study
Silica Aerogel	4-BP	65	Current study

where,  $k_i$  is the intra-particle diffusion rate constant ( $\text{mg}/\text{g}\cdot\text{min}^{0.5}$ ) and  $C$  (mg/g) is the boundary layer diffusion effects. Parameter  $C$  is representative of the boundary layer thickness. In other words, the greater value of parameter  $C$  indicates that the thickness of the adsorbent layer, in which the adsorption occurs, is larger.

The results of applying kinetics models to correct the data are given in Table 3.

### 3.6. Comparison with other adsorbents

As mentioned previously, the adsorption capacity depends on various factors such as interaction type, pH, initial concentration, etc. Hence, comparison must be made under completely equal conditions. Table 4 shows a comparison of the adsorption capacity of various adsorbents for halophenols.

## 4. Conclusion

In this study, the adsorption of phenolic component from aqueous solution using silica aerogel was investigated. Contact angle, SEM, BET, BJH, and TG/DTA tests were used to characterize the properties of the synthesized aerogel. The silica aerogel is applied as an adsorbent. The results indicate that the adsorption capacity of the adsorbent was considerably influenced

by initial pH, initial concentration and contact time. The outcomes show that the amount of halophenol adsorption increased by the rising of initial concentration. The results also indicated that the uptake of halophenol took place at a pH of 5, and, then, the adsorption of phenol decreased by pH increasing. Equilibrium data fitted very well in a Freundlich isotherm equation, confirming the heterogeneous distribution on the adsorbent.

The pseudo-first-order, pseudo-second-order, elovich and intra-particle diffusion kinetic models were used to analyze the data obtained for 4-CP and 4-BP adsorption onto silica aerogel. The results show that the intra-particle diffusion and pseudo-second-order model provided the best correlations for the adsorption data. Future studies should focus on a scale up of the setup, and evaluation of the adsorption capacity of silica aerogel for removing phenolic compounds from wastewater. Also, adsorption of halophenols using a modified silica aerogel with amine groups and their composites is suggested for future work.

## Nomenclature

4-CP	4-Chloro phenol
4-BP	4-Bromophenol



NH <sub>4</sub> OH	Ammonium hydroxide
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
$q_e$	Adsorption capacity of adsorbent at equilibrium (mg/g)
$q_t$	Adsorption capacity of adsorbent at time $t$ (mg/g)
$C_0$	Initial concentration (mg/L)
$C_e$	Equilibrium concentration (mg/L)
$C_t$	Concentration at time $t$ (mg/L)
$V$	Volume (L)
$m$	Mass of adsorbent (g)
$q_m$	Langmuir isotherm constant (mg/g)
$K_L$	Langmuir isotherm constant (L/mg)
$k_F$	Freundlich constant
$n$	Freundlich constant
$t$	Time (hr)
$k_1$	Rate constant of pseudo-first-order sorption (hr <sup>-1</sup> )
$k_2$	Rate constant of pseudo-second-order sorption (g/mg.hr)
$\alpha$	Initial sorption rate in Elovich model (mg/g.hr)
$\beta$	Extent of surface coverage in Elovich model (g/mg)
$k_i$	Intra-particle diffusion rate constant (mg/g.min <sup>0.5</sup> )
$C$	Boundary layer diffusion effects in intra-particle diffusion model (mg/g)

## References

- Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Haya-neh, O. "Adsorption of phenol by bentonite", *Environmental Pollution*, **107**, pp. 391-398 (2000).
- Cermola, F., Dellagrecia, M., Iesce, R., Montella, S., Pollio, A. and Temussi, F. "A mild photochemical approach to the degradation of phenols from olive oil mill wastewater", *Chemosphere*, **55**, pp. 1035-1041 (2004).
- Rengaraj, S., Moon, S.H., Sivabalan, R., Arabindoo, B. and Murugesan, V. "Agricultural solidwaste for the removal of organics: Adsorption of phenol from water and wastewater by palm seed coat activated carbon", *Waste Manage.*, **22**, pp. 543-548 (2002).
- Polat, H., Molva, M. and Polat, M. "Capacity and mechanism of phenol adsorption on lignite", *Int. J. Miner. Process*, **79**, pp. 264-273 (2006).
- Bevilaqua, J.V., Cammarota, M.C., Freire, D.M.G. and Sant'Anna Jr., G.L. "Phenol removal through combined biological and enzymatic treatments", *Braz. J. Chem. Eng.*, **19**(2), pp. 151-158 (2002).
- Sobecka, B.S., Tomaszewska, M. and Morawski, A.W. "Removal of micropollutants from water by ozonation/biofiltration process", *Desalination*, **182**, pp. 151-157 (2005).
- Yang, C., Qian, Y., Zhang, L. and Feng, J. "Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater", *Chemical Engineering Journal*, **117**(2), pp. 179-185 (2006).
- Yavuz, Y., Koparal, A.S. and Ögütveren, Ü.B. "Phenol removal through chemical oxidation using Fenton reagent", *Chemical Engineering & Technology*, **30**(5), pp. 583-586 (2007).
- Shawabkeh, R.A., Khashman, O.A. and Bisharat, G.I. "Photocatalytic degradation of phenol using Fe-TiO<sub>2</sub> by different illumination sources", *International Journal of Chemistry*, **2**, pp. 10-18 (2010).
- Zazouli, M.A. and Taghavi, M. "Phenol removal from aqueous solutions by electrocoagulation technology using iron electrodes: Effect of some variables", *Journal of Water Resource and Protection*, **4**, pp. 980-983 (2012).
- Carmona, M., De Lucas, A., Valverde, J.A., Velasco, B. and Rodríguez, J.F. "Combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420", *Chemical Engineering Journal*, **117**, pp. 155-160 (2006).
- Körbahti, B.K. and Tanyolaç, A. "Continuous electrochemical treatment of phenolic wastewater in a tubular reactor", *Water Research*, **37**, pp. 1505-1514 (2003).
- Yavuz, Y., Koparal, A.S. and Ögütveren, Ü.B. "Phenol removal through chemical oxidation using Fenton reagent", *Chem. Eng. Technol.*, **30**(5), pp. 583-586 (2007).
- Akgerman, A. and Zardkoohi, M. "Adsorption of phenolic compounds on fly ash", *J. Chem. Eng. Data*, **41**, pp. 185-187 (1996).
- Štandeker, S., Novak, Z. and Knez, Ž. "Adsorption of toxic organic compounds from water with hydrophobic silica aerogels", *Journal of Colloid and Interface Science*, **310**, pp. 362-368 (2007).
- Theopharis, G.D., Traiantafyllos, A.A., Petrakis, D.E. and Pomonis, P.J. "Removal of chlorinated phenols from aqueous solutions by adsorption on alumina pillared clays and mesoporous alumina aluminum phosphates", *Water. Res.*, **32**(2), pp. 295-302 (1998).
- Kamble, S.P., Mangrulkar, P.A., Bansiwai, A.K. and Rayalu, S.S. "Adsorption of phenol and o-chlorophenol on surface altered fly ash based molecular sieves", *Chem. Eng. J.*, **138**, pp. 73-83 (2008).
- Kuleyin, A. "Removal of phenol and 4-chlorophenol



- by surfactant-modified natural zeolite”, *J. Hazard. Mater.*, **144**, pp. 307-315 (2007).
19. Abburi, K. “Adsorption of phenol and p-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin”, *J. Hazard. Mater. B*, **105**, pp. 143-156 (2003).
  20. Pan, B.C., Zhang, X., Zhang, W.M., Zheng, J.Z., Pan, B.J., Chen, J.L. and Zhang, Q.X. “Adsorption of phenolic compounds from aqueous solution onto a macroporous polymer and its aminated derivative: isotherm analysis”, *J. Hazard. Mater. B*, **121**, pp. 233-241 (2005).
  21. Liu, H., Sha, W., et al. “Preparation and characterization of a novel silica aerogel as adsorbent for toxic organic compounds”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **347**, pp. 38-44 (2009).
  22. Bargozin, H., Amirkhani, L., Moghaddas, J.S. and Ahadian, M.M. “Synthesis and application of silica aerogel-MWCNT nanocomposites for adsorption of organic pollutants”, *Scientia Iranica*, **17**(2), pp. 122-132 (2010).
  23. Bargozin, H. and Moghaddas, J.S. “Wettability alteration with silica aerogel nanodispersion”, *Journal of Dispersion Science and Technology*, **34**, pp. 1130-1138 (2013).
  24. Bargozin, H. and Moghaddas, J.S. “Stability of Nanoporous Silica Aerogel Dispersion as Wettability Alteration Agent”, *Journal of Dispersion Science and Technology*, **34**, pp. 1454 -1464 (2013).
  25. Annual Book of ASTM Standards, Part 31, ”Water”, Standard D 1783-70, p. 553 (1976).
  26. *Standard Methods for the Examination of Water and Wastewater*, 14th Edn., pp. 574-581, Method 510 through 510C (1975).
  27. Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O. “Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn<sup>2+</sup> unto phosphoric acid modified rice husk”, *IOSR Journal of Applied Chemistry (IOSR-JAC)*, **3**, pp. 38-45 (2012).
  28. Langmuir, I. “The constitution and fundamental properties of solids and liquids”, *Journal of the American Chemical Society*, **38**, pp. 2221-2295 (1916).
  29. Yang, R.T., *Adsorbents: Fundamentals and Applications*, 1st Edn., Wiley, New Jersey, USA (2003).
  30. Vazquez, I., Rodriguez-Iglesias, J., Maranon, E., Castillon, L., and Alvarez, M. “Removal of residual phenols from coke wastewater by adsorption”, *Journal of Hazardous Materials*, **147**, pp. 395-400 (2007).
  31. Gerente, C., Lee, V.K.C., Le Cloirec, P. and McKay, G. “Application of Chitosan for the removal of metals from wastewaters by adsorption-mechanisms and models review”, *Critical Reviews in Environmental Science and Technology*, **37**, pp. 41-127 (2007).
  32. Ho, Y.S. and McKay, G. “Pseudo-second-order model for sorption process”, *Process Biochem.*, **34**, pp. 451-465 (1999).
  33. Chien, S.H. and Clayton, W.R. “Application of Elovich equation to the kinetics of phosphate release and sorption on soils”, *Soil Sci. Soc. Am. J.*, **44**, pp. 265-268 (1980).
  34. Treybal, R.E., *Mass Transfer Operations*, 3rd Edn., McGraw Hill, New York, USA (1981).
  35. McKay, G. and Poots V.J. “Kinetics and diffusion processes in color removal from effluent using wood as an adsorbent”, *J. Chem. Technol. Biotechnol.*, **30**, pp. 279-292 (1980).
  36. Lawrence, M.A.M., Kukkadapu, R.K. and Boyd, S.A. “Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium- and tetramethylphosphonium-exchanged montmorillonite”, *Applied Clay Science*, **13**(1), pp. 13-20 (1998).
  37. Akçay, M. and Akçay, G. “The removal of phenolic compounds from aqueous solutions by organophilic bentonite”, *Journal of Hazardous Materials B*, **113**, pp. 189-193 (2004).
  38. Bhatnagar, A. “Removal of bromophenols from water using industrial wastes as low cost adsorbents”, *Journal of Hazardous Materials*, **139**, pp. 93-102 (2007).

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