

ORIGINAL RESEARCH PAPER

Adsorption of Phenol by Super Hydrophobic Phenol-Formaldehyde/Silica Hybrid Aerogel

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ABSTRACT

Phenol-formaldehyde/silica hybrid gel with hydrophobic character, high porosity, and the small pore size mean was prepared via sol-gel polymerization under solvent saturated vapor atmosphere and was dried by ambient drying method. The silica sols were prepared based on Tetraethoxysilane (TEOS) and Methyltrimethoxysilane (MTES) as hydrophilic and hydrophobic precursors, respectively. Phenol-formaldehyde resin was used as organic phase to achieve suitable physical properties. The contact angle of this aerogel was about 147° and it is a result of formation of CH₃ groups on the pore walls. The results of FESEM and nitrogen adsorption indicated that the structure of this aerogel is highly porous, uniform, and colloid like network. The Phenol-formaldehyde/silica hybrid aerogel was used for removal of phenol from aqueous solution. The study was carried out as functions of contact time, pH and initial phenol concentration. The experiments demonstrated that maximum phenol removal was obtained at neutral pH in unbuffered condition and it takes 40 min to attain equilibrium. Langmuir, Freundlich and Temkin isotherm models were applied to fit adsorption equilibrium data. The best-fitted data was obtained with the Langmuir model and the adsorption capacity was 97.09 mg g⁻¹. Kinetic studies indicated that the adsorption process was described better by pseudo-second-order model.

Keywords: Adsorption; Silica-based aerogel; Equilibrium isotherm; Kinetic; Phenol; Removal.

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INTRODUCTION

Nowadays, phenolic compounds with a wide spectrum of water solubility, high toxicity, high volatility and reactivity are one of the most important water pollutants. The presence of phenol derivatives with different concentrations in the agricultural, pharmaceutical, and petrochemical industry

wastewater leads to a huge environmental and human health hazardous effects [1, 2]. Therefore, phenol derivatives have been listed as priority pollutants by the environmental protection and health Agencies. A lot of researches have been carried out to find and modification of processes to achieve high capacity of phenol removal from wastewaters [1]. The physical, chemical and biological water waste treatments have been applied to removal of phenol derivatives. Adsorption

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technique is an effective conventional physical method for removal of organic compounds from water. This method has a proper effectivity for phenol removal from aqueous solutions in a wide range of phenol concentration [3]. The mechanism of adsorption method is based on the type and magnitude of molecular interactions between adsorbent surface and dissolved adsorbate molecules in the liquid. In the last decades, a huge number of adsorbents and their capacity have been investigated for phenol included wastewater treatment [4]. Activated carbon is the most popular adsorbent for phenol adoption [5]. In despite of high capacity of activated carbon for phenol removal the non-selective chemical structure of these materials induced researchers to synthesis

of novel selective nanostructures. Recently, new porous silica based nanostructures, silica aerogel and xerogels, with ultralow density, high porosity, high Surface area and controllable microstructure and chemical functionality have been interested for selective removal of phenol derivatives, which some of them are summarized in Table 1. According to these researches, the tailoring of silica structure to achievement of various hydrophobicity is related to amphiphilic properties of phenol derivatives. In addition, aerogels with high concentration of hydrophobic surface groups such as CH_3 can control the diffusion of water and phenol derivatives into the aerogel pores and it leads to increasing of organic compounds entering to the porous structure in comparison of water molecules.

Table 1. Summary of properties and performance of silica based aerogel as phenol adsorbent

Adsorbent aerogel	Precursor	S_{BET} (m^2g^{-1})	Contact angle ($^\circ$)	Phenol deriv- ative	Adsorption capacity (removal)Experimental condition	Ref
Hydrophobic silica aerogel	MTMS	512.4	-	phenol	21.1 mg g^{-1} contact time: 1 h	[6]
Hydrophobic silica xerogel	MTMS	426.5	-	phenol	4.9 mg g^{-1} contact time: 1 h	[6]
Hydrophobic silica aerogel	TEOS, TMCS	251-692	-	phenol	142 mg g^{-1} contact time: 25 h	[7]
Silica aerogel	MTMS, TMOS, β -CD	843- 938	35-107	Phenol, p-Cresol, 4-Chlorophenol, SDBS	117.8 mg g^{-1} contact time: 6 h	[8]
Water glass-based silica aerogel	TMCS, sodium silicate	579	143	phenol	38.46 mg g^{-1} contact time: 6 h	[9]
Water glass-based silica aerogel/activated carbon (AC) composite	TMCS, sodium silicate, AC	-	-	phenol	38.46 mg g^{-1} contact time: 6 h	[9]
Silica aerogel	sodium silicate	600-850	143	4-chlorophenol, 4-bromophenol	270.2703 mg g^{-1} contact time: 20 h	[10]
Silica Aerogel-Activated	TMOS, MTMS	916	-	phenol	309.7 mg g^{-1} contact time: 23 h	[11]
Carbon Nanocomposite						
graphene aerogels-mesoporous silica	TEOS, Graphite	1000.80	-	Phenol, Catechol, Resorcinol, Hydroquinone	10.46 mg g^{-1} -	[12]

Recently, the preparation of polymer/silica hybrid aerogels has been attracted due to their unique properties and applications [13, 14]. In addition, Phenol-formaldehyde/silica aerogels with controllable microstructural properties has been synthesized successfully. The combination of polymeric phase through silica network leads to less shrinkage during the ambient drying and helps to prepare an ultralight, hyper porous nanostructure with a lower cost in comparison of supercritical drying [15]. Previously, we investigated the effect of process parameters on the microstructure and properties of phenol-formaldehyde (PF)/silica aerogels. The results showed that the increasing of hydrophobic characters on the pore walls cause to decreasing of surface area and the aerogel structure goes to polymeric hybrid system [16].

In this paper, we investigate the removal capacity and isotherms of phenol removal by a new type of hybrid hyper porous nanostructure, PF/silica aerogels. To obtain the effective amphiphilicity and nanostructure, TEOS, PF resin, and MTES were used as co-precursors for the formation of OH and CH₃ groups. The preparation process was selected according to the best condition that is led to high porosity and surface area with high hydrophobicity properties. The equilibrium and kinetic studies were carried out for investigation of prepared aerogel's ability for phenol adsorption from aqueous solutions.

EXPERIMENTAL

Materials and aerogel preparation method

Phenol-formaldehyde resin (IP 502 Resitan Co. Iran) was used as polymeric thermoset phase. The amount of HMTA (hexamethylenetetramine) as crosslinking agent was 9 wt. % in the PF powder. Tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) (Merck) were used as inorganic precursor and co-precursor, respectively. 2-propanol was purchased from Merck and was used as solvent. Analytical grade of hydrochloric acid (Merck, Germany) was used as hydrolysis catalyst. Preparation of aqueous phenol solutions, analytical grade phenol (99%) was obtained from Merck. The preparation of hydrophobic hybrid aerogel was conducted by the demonstrated method in our previous work [16]. First of all, three solutions of TEOS, MTES, and, were prepared. Hydrophilic silica based sol prepared with mixing of TEOS, 2-propanol, deionized water and HCl. The molar ratio of

TEOS/H₂O/HCl was 1:4:0.00018. Hydrophobic silica based sol was prepared by mixing of MTES, 2-propanol, deionized water and HCl. The molar ratio of MTES/H₂O/HCl was 2.5:1.5:0.0001. Organic sol was prepared by dissolving PF resin in 2-propanol. Then, these three solutions were mixed together at optimum concentration for obtaining 3/1 mass ratio of TEOS and MTES. The solid content in the final mixture was kept at 10 wt. %. After it, the final solution, stirred and was cast into polypropylene mold and placed into an autoclave containing small amount of pure 2-propanol. The sol-gel polymerization was conducted for 20 hours at 120°C. The synthesized gel was dried at ambient conditions and the final aerogel monolith was powder. To remove of impurities, the final powder was washed for two times and was dried.

Adsorbents characterization

Field emission scanning electron microscopy (MIRA3 TESCAN-RMRC) were used to characterization of microstructure and morphology of hybrid aerogel. EDX analysis was used for investigation of the silica fracture on the surface of aerogel. Pore size distribution and specific surface area were measured using the BET adsorption theory and the BJH desorption technique (Belsorp mini II, Japan). Water contact angle was measured with a Data physics OCA 15 plus (Germany) instrument.

Determination of organic compound concentration

The adsorption of phenol from aqueous solutions was carried out at 25°C. In general, 0.03 g of dry PF/silica aerogel pre-washed with distilled water (to eliminate impurities) was added to a 50 mL solution mixture of phenol (20 mg L⁻¹) without pH adjustment and stirred for 40 min at 200 rpm. PF/silica aerogel were simply separated by passing the sample solution through an ordinary filter paper. The pH of the test solutions did not change during the removal experiments and remained nearly constant at about 7. The solution pH was measured by a Metrohm digital pH meter Model 632 (Herisau, Switzerland) using a combined glass electrode. The concentrations of phenol were determined by using a UV-Vis spectrophotometer model Jenway 620 (Stone, UK) using 10 mm path length quartz cell. The concentrations used in the calibration curves were in the range of 1-60 mg L⁻¹ for phenol. The solutions were analyzed by measuring the absorbance at 270 nm.

The percentage of adsorbate removed from the aqueous solution was calculated using Eq. (1), where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium adsorbate concentrations, respectively.

$$R (\%) = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

RESULT AND DISCUSSION

Characterization of the synthesized aerogel

As seen in the FESEM images, the solid phase of PF/silica aerogel is made of spherical particles with a varying size distribution. The distribution of particle size is due to the different chemistry and

mechanism of sol-gel polymerization for organic and inorganic phases (Seraji et al. 2017). The particles with bigger dimensions attributed to the phenol/formaldehyde phase. As shown, the organic phase has been covered with amphiphilic porous silica phase (Fig. 1). In addition, the 3-D network created with nanoparticles, leads to nano order open pores.

The EDX spectrum and element mapping of aerogels (Fig. 2) shows that the silica phase is dispersed in polymeric phase. The same distribution of Si and O in the mapping element shows the hydrophilic silica phase that is attributed to the Si-OH groups.

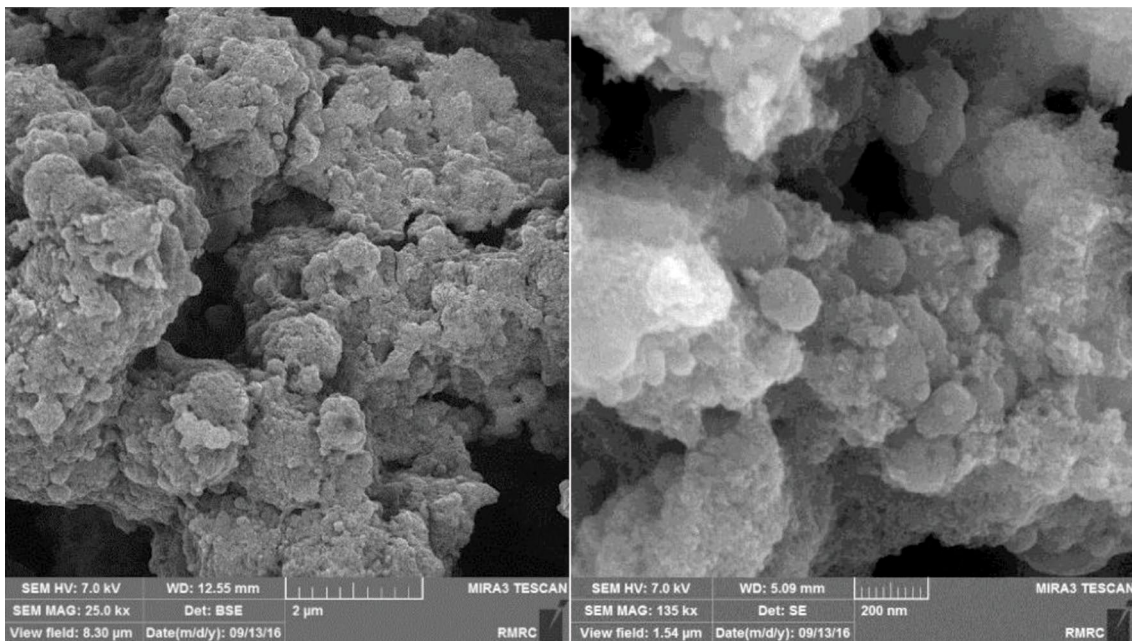


Fig. 1. FESEM micrograph of prepared aerogel.

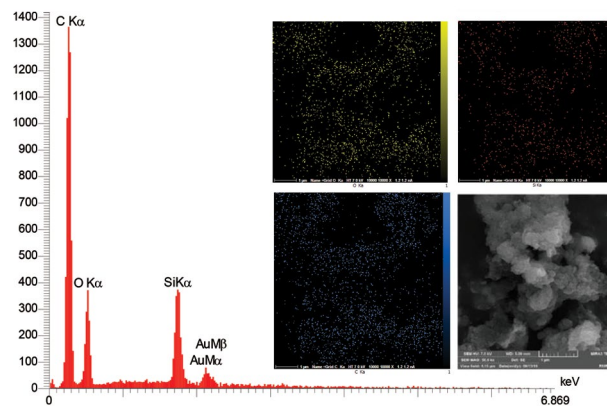


Fig. 2. EDX spectra and element mapping of aerogels.

According to the Fig. 3 the maximum pore size distribution occurs in a range less than 10 nm. The presence of micropores in the aerogel structures lead to formation of adsorption layer on the surface of pore's wall and it can be causes to more phenol removal by occurring of capillary condensation [17]. In despite of presence of micropores in PF/silica hybrid aerogel, one of the most important mechanisms for phenol removal by aerogels is

filling of micropores with size smaller than 1.4 nm.

The Fig. 4 obviously shows that the PF/silica hybrid aerogel is strongly hydrophobic. The contact angle of this aerogel is about 147°. This strong hydrophobicity is due to the fact that the OH groups that formed by TEOS condensation have been replaced end CH₃ groups while [6, 7]. On the other hand, the presence of remained OH groups of silica phase account as hydrophobic characters.

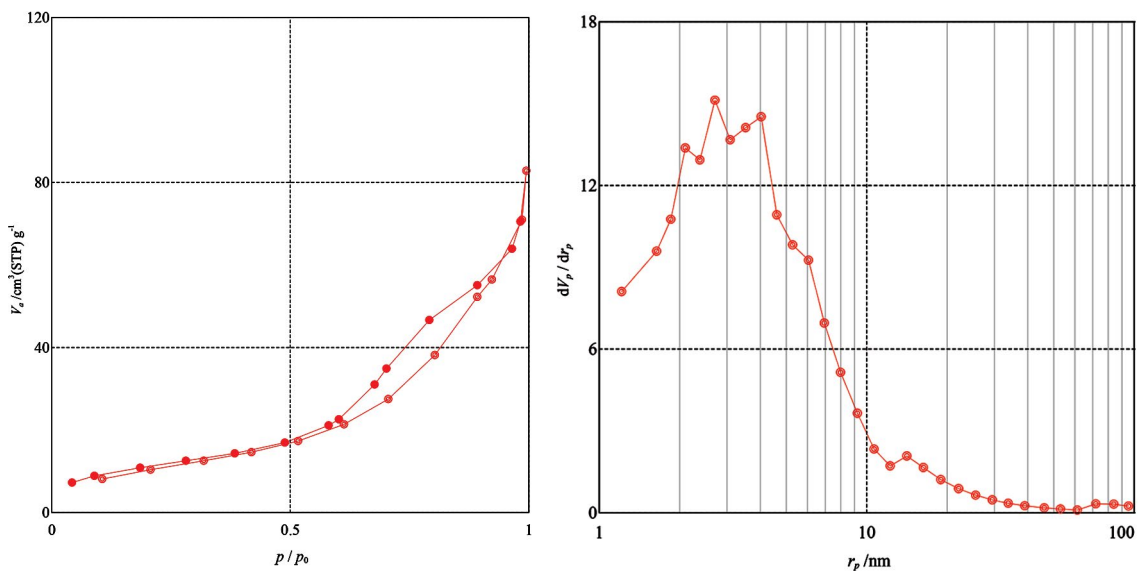


Fig. 3. Pore size distribution obtained by nitrogen gas desorption for prepared aerogel.

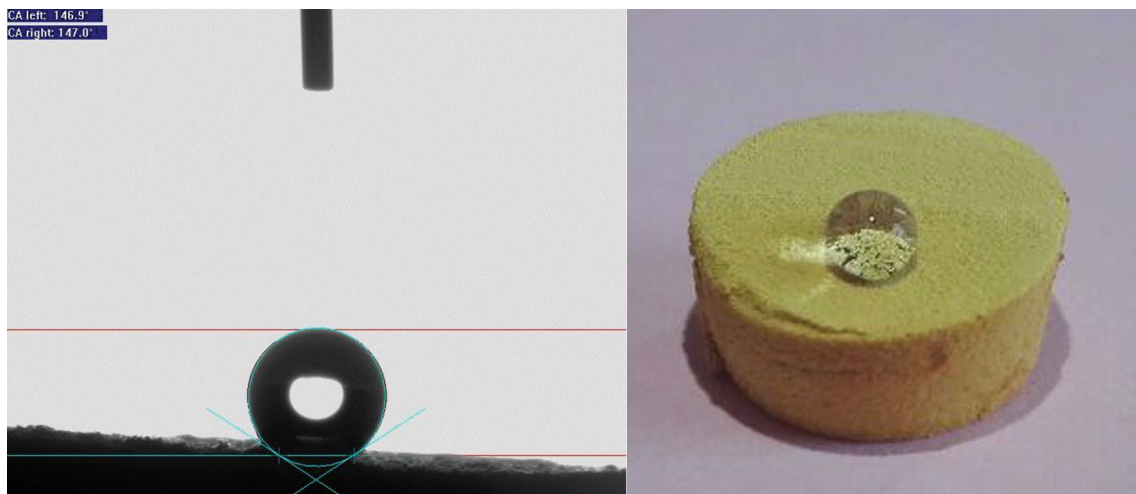


Fig. 4. Water droplet on the monolith surface and the image of contact angle test.

Phenol removal

Effect of pH

The effect of pH on the adsorption of phenol was determined within the pH range of 2-10. The results are represented in Fig. 5. The maximum adsorption was determined at pH 7 that means the adsorption is higher at neutral pH. The optimum adsorption of phenol at pH 7.0 can be attributed to the phenol ionization capacity and point zero charge (pH_{pzc}) of PF/Silicate. The pH_{pzc} for PF/Silicate was obtained about 8.5. While the pH of the solution increases, the percentage of the ionized species increased; this is due to the fact that the pKa value of phenol is about 9.98 [17]. At pH 7.0 ($pH < pK_a$), there is no electrostatic repulsion between the unionized phenol species and the PF/Silicate surface and thus adsorption is higher. Therefore, all the adsorption experiments were carried out in unbuffered condition at neutral pH ($pH \sim 7$) where the highest adsorptions were obtained.

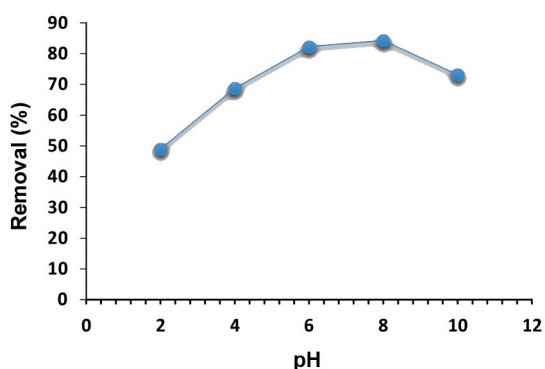


Fig. 5. The effect of pH on phenol removal by 0.03 g of PF/Silicate adsorbent at 25°C.

Effect of contact time

The effect of contact time on the adsorption of phenol was investigated to determine the optimum time. Equilibrium adsorption curves of phenol, were obtained by following the same procedure with different contact time varying between 1 and 90 minutes. The adsorbate uptake (q_e), expressed as adsorbate removal per unit mass of adsorbent ($mg\ g^{-1}$), was calculated according to Eq. (2), where C_0 is the initial adsorbate concentration ($mg\ L^{-1}$), C_e the equilibrium concentration ($mg\ L^{-1}$), V the batch volume (L) and m the adsorbent mass (g).

$$q_e = (C_0 - C_e)V/m \quad (2)$$

As shown in Fig 6, the amount of phenol adsorbed increases with contact time and attains equilibrium at about 40 min for same initial concentrations.

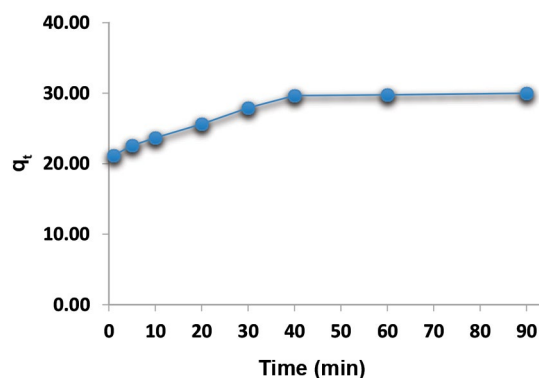


Fig. 6. The effect of time on the removal of phenol by 0.03 g of PF/Silica adsorbent at pH 7 and 25°C.

Effect of initial phenol concentration

The effect of initial phenol concentration on the removal of phenol was investigated by following the same procedure with different concentration varying between 5 and 60 $mg\ L^{-1}$. The adsorption of phenol on PF/Silica decreases with increase in the phenol concentration, indicating that the adsorption is dependent upon the availability of the binding site (Fig. 7). That means once adsorbate bind with the active site of adsorbent, the active site of PF/Silica is blocked. There is no further adsorption takes place to increase in concentration of phenol. Fig. 8 showed the decrease in adsorption with increase in the phenol concentration in the range 5-60 $mg\ L^{-1}$.

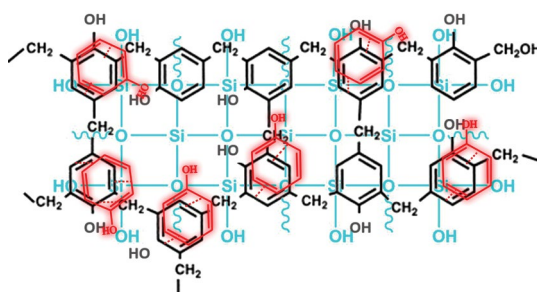


Fig. 7. Schematic representation of adsorption of phenol on PF/Silica adsorbent. (Black: Novolac, cyan: Silica, and red: Phenol).

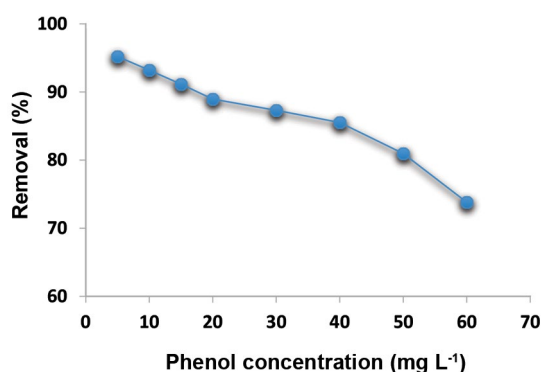


Fig. 8. The effect of initial phenol concentration at pH 7 and temperature: 25°C.

Adsorption isotherms

Equilibrium parameters and adsorption properties of each isotherm model give useful information about the nature of interaction and indicate the interaction of adsorbent-adsorbate. For describing of relationship between the amount of phenol adsorbed on the PF/Silica and the phenol concentration; we need to use isotherms. The adsorption phenomena at the adsorbent surface are commonly described by Langmuir, Freundlich and Temkin isotherms [18-21]. The Langmuir is the main monolayer adsorption model that its linear form is written as Eq. (3):

$$C_e/q_e = 1/(K_L q_m) + C_e/q_m \tag{3}$$

Where q_e is the equilibrium adsorption amount of phenol (mg g^{-1}), C_e is the equilibrium phenol concentration in the solution ($\mu\text{g mL}^{-1}$), q_m is the maximum adsorption amount of phenol per gram of adsorbent (mg g^{-1}), and K_L is the Langmuir adsorption equilibrium constant (L mg^{-1}). The correlation coefficient was found to be 0.9967. The Freundlich isotherm is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as Eq. (4):

$$q_e = kC_e^{1/n} \tag{4}$$

The equation may be linearized by taking the logarithm of both sides of Eq. (4) and linear form of Freundlich isotherm can be given as Eq. (5):

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{5}$$

Where C_e is equilibrium concentration, q_e designates the amount of phenol adsorbed at equilibrium in mg g^{-1} , K_F is the sorption capacity (mg g^{-1}) and n is an empirical parameter. Adsorption data were also correlated with Freundlich model and a curve of $\ln q_e$ vs. $\ln C_e$ was constructed. The Temkin isotherm describes the adsorption behavior on heterogeneous surfaces and is expressed by a linear Eq.

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{6}$$

Where $B_T = RT/b_T$, T is the absolute temperature in 298K and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K_T is the equilibrium binding constant (L mg^{-1}) and B_T is related to the heat of adsorption. The values of the constants for isotherms were obtained from the slope and intercept of the curves of Langmuir, Freundlich, and Temkin isotherms have been shown in figs 9, 10, and 11, respectively.

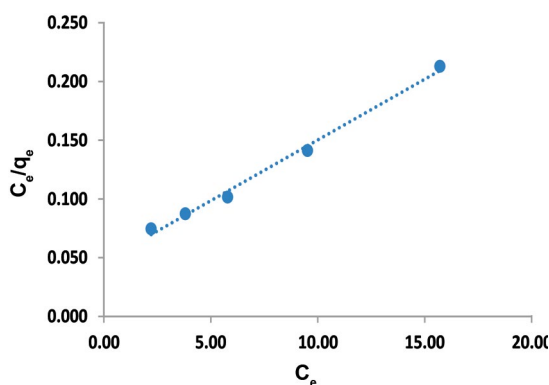


Fig. 9. The Langmuir isotherm plot for phenol adsorption on PF/Silica adsorbent. Amount of adsorbent: 0.03 g, pH 7, agitation speed: 200 rpm and temperature: 25°C.

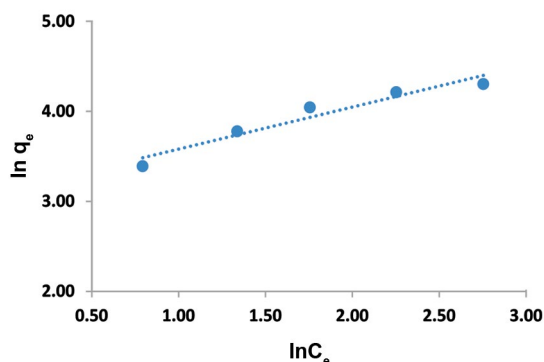


Fig. 10. The Freundlich isotherm plot for phenol adsorption on PF/Silica adsorbent. Amount of adsorbent: 0.03 g, pH 7, agitation speed: 200 rpm and temperature: 25°C.

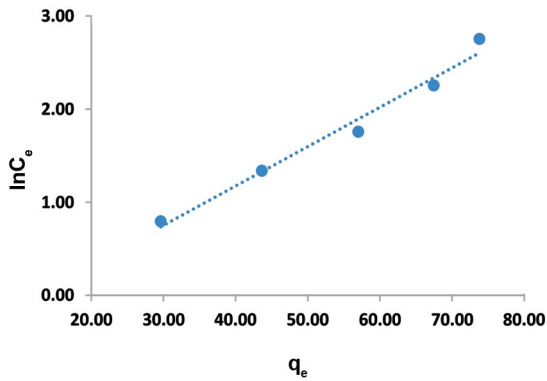


Fig. 11. The Temkin isotherm plot for phenol adsorption on PF/Silica adsorbent. Amount of adsorbent: 0.03, pH 7, agitation speed: 200 rpm and temperature: 25°C.

The calculated constant values of the Langmuir, Freundlich, and Temkin isotherms along with their correlation coefficients are given in Table 2.

Kinetics of adsorption

The kinetic models were used to predict the variation of adsorbed phenol with time using PF/Silica. The rate constants of chemical adsorption were determined using the equations of the pseudo-first-order and pseudo-second-order models. Among procedures for the adsorption of a solute from aqueous solution, Pseudo-first-order model

is one of the most widely used. The pseudo-first-order kinetic model of Lagergren can be given as Eq. (6):

$$\log(q_e - q_t) = \log q_e - (K_1 t)/2.303 \tag{7}$$

Where q_e and q_t are the amounts of phenol adsorbed onto PF/Silica (mg g^{-1}) at equilibrium and at time t , respectively, and K_1 ($1/\text{min}$) is first-order rate constant for adsorption. The rate constant, K_1 , can be calculated from the plots of $\log(q_e - q_t)$ vs. t . Pseudo-second-order kinetics may be expressed as Eq. (7):

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{8}$$

Where k_2 is the rate constant of the second-order adsorption ($\text{g mg}^{-1} \text{min}$). The straight-line plots of t/q_t against t have been tested to obtain rate parameters. The pseudo-first-order and pseudo-second-order kinetic models for phenol removal by PF/Silica were investigated using the above equations. The results indicate that the adsorption of phenol on PF/Silica is not fitted to a first-order model. However, the correlation coefficients for the second-order kinetic model were higher than 0.99 indicating the applicability of this kinetic model with the adsorption process of phenol on PF/Silica adsorbent.

Table 2. Summary of properties and performance of silica based aerogel as phenol adsorbent

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_m (mg g^{-1})	K_L (L mg^{-1})	R	K_f (mg g^{-1})	N	r	B_T (J mol^{-1})	K_T (L g^{-1})	r
97.09	0.22	0.9967	22.51	0.233	0.9682	23.64	1.68	0.9889

It was observed that the experimental data are better fitted with the Langmuir isotherm ($r=0.9959$) for the adsorption of phenol on the PF/Silica.

Table 3. Kinetic parameters for the adsorption of phenol on PF/Silica adsorbent

C_0 (mg L^{-1})	Pseudo-first-order equation			Pseudo- second-order equation		
	K_1 (10^{-3} min^{-1})	q_e (mg g^{-1})	R^2	K_2 ($10^{-2} \text{ min}^{-1} \text{ g mg}^{-1}$)	q_e (mg g^{-1})	R^2
20	0.052	9.57	0.962	0.03	28.25	0.9951

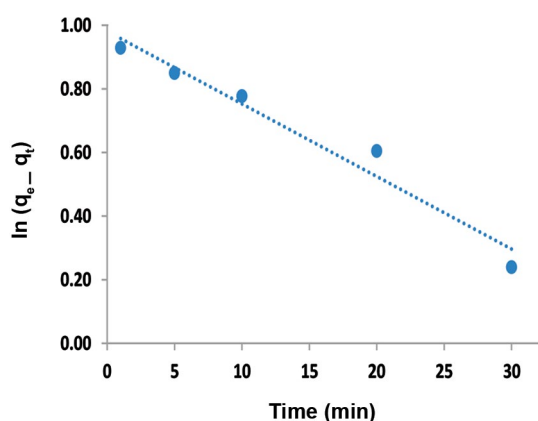


Fig. 12. Representative plot of the fit of linearized forms of pseudo-first-order equation to experimental adsorbed amounts of phenol on PF/Silica.

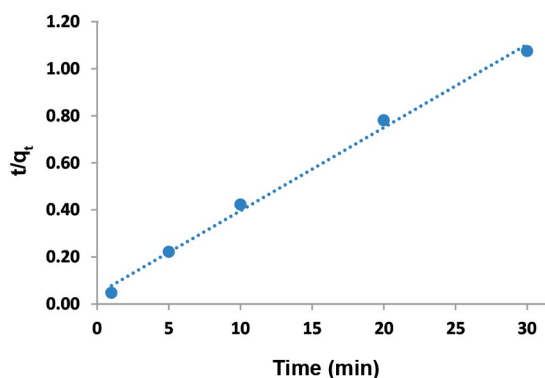


Fig. 13. Representative plot of the fit of linearized forms of pseudo-second-order equation to experimental adsorbed amounts of phenol on PF/Silica.

CONCLUSION

The super hydrophobic PF/silica hybrid aerogel prepared in this work indicate mesoporous structures, high surface area, and high level of hydrophobicity. Adsorption studies of phenol under different experimental conditions on PF/silica adsorbent have been undertaken. The percentage phenol removal is maximal at pH value of around 7, therefore, all the adsorption experiments were carried out at neutral pH in unbuffered condition. Adsorption kinetic by PF/silica adsorbent follows pseudo-second-order kinetic and interparticle diffusion model. The equilibrium data are analyzed using Langmuir, Freundlich and Temkin isotherm equations. The result shows that the experimental data are best correlated by Langmuir isotherm on PF/silica adsorbent.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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