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RESEARCH ARTICLE

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Aminoantipyrine Functionalized Mesoporous Silica: An Effective Sorbent for Removing Phenolic Compounds from Aqueous Medium

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Abstract : Phenolic compounds are among the most hazardous pollutants in industrial effluents, posing severe risks to both aquatic ecosystems and human health due to their carcinogenic properties. Their removal from water sources is thus a critical environmental challenge. Adsorption is widely recognized as an efficient technique for eliminating such contaminants. In this study, mesoporous silica functionalized with aminoantipyrine (Aminoantipyrine-MCM-41) was investigated as a potential adsorbent for the removal of phenolic compounds from aqueous solutions. The synthesized material exhibited a significant adsorption capacity of 104.4 mg g^{-1} for phenol. Adsorption kinetics followed the pseudo-second-order model, indicating that chemisorption was the rate-limiting step, while equilibrium data were best described by the Langmuir isotherm model, suggesting monolayer adsorption on a homogenous surface. The high adsorption efficiency, coupled with excellent selectivity for phenolic compounds, was further validated by testing the adsorbent in real environmental samples, including wastewater and groundwater. The results demonstrated that Aminoantipyrine-MCM-41 is a highly effective material for removing phenolic pollutants and holds promise for practical applications in water purification processes.

Keywords: Phenolic Compounds, Aminoantipyrine, Mesoporous Silica, Adsorption Kinetics, Water Purification.

1.Introduction

Organic substances with a hydroxyl group joined to one or more aromatic rings are known as phenolic compounds. The primary component of their structure is benzene ring with a -OH group attached. Phenols are a broad class of chemicals with this base structure (Fig. 1). The U.S. EPA and the European Union (EU) both classify these substances as persistent organic pollutants (POPs) due to their strong affinity for water [1]. Water contains phenols as a result of both natural and man-made processes.

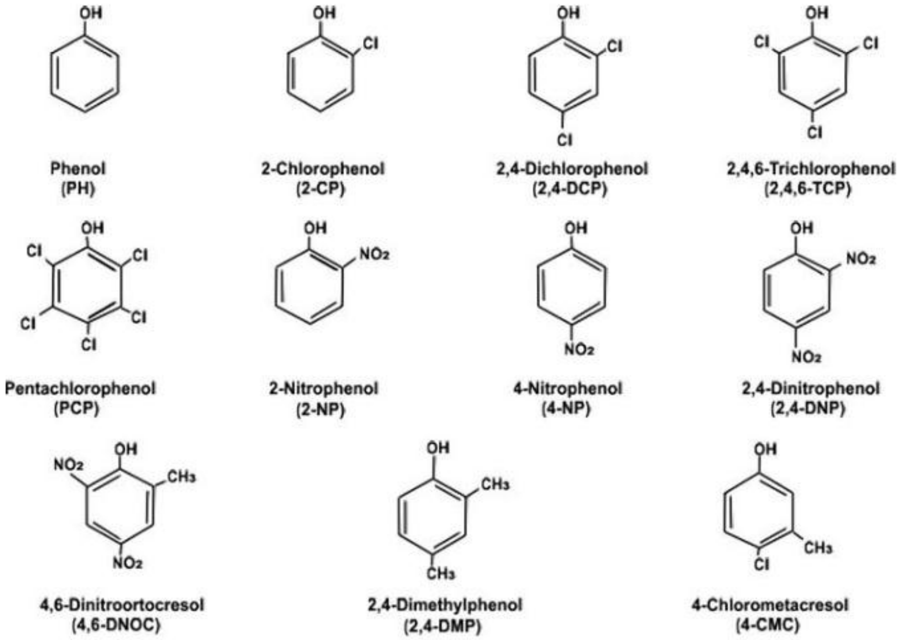


Figure 1. Phenolic compounds structures can be found in water [2].

Phenols that are typically found in nature as a result of the breakdown of polyphenols, which are primarily produced by plants and serve as antioxidants. Apart from their role as antioxidants, phenolic compounds have numerous other uses for people. The primary issue with phenolic chemicals is that they bioaccumulate in our water sources as a result of the fecundity of aquatic life. This deterioration may be brought on by the naturally occurring acids in water or by direct sun exposure. [3-5].

One source of phenolic chemicals in water that take the form of polymers is industrial phenol [6]. Devices and coatings for certain items are typically made using phenolic polymers [7]. Consequently, industrial phenols contaminated water sources either directly or indirectly by wastewater discharge, herbicide and insecticide application, or polymer breakdown in water [8].

Owing to the harmful effects of phenols, stringent regulations that restrict the presence of phenolic compounds in drinking water, and the difficulty of removing, recovering, or quantifying phenolic chemicals[2]. It was discovered that the best method for removing phenol from water was solid phase extraction (SPE) [4]. Because of their high surface area and large pore volume, silica-based sorbents like SBA-15 and MCM-41 are well-known for their exceptional ability to extract phenolic compounds. Mesoporous materials are also very easy to purchase and affordable [9, 10].

This study assessed the capability of aminoantipyrine–MCM-41 to remove phenolic compounds from the water and pHs influence on the extraction efficiency was evaluated. The linearized Langmuir and Freundlich equations were used to fit the equilibrium isotherms. Kinetic data were analysed by pseudo-first, pseudo-second to obtain the kinetic constants. These data contribute to the understanding of mechanisms involved in mesoporous silica and provide some practical clues to improve the adsorption efficiency (uptake capacity and kinetics) of phenolic compounds from water Samples. The selectivity of phenolic compound extraction by this sorbent was evaluated by using apply this method in real samples, particularly, from wastewater and groundwater was studied.

2. Experimental

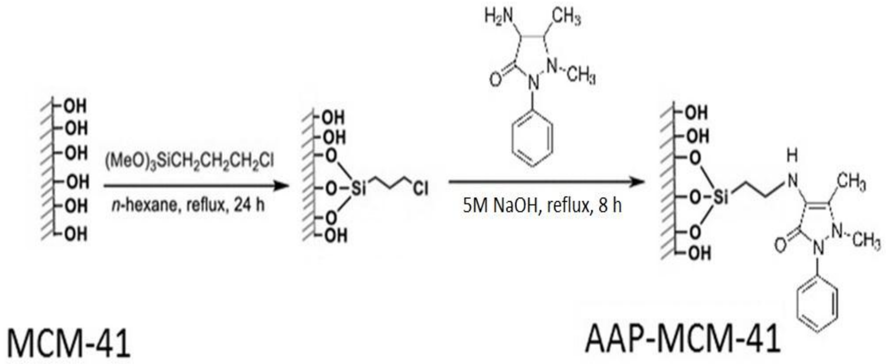
2.1. Materials and reagent

Cetyltrimethylammonium bromide (CTAB), 98%, was supplied by BDH. Aqueous ammonia (30% NH_3), 4-Aminoantipyrene (98%) was purchased from Acros Organic, USA, Ammonium Chloride was purchased from Altay Scientific, Italy, Ammonium Hydroxide (25%) was purchased from Riedel Dean, Germany, Potassium ferricyanide (99%) was purchased from BDH, England, Phenol (Pure) was purchased from Alpha Co., India, Sodium hydroxide (96%) was purchased from ADWIC, Egypt, Hydrochloric Acid (36-38%) was purchased from Hamilton Co., Newzland. Glassware was soaked in 5% HNO_3 overnight and cleaned with deionised water before use. All products were used as supplied and deionised water was used throughout this work.

2.2. Mesoporous silica preparations and functionalisation

The synthesis method and functionalization MCM-41 was prepared according to the method reported in ref [10]. Approximately 10 g of CTAB was dissolved under slight warming (35 °C) in a mixture of 250 mL of distilled H_2O and 100 mL of aqueous NH_3. To this clear solution, 50 mL of TEOS was slowly added under stirring. After further stirring for 4 h, the gel was aged at room temperature for 48 h in a closed container. The product was obtained by filtration, washed with 800 mL of distilled H_2O, and dried in air at room temperature. To remove the surfactant microwave digestion (MWD) was performed by using a MARS 5 microwave digestion system (CEM Corporation, Buckingham, UK) was used at an operating power of approximately 1600 W. The pressure and temperature inside the microwave were controlled to be lower than 1.3 MPa and 200 ^{o}C, respectively. Samples (approx. 0.1 g) were added to multiple Teflon vessels to which 1.5 mL of HNO_3 and 0.70 mL of H_2O_2 were added. Microwave digestion was operated at a working frequency of 2450 MHz and 220 V for 15 min. The product (MCM-41) was filtered, washed with copious amounts of distilled H_2O and dried at 100 ^{o}C for 2 h. .

Surface modification of MCM-41 was carried out by grafting method using 3-Chloropropyltrimethoxysilane in n-hexane and refluxing for 24 h to produce chloro-functionalized MCM-41 (Cl-MCM-41). Then, approximately 10 g of Cl-MCM-41 was immersed in 80 cm^3 of distilled water and 2 g of 4-Aminoantipyrene and 2 cm^3 of 5M NaOH were added, in a 250 cm^3 flask. The mixture was refluxed for 8 h and the solid produced was filtered, washed with 100 cm^3 ethanol, and oven-dried at 80 ^{o} C for 8 h to produce a AAP-MCM-41 sorbent (scheme 1).



Scheme 1. Functionalisation of MCM-41 by 4-Aminoantipyrene

2.3 Characterisation and Analysis

Powder X-ray diffraction (PXRD) profiles were recorded on a Philips X'Pert diffractometer, equipped with a Cu Kα radiation source and accelerator detector. Incident and reflected Stöller slits of 0.2 ° were used with a programmable divergent slit (a constant 10 mm sample footprint). The surface area of the microwave digestion and calcined mesoporous silicas were measured using nitrogen physisorption isotherms on a Micromeritics Gemini 2375 volumetric analyser. Each sample was degassed prior to analysis for 6 h at 200 ° C. The Brumauer– Emmett–Teller (BET) surface areas were calculated using experimental points at a relative pressure (P/P_0) of 0.05–0.25. The total pore volume was calculated from the N_2 amount adsorbed at the P/P_0 of 0.99 for each sample and the average pore size distribution of the materials was calculated using the Barrett–Joyner–Halanda (BJH) model from a 30-point BET surface area plot. All the mesoporous silicas exhibited a Type IV adsorption isotherm typical of mesoporous solids. Desorption isotherms were used to calculate the pore diameters. Infrared spectra of all samples were obtained in KBr pellets in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 64 scans using an ATI Mattson FTIR spectrophotometer.

Analysis of phenol in water samples were conducted according ASTM Standards D 1783-70 [11]. Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown coloured antipyrine dye. The amount of colour produced is a function of the concentration of phenolic material. Briefly, 50 µL buffer solution (17 g NH_4Cl in 150 mL conc. NH_4OH and dilute to 250 cm^3 with distilled water) to 1 cm^3 of standard or water sample o adjust the pH to 10. Then add 50 µL 4-aminoantipyrine solution (2 g of 4AAP in in 100 cm^3 distilled water) and finally add 50 µL potassium ferricyanide solution (8 g of $K_3Fe(CN)_6$ in 100 cm^3 distilled water), after 15 minutes read absorbance at 510 nm. The concentration of phenol or phenolic compound in water can be obtained directly from standard curve by plotting the absorbance value of standards (0.5, 1.0, 5 and 10 µg cm^{-3}) versus the corresponding phenol concentrations. The UV-Vis Spectrophotometer used in this work is Lovibond Spectro-Direct single-beam spectrophotometer.

2.4.Effect of pH and Adsorption process

Effect of pH for phenolic compounds extraction was examined at various pH values (3, 5, 7 and 9) with solution modification achieved via the addition of small amounts of 1M sodium hydroxide.

2.5Adsorption isotherms

To study the adsorption isotherms, Langmuir [12] or Freundlich [13] models were used to determine type of adsorption and eventually information about adsorption capacity. Solutions have 10, 50, 100 or 200 µg cm^{-3} of phenol in water was used as initial concentrations. 0.10 g of AAP-MCM-41 was added and stirred at 250 rpm for 40 min at pH of 3, then the solution was removed and analysed for phenol by UV-Vis Spectrophotometer. The experimental q_e (mg/g) were calculated using Eq. (1):

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

where C_0 and C_e (mg/g) were the initial and equilibrium concentrations of the Phenol respectively. V is the volume of the solution (cm^3), and W is the mass of sorbent (g). Langmuir Eq. (2) and Freundlich Eq. (3) isotherm models [14] were determined according to these equations.

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right) C_e \tag{2}$$

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

where q_m in Eq. 1 and K_f in Eq. 2 (mg/g) are the theoretical maximum adsorption capacity [15, 16].

2.6.Adsorption kinetics study

6 Solutions were prepared to study kinetic were prepared with the same initial Phenol concentration of 200 µg cm^{-3} and each one stirred with 0.10 g AAP-MCM-41 at 250 rpm. After each time period (1, 5, 10, 20, 30 or 40 min), one of solutions at a time was filtered and analyzed by spectrophotometer to determine remained Phenol in solution.

The pseudo first-order equation (Eq.1) [17], The pseudo second-order equation (Eq.2) [18] were used for kinetic study:

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t \tag{4}$$

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_1 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_e and q_t are the adsorption capacity (mg g^{-1}), at equilibrium and at time t, respectively, k_1 is the rate constant of pseudo first-order adsorption (L min^{-1}).

2.7.Extraction of phenolic compounds from real samples

To examine the efficiency of the APP-MCM-41 for real application and environment, 0.1 g from sorbent was added to three different ground water samples which found polluted by phenolic compounds and sample of wastewater. Solutions were stirred at 25 ° C and pH 3, for 40 min. After time period, solutions were filtered and analyzed by spectrophotometer to determine the concentration of Phenolic compounds in solution.

3. Results and discussion

3.1. MCM-41 characterisation by XRD and N2 adsorption isotherm

XRD patterns of AAP-MCM-41 and MCM-41 samples, shown in Fig. 2, indicated that the adsorbent materials possessed a hexagonal mesophase structure with a clear (1 0 0) peak and weaker reflections assignable to (1 1 0) and (2 0 0) reflections with weaker peaks in AAP-MCM-41 due to functionalisation.

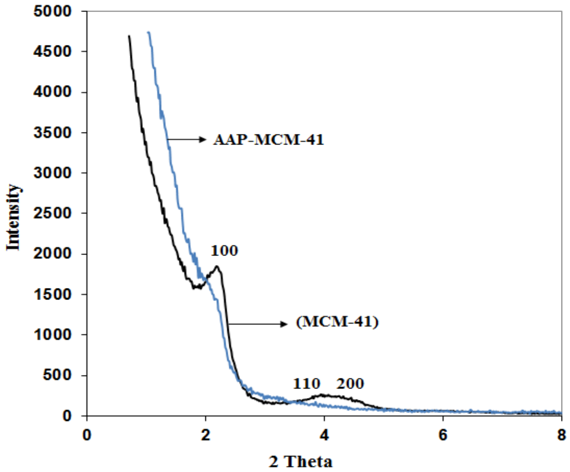


Figure 2. XRD Patterns of MCM-41, AAP-MCM-41.

The physicochemical properties of the materials are summarized in Table 1 and indicate that the surface area of MCM-41 reduced slightly for functionalised material compared to original MCM-41 that because the surface was occupied by functional groups.

Table 1. Physicochemical properties of MCM-41 and AAP- MCM-41.

Sample Name	BET Surface Area (m^2 g^{-1})[a]	Pore Size (nm)[b]	Pore Volume (cm^3 g^{-1})[c]
MCM-41	760	6.74	0.99
AAP-MCM-41	430	4.39	0.69

[a] Calculated by the linear BET equation from sorption data in a relative pressure range from 0.05–0.25.

[b] Calculated by the BJH model from the adsorption branches of isotherms.

[c] Calculated from N_2 amount adsorbed at a relative pressure P/P_0 of 0.99.

The N_2 sorption isotherms (Fig. 3) were type IV confirming their mesoporous nature, however slightly different capillary condensation steps were noted at relative pressures of 0.31–0.38 and 0.55-0.69 for the MCM41and AAP-MCM-41products, respectively, suggesting that the MCM41 lost some volume due to occupation by functional groups. This was confirmed by examination of the pore distribution plots (top left in Fig. 3). These results for MCM-41 with larger mesopores (or even mesotunnels) in an adsorbent material would be highly desirable if it were to be surface functionalised and used to provide a higher number of chelating groups that could extract phenolic compounds from a contaminated matrix.

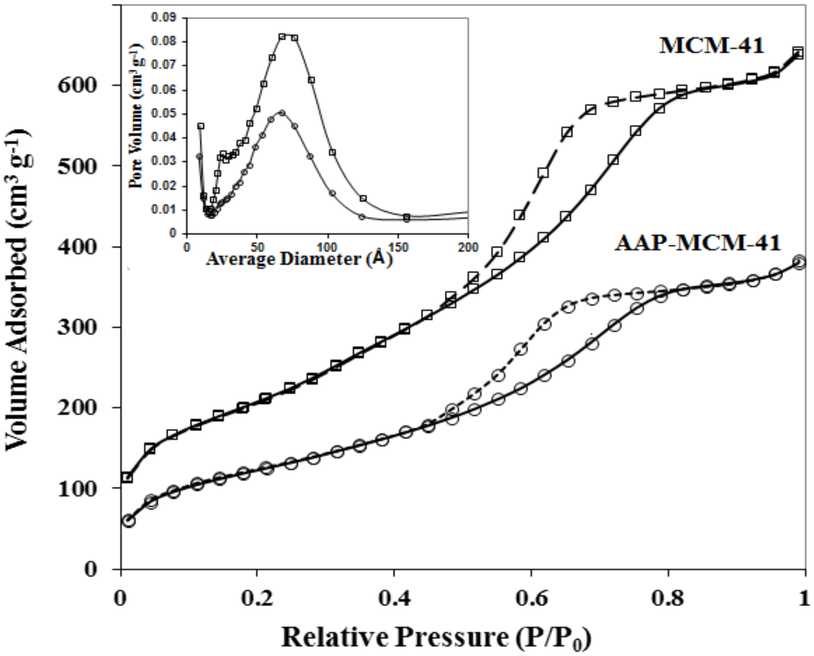


Figure 3. N_2 adsorption isotherms of MCM-41, AAP-MCM-41.

The FTIR spectra of for both MCM-41 and AAP-MCM-41 (Fig 4) contain similar features expected of a silica containing material associated with the inorganic backbone such as (i) a large broad band between 3500 and 3200 cm^{-1} which is assigned to the O–H stretching mode of silanol groups and also to some adsorbed water, (ii) several absorption bands at around 1030-1240 cm^{-1} which can be assigned to the Si–O–Si stretching and (iii) the water bending mode band around 1650 cm^{-1} [25]. In addition to those peaks the spectrum of AAP-MCM-41 showed extra bands at 2850 and 2930 cm^{-1} which behalf to amino groups confirmed successes functionalisation.

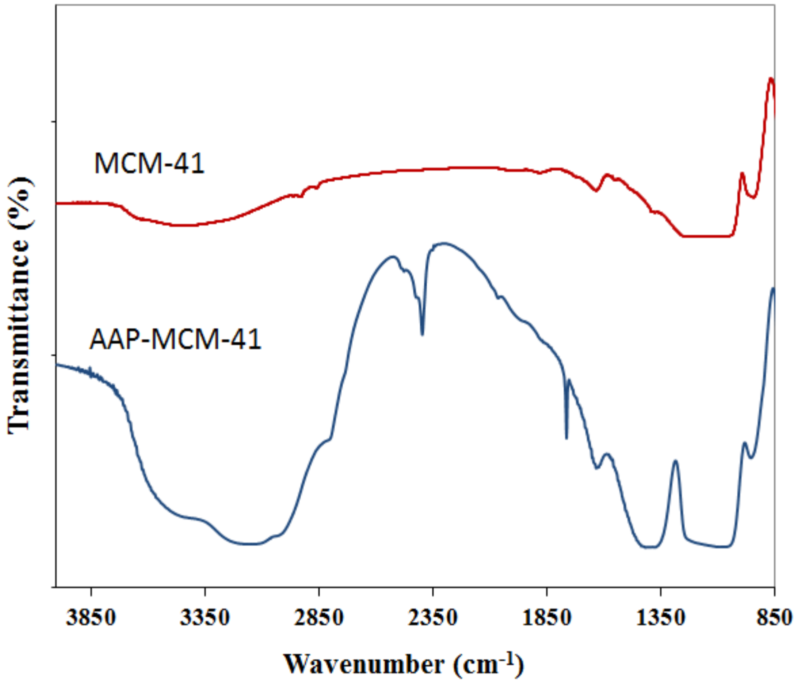


Figure 4. FTIR spectra of MCM-41 and AAP-MCM-41

3.2 Effect of pH on Phenolic compounds adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption processes.

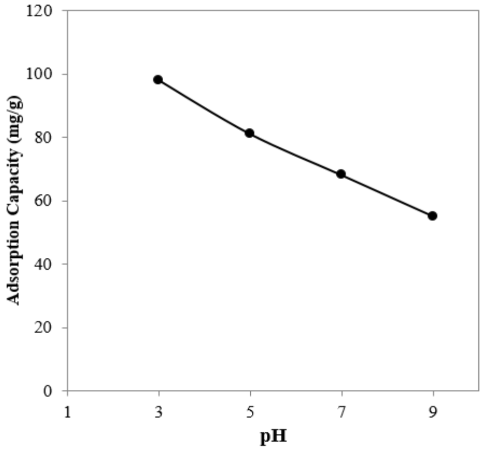
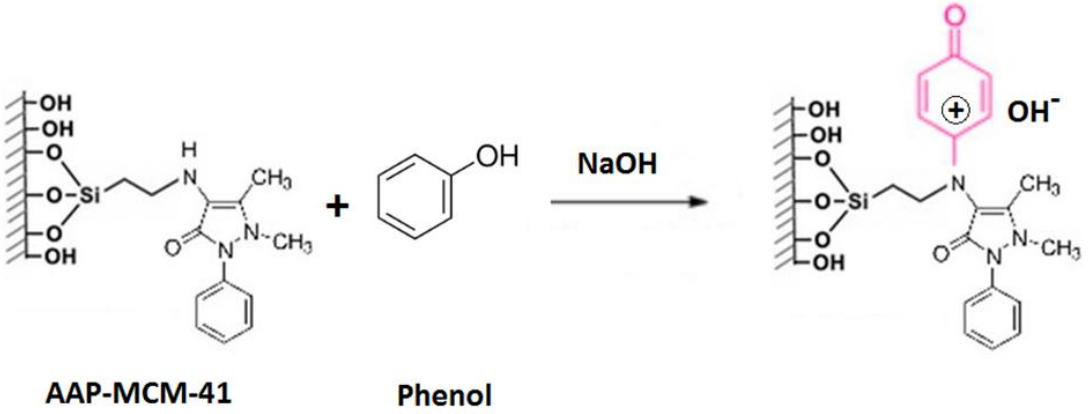


Figure 5. Adsorption capacities of functionalised MCM-41 for Phenolic compounds extraction over different pH values.

Fig. 5 shows that the number of Phenolic compounds adsorbed on AAP-MCM-41 increases with decreasing the pH. This phenomenon appears to be due to the fact that functional group in the surface of mesoporous silica were more active in present of hydrogen in the secondary amine which is the active site to attract phenolic compounds from aqueous media as shown in scheme 2.



Scheme 2. The mechanism of extraction phenolic compounds from aqueous media.

Thus, at higher pH values the OH^- ions compete with Phenolic compounds for the exchange sites in AAP-MCM-41 leading to a low removal of the Phenolic compounds.

3.3 Adsorption isotherms

The adsorption isotherms were studied to find the relationship between equilibrium adsorption capacity and equilibrium concentration at a certain temperature. Langmuir and Freundlich isotherms are the most commonly used isotherms for different adsorbent/adsorbate systems to explain solid-liquid adsorption systems and to predict their equilibrium parameters [19-21].

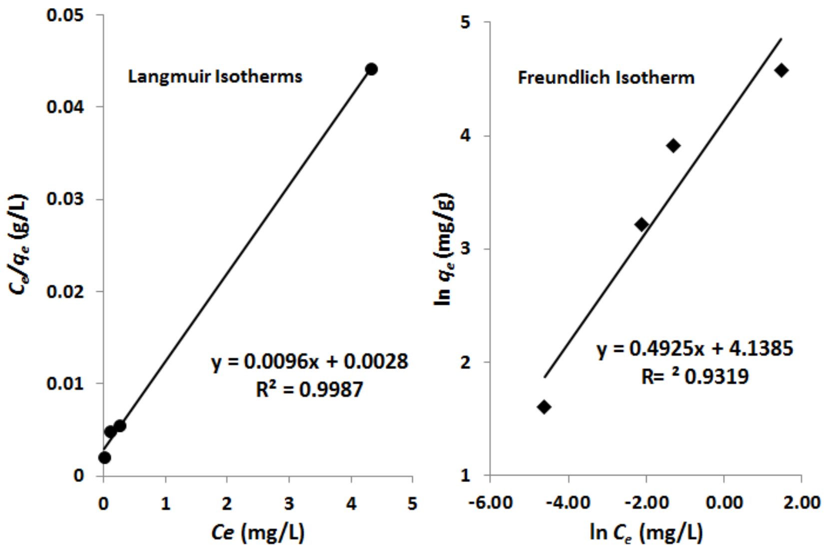


Figure 6. Langmuir and Freundlich isotherms for Phenolic compounds sorption on functionalized mesoporous silica.

Langmuir and Freundlich isotherms (Fig.6) showed that the R^2 values obtained from the Langmuir model are much closer to one than are those from the Freundlich model, suggesting that the adsorption can be described by the Langmuir isotherm and the phenolic compounds adsorption occurs on a homogeneous surface by monolayer sorption with adsorption capacity reached 104.4 mg/g [22]. The relevant parameters for these isotherms are presented in table 2.

Table 2. Isotherm parameters for Phenolic compounds sorption on functionalized mesoporous silica.

Adsorbents	Langmuir				Freundlich		
	q_m(mg/g)	b(L/mg)	R_L	R^2	K_f(mg/g)	n(L/mg)	R^2
AAP-MCM-41	104.4	3.43	0.74	0.9987	31.6	2.0	0.9319

3.4 Adsorption kinetics

The experimental kinetic data were fitted using a pseudo-first -order kinetic model and pseudo-second-order kinetic model. The results are shown in Fig. 7.

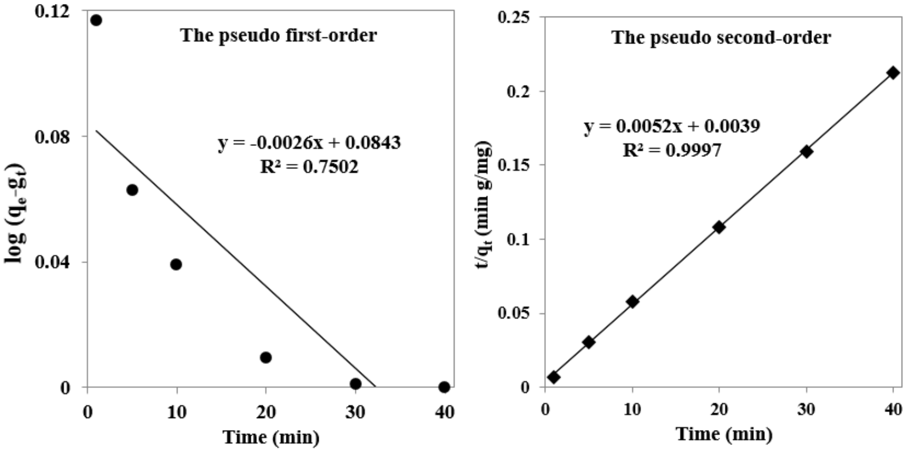


Figure 7. A pseudo-first-order and pseudo-second-order kinetic models for adsorption of phenolic compounds from water.

From table 3 the obtained R^2 values of the pseudo-second-order model (0.9997) were better than the pseudo-first – order model (0.7502) for AAP-MCM-41 adsorbents, suggesting that the adsorption process is second-order. Moreover, the calculated q_e values were much closer to the experimental values in the pseudo-second-order kinetic model than the pseudo-first -order kinetic model indicating that the adsorption process is second-order and it was clear from the rate of reaction (0.005 min^{-1}) that the available active sites on the adsorbents are saturated rapidly by phenolic compounds and the adsorption process was depends on both phenolic compounds present in solution and active sites available on the sorbent surface.

Table 3. Kinetic parameters for the adsorption of phenol on the AAP-MCM-41.

Adsorbents	q_e (exp) (mg/g)	k_1 (min^{-1})	q_e (cal) (mg/g)	R^2
The pseudo first-order	88.45	0.015	1.62	0.7066
The pseudo second-order		0.005	92.93	0.9984

3.5 Adsorption of phenolic compounds from real samples

To study the performance of AAP-MCM-41 in real samples application, two types of samples were used in this study:

1)Ground water (Three different samples).

2) Sewage water (one sample).

Table 4. Efficiency of AAP-MCM-41 for extraction phenolic compounds from real samples

No.	Type of sample	Concentration of phenolic compound in sample before extraction (μg/mL)	Concentration of phenolic compound in sample After extraction (μg/mL)
1	Ground water 1	0.152	ND*
2	Ground water 2	0.127	ND*
3	Ground water 3	0.166	ND*
4	Wastewater	5.24	ND*

*ND=Not detected (limit of detection (0.011)

The results showed in table 4. It was clear that the sorbent used showed excellent performance toward elective extraction of phenolic compounds from real samples even with those type of samples contain lots of different ions may compete the phenolic compounds to occupied the active cites on the sorbent.

3.6 Comparison with other adsorbents

The value of q_e (mg/g) is useful in identifying the sorbent with the highest adsorption capacity when considering scale-up. Table 5 compares the adsorption capabilities of several adsorbents for removing phenolic compounds from water samples.

Table 5. Comparison of adsorption capacity of phenolic compounds onto some adsorbents.

No.	Adsorbent	q_e (mg/g)	Reference
1	NH_2–activated silica	12	[23]
2	NH_2–SBA-15	30.0	[24]
3	NH_2–SBA-15	72.1	[25]
4	N,N-dimethyldodecylamine-MCM-41	88	[26]
5	Aminoantipyrine-MCM-41	104.4	This work

4. Conclusions

In this work, AAP-MCM-41 was prepared, and its ability to adsorb phenolic compounds from aqueous medium was examined. The adsorption capability of phenolic compounds showed considerable pH dependence, with pH 3 yielding the highest findings. The maximum adsorption capacity of phenolic compounds was 104.4 mg/g, and the equilibrium data fit the Langmuir sorption isotherms. The fact that the adsorption date fit the Langmuir model suggests that monolayer sorption takes place on a homogeneous surface during adsorption, with no interaction amongst the adsorbed phenolic compounds. A pseudo-second-order kinetic model was better to describe the process than pseudo-first-order kinetic model with rate constant (k) 0.005 min^{-1} suggesting that phenolic compounds quickly saturate the available active sites on the adsorbents, and that the adsorption process depends on both the presence of phenolic compounds in solution and the active sites that are available on the sorbent surface. The effectiveness of this sorbent was tested in actual samples, such as groundwater and wastewater, and the findings verified that it could be used to remove phenolic chemicals from a variety of water sources.

Reference

[1] M. Jahandar Lashaki, A. Sayari, Chemical Engineering Journal, 334 (2018) 1260-1269.
[2] E. Ramírez, M. Asunción, V. Rivalcoba, A. Hernández, C.Santos, Removal of Phenolic Compounds from Water by Adsorption and Photocatalysis, in, IntechOpen, Rijeka, 2017.
[3] A. Tanimu, S.M.S. Jillani, A.A. Alluhaidan, S.A. Ganiyu, K. Alhooshani, Talanta, 194 (2019) 377-384.
[4] M. Mezcua, M.A. Martínez-Uroz, M.M. Gómez-Ramos, M.J. Gómez, J.M. Navas, A.R. Fernández-Alba, Talanta, 100 (2012) 90-106.
[5] X. Ye, L.J. Tao, L.L. Needham, A.M. Calafat, Talanta, 76 (2008) 865-871.
[6] G. Galati, P.J. O'Brien, Free Radical Biology and Medicine, 37 (2004) 287-303.
[7] O.R. Alara, N.H. Abdurahman, C.I. Ukaegbu, Current Research in Food Science, 4 (2021) 200-214.
[8] Y. Zhu, Z. Cheng, Q. Xiang, Y. Zhu, J. Xu, Sensors and Actuators B: Chemical, 256 (2018) 888-895.
[9] M.R. Ganjali, V.K. Gupta, M. Hosseini, Z. Rafiei-Sarmazdeh, F. Faridbod, H. Goldooz, A.R. Badiei, P. Norouzi, Talanta, 88 (2012) 684-688.

[10] S.A. Idris, C.M. Davidson, C. McManamon, M.A. Morris, P. Anderson, L.T. Gibson, Journal of Hazardous Materials, 185 (2011) 898-904.
[11] ASTM (Standard Test Methods for Phenolic Compounds in Water) D 1783 – 01.
[12] I. Langmuir, J. Am. Chem. Soc., 40 (1918) 1361-1403.
[13] J.-u.-R. Memon, S.Q. Memon, M.I. Bhanger, M.Y. Khuhawar, J. Hazard. Mater., 163 (2009) 511-516.
[14] G. Zolfaghari, A. Esmaili-Sari, M. Anbia, H. Younesi, S. Amirmahmoodi, A. Ghafari-Nazari, Journal of Hazardous Materials, 192 (2011) 1046-1055.
[15] T.Y. Guo, Y.Q. Xia, G.J. Hao, M.D. Song, B.H. Zhang, Biomaterials, 25 (2004) 5905-5912.
[16] J. Pan, X. Zou, X. Wang, W. Guan, Y. Yan, J. Han, Chem. Eng. J. (Lausanne), 162 (2010) 910-918.
[17] S. Lagergren, Handlingar, 24 (1898) 1-39.
[18] S. Ho, G. Mckay, D. Wase, C. Foster, Adsorption Science and Technology, 18 (2000) 639-650.
[19] Y.-S. Ho, W.-T. Chiu, C.-S. Hsu, C.-T. Huang, Hydrometallurgy, 73 (2004) 55-61.
[20] Y.-S. Ho, Water Research, 37 (2003) 2323-2330.
[21] S. Hong, C. Wen, J. He, F. Gan, Y.-S. Ho, Journal of Hazardous Materials, 167 (2009) 630-633.
[22] Y. Sağ, Y. Aktay, Process Biochemistry, 36 (2001) 1187-1197.
[23] M.R. Oliveira, M.M. Oliveira, R.J. Oliveira, A. Dervanoski, E. Franceschi, S.M. Egues, J.F.D. Conto, CHEMICAL ENGINEERING COMMUNICATIONS, 206 (2019) 1554-1569.
[24] J. Toufaily, B. Koubaissy, L. Kafrouny, H. Hamad, P. Magnoux, L. Ghannam, A. Karout, H. Hazimeh, G. Nemra, M. Hamieh, N. Ajouz, T. Hamieh, Central European Journal of Engineering, 3 (2013) 126-134.
[25] M. Anbia, S. Amirmahmoodi, Scientia Iranica, 18 (2011) 446-452.
[26] A. Morsli, A. Benhamou, J.-P. Basly, M. Baudub, Z. Derriche, The Royal Society of Chemistry, 5 (2015) 41631–41638.