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Remediation of oil refinery wastewater implementing functionalized mesoporous materials MCM-41 in batch and continuous adsorption process

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ABSTRACT

The current study investigated the performance of the adsorption process for the remediation of secondary treated wastewater from the Al-Daura Oil Refinery in Central Iraq, employing batch and continuous (fixed-bed column) adsorption systems. A functionalized mesoporous material with amine groups (NH_2-MCM-41) was used as an efficient adsorbent for the removal of various types of polycyclic aromatic hydrocarbons (PAHs) compounds. The highest removal efficiency of PAHs in batch and continuous adsorption systems were 85.7% and 74.24%, respectively. The batch adsorption system was operated based on our earlier work, using the NH_2-MCM-41 dosage = 0.4 g/L, time = 50 min, rpm = 200, and pH = 7. For this case, the removal efficiency of the chemical oxygen demand was 45%. The fixed-bed column (i.e., bed height = 8 cm, flow rate = 1 mL/min, and pH = 7) showed a removal efficiency of 40%–66% for the chemical oxygen demand as well as 74.24% PAHs degradation. The results indicated that functionalized MCM-41 can be used as an effective adsorbent for the removal of different types of polycyclic aromatic hydrocarbons compounds using either batch or continuous (fixed-bed column) adsorption systems in oil refineries.

Keywords: Batch and fixed-bed adsorption; Functionalized mesoporous MCM-41; Organic removal; Polycyclic aromatic hydrocarbons; Refinery wastewater; Wastewater treatment

1. Introduction

A large quantity of organic and chemical pollutants from wastewater has been produced in the wastewater by the crude oil refining process [1]. These pollutants include different types of polycyclic aromatic hydrocarbons (PAHs) compounds, such as phenols, surface-active substances, metal derivatives, naphthenic acid, sulfides, etc. [2–4]. Polycyclic aromatic hydrocarbons are typically detected in crude oil and usually form as a derivative due to the partial combustion of fossil fuels in the cracking processes and during storage [5,6]. Presently, PAHs compounds from oil refinery wastewater treatment plants are discharged into a nearby water source [7]. PAHs decompose slowly in the aerobic conditions of aquatic environments due to PAHs' high number of aromatic rings, meaning that they can remain in the environment from three months to several years [8]. Furthermore, oil refineries produce contaminated wastewater that contains a biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of around 150–250 ppm and 300–600 ppm, respectively [7,9–11]. These contaminated wastewaters are highly inhibitory and toxic to microbial activity and make wastewater treatment in the oil refinery unit even more challenging [12,13]. Recently, there are new and promising treatments [9,14], such as membrane bioreactors [15], adsorption [16], biodegradation, ion

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exchange and flotation, electrochemical separation, biological activated carbon (AC), advanced oxidation techniques [17], and activated sludge system [18]. Nevertheless, there are obvious limits to these techniques due to the high cost of membrane and fouling problems, chemical agents, and activated carbon, etc. [19–22].

Adsorption is one of the major potential methods for managing PAHs that is both environmentally friendly and efficient because of the useful properties of adsorbents as well as their low cost, adaptability, and simplicity [23,24]. Cavalcanti et al. [25] investigated the adsorption of wastewater contaminants from petroleum refineries by organoclay and was able to eliminate highly toxic organic elements, such as mixtures of benzene, toluene, and xylene and phenols. Alardhi et al. [19] verified a matched pair method using ozone with activated carbon (AC) for refinery wastewater processing and accomplished a powerful COD elimination (90%) [26]. An additional new investigation applied adsorption after the biological treatment for dyeing and COD removal from wastewater, with 96% COD removal [26–28]. Mesoporous inorganic silicas, such as HMS, M41S, SBA, and MSU, are especially desirable adsorbents because of their high adsorption capacity, pore-volume, large surface area, and uniform pore size [29]. The cyclic mesoporous elements (i.e., MCM-41) are deemed profoundly attractive for several technological processes [1]. The construction of the hexagonal mesoporous MCM-41 consists of the hexagonal filler of one-dimensional channels, with a pore volume above 0.3 cm^3/g and a pore diameter from 1.5–10 nm. There are few studies on the adsorption of PAHs by MCM-41 using real wastewater from an oil refinery, and none exclusively studying the adsorption of PAHs by functionalized MCM-41. Therefore, there is a significant interest in developing functionalized MCM-41 for adsorbing PAHs [30,31].

Many pollutants are discharged from the refinery wastewater; however, this research focuses on the removal of PAHs. The concentrations of these contaminants PAHs in treated WW effluents must be reduced to acceptable limits before discharging the water into the environment.

This study aims to investigate the performance of functionalized MCM-41 for the adsorption of PAHs that are exist in the real wastewater from the Al-Daura Oil Refinery in Central Iraq, employing batch and continuous (fixed-bed column) adsorption systems.

2. Materials and methods

2.1. Chemicals

Cetyltrimethylammonium bromide (≥ 99%; Sigma-Aldrich, Germany) and tetraethoxysilane (TEOS), $(C_2H_5)4SiO_4$ (98%; Sigma-Aldrich, Germany) were used as reagents for fabricating MCM-41 (Section S1 – Preparation of MCM-41). PAHs (≥ 99.5%) was also supplied by Sigma-Aldrich (Germany).

2.2. Characteristics of the adsorbent material

The characterizations of the functionalized mesoporous material MCM-41 were accomplished according to the traditional method and had been achieved in our previous work [1] (Section S1 – Preparation of MCM-41).

2.3. Characterization of refinery wastewater

The effluent utilized in this study was obtained at the discharge point of the biological processing unit in the treatment plant of the Al-Daura Oil Refinery in Baghdad, Iraq. Using secondary treated wastewater samples, concentrations were recorded and analyzed in triplicate according to the Standard Methods [31–33]. The BOD_5, COD, and NH_3–N were measured using an ultraviolet-visible spectrum (UV-vis) spectrophotometer (DR-3600, Germany). The concentrations of PAHs in the real wastewater samples were measured using high-performance liquid chromatography (HPLC) (SYKNM S-31155; Germany) in the Ministry of Science and Technology, Baghdad, Iraq. Additionally, removal efficiencies of PAHs, COD, and other tested parameters were calculated as follows:

$$\text{Removal } \% = \frac{X_{\text{inlet}} - X_{\text{outlet}}}{X_{\text{inlet}}} \times 100\% \quad (1)$$

2.4. Batch adsorption of the Al-Daura Oil Refinery wastewater

The experimental work was performed to remove PAHs from secondary (biologically) treated wastewater samples. All samples were filtered using 0.45-micron filtration paper before the adsorption experiment to remove the insoluble materials in order to obtain soluble PAHs.

The first step entailed a batch adsorption process using functionalized MCM-41 adsorbents as an efficient adsorbent. At the same time, NH_2-MCM-41 was evaluated under the optimal conditions obtained from the kinetics and isotherms adsorption of our previous work, as shown in Table 1 [1].

2.5. Continuous adsorption of Al-Daura Oil Refinery wastewater

The process took place in a continuous fixed-bed system 100 cm in length and a 0.7 cm internal diameter. The column was filled with functionalized MCM-41 obtained from our previous study [1]. The fixed bed consisted of the column packed with 6 g of functionalized MCM-41, providing a total bed height of 8 cm. The effluent wastewater from the oil refinery was filtered before the treatment and then drawn into the adsorption column at a flow rate of 1 mL/min. Afterward, the wastewater was transferred to the last collecting container, as shown in Fig. 1.

3. Results and discussion

3.1. Characterization of adsorbents

The Brunauer–Emmett–Teller surface area, pore-volume, and pore diameter of the NH_2-MCM-41 sample were measured, and the results are outlined in Table 2.

3.2. Analysis of oil refinery wastewater

The characterization of secondary wastewater of Al-Daura Oil Refinery was tested, as shown in Table 3. The major peaks before treatment have been labeled and named, as shown in Figs. 2a and 3a, which provide a good view of the 16 PAHs present in the wastewater. The total PAHs

Table 1
Operating conditions of the adsorption of PAHs by functionalized MCM-41

Process factors	Conditions
Initial pH = (3, 4, 5, 7, 9 and 10)	Temperature = (25°C ± 2°C); agitation = 200 rpm; MCM-41 dosage = 0.02 g; initial PAHs concentration = 15 mg/L; contact time = 50 min
Agitation speed = (100, 150, 175, 200 and 250 rpm)	Temperature = (25°C ± 2°C); pH = 4; MCM-41 dosage = 0.02 g; initial PAHs concentration = 25 mg/L; contact time = 50 min
MCM-41 dosages = (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 g)	Temperature = (25°C ± 2°C); agitation = 200 rpm; initial PAHs concentration = 25 mg/L; initial pH = 4; contact time = 50 min
Different PAHs concentrations = (2.5, 5, 10, 15, 20, 25, 30, 40 and 50 mg/L)	Temperature = (25°C ± 2°C); MCM-41 dosage = 0.02 g; agitation = 200 rpm; initial pH = 4; contact time = 50 min
Optimum conditions	Temperature = (25°C ± 2°C); MCM-41 dosage = 0.02 g; agitation = 200 rpm; initial pH = 4; contact time = 50 min

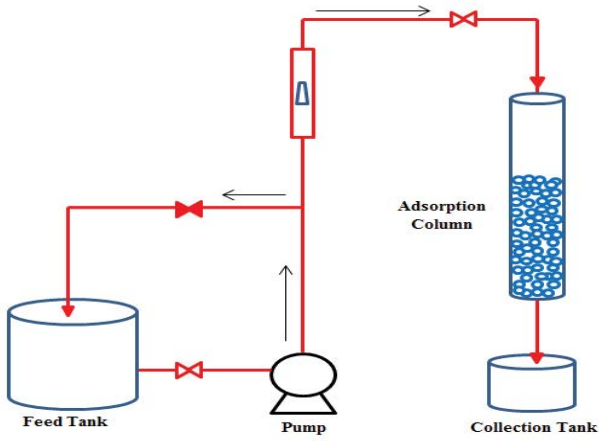


Fig. 1. A flow diagram of the continuous fixed-bed treatment operation.

levels in the present study were greater than the highest allowable concentrations of the Environmental Quality Criteria of the United States, which is Σ PAHs = 0.03 μg/L [6]. Such PAHs have polluted the Tigris River, according to the World Health Organization (WHO) [34], which considers water to be heavily polluted when the concentration of total PAHs exceeds 2.2 μg/L. Similar results were obtained in the Ruwais Refinery Wastewater Treatment Plant in Abu Dhabi [7] and also in the Shatt Al-Arab River, Northwest Arabian Gulf [35–38], and Langkawi Island of Malaysia [38]. BOD_5 and NH–N were also measured before and after the experiment, and it was found that no change in their values was noticed as there was no biological treatment involved in our experiments.

3.3. Secondary treated wastewater treatment using a batch process

A very low fixed mass-functionalized MCM-41 of 0.4 g/L under pH = 7 at lab temperature (25°C ± 2°C) and 200 rpm was applied as the best-operating conditions. Under those conditions, the factory wastewater processing removed more than 85% of PAHs along with a 45% COD removal with a contact time of 50 min, as shown in Figs. 2b, 3b and Table 4. Table 4 represents the quality of the treated PAHs samples and the percentage removal of the pollutants, showing that most of the PAHs compounds were separated effectively, with their concentrations reduced to zero. This can be illustrated as follows, functionalized MCM-41 had many Si–O–Si bonds in its frame-work and had many hydroxyl groups (OH) and amino groups (NH_2) at the pore surface, which has some hydroscopic features; the PAHs could interact with groups by hydrophobic interactions which result in significant adsorption.

3.4. Secondary treated wastewater treatment using a continuous fixed-bed process

Before treatment, the chromatogram of the Al-Daura Oil Refinery wastewater and major peaks were labeled as shown in Figs. 4a and 5a, according to HPLC identification. Figs. 4b and 5b demonstrate that sorption by a continuous fixed-bed process reduced the concentration of PAHs compounds by 74.24% this indicates an excellent efficacy to treat wastewater in the continuous mode of operation.

Table 2
Structure properties of functionalized MCM-41

Material	S_{BET} (m^2/g)	V (cm^3/g)	D_{BJH} (nm)	Particle size (nm)	d_{100} (nm) XRD	a_0 (nm) XRD	W_t (nm)	O_2 wt.% EDX	Si wt.% EDX
Functionalized MCM-41	300	0.68	3.0776	19.748	4.41	5.09	2.012	52	48

d_{100}: $d_{(100)}$ spacing; a_0: center–center distance ($a_0 = (2/\sqrt{3})$) d; S_{BET}: BET surface area; V: volume of the pore; D_{BJH}: diameter of the pore; W_t: thickness of wall, computed as $a_0 - D_{BJH}$.
XRD: X-ray diffraction; EDX: energy-dispersive X-ray analysis; BET: Brunauer–Emmett–Teller; BJH: Barrett–Joyner–Halenda.

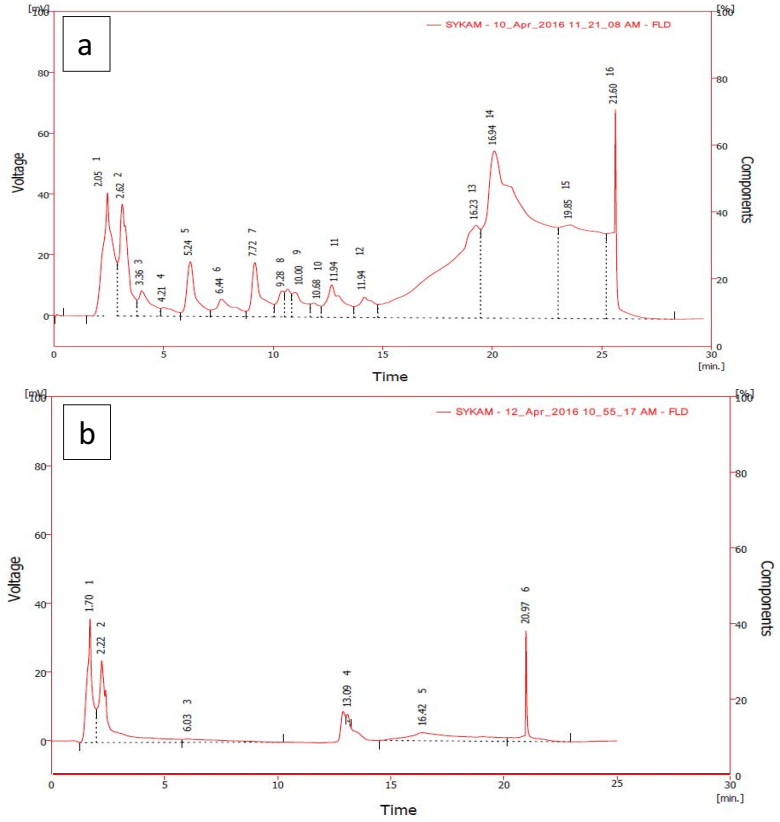


Fig. 2. Chromatogram of Al-Daura Oil Refinery wastewater (a) before batch process treatment and (b) after treatment batch process.

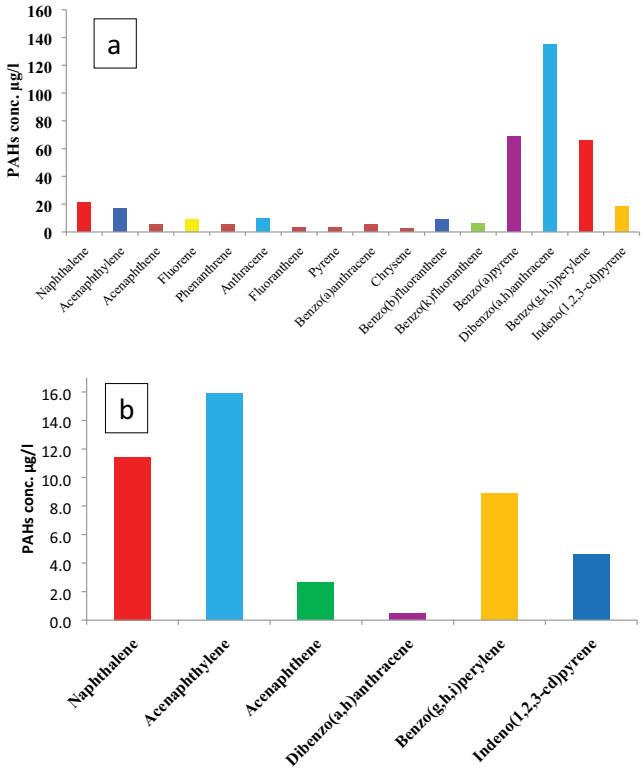


Fig. 3. Major peaks of Al-Daura Oil Refinery wastewater (a) before batch process treatment and (b) after batch process treatment.

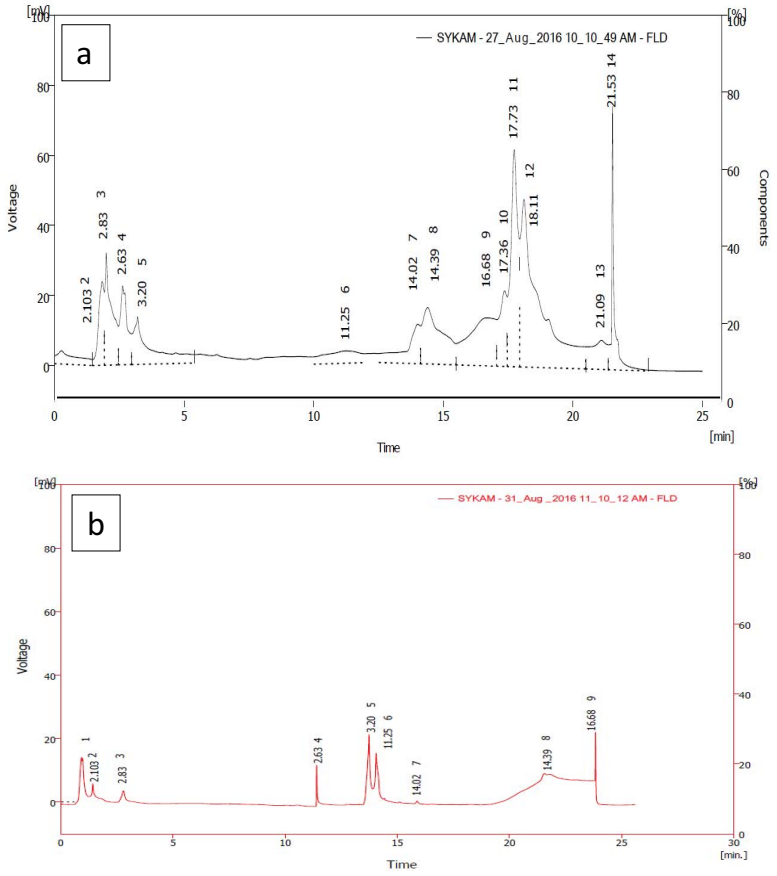


Fig. 4. Chromatogram of Al-Daura Oil Refinery wastewater (a) before fixed-bed treatment and (b) after fixed-bed treatment.

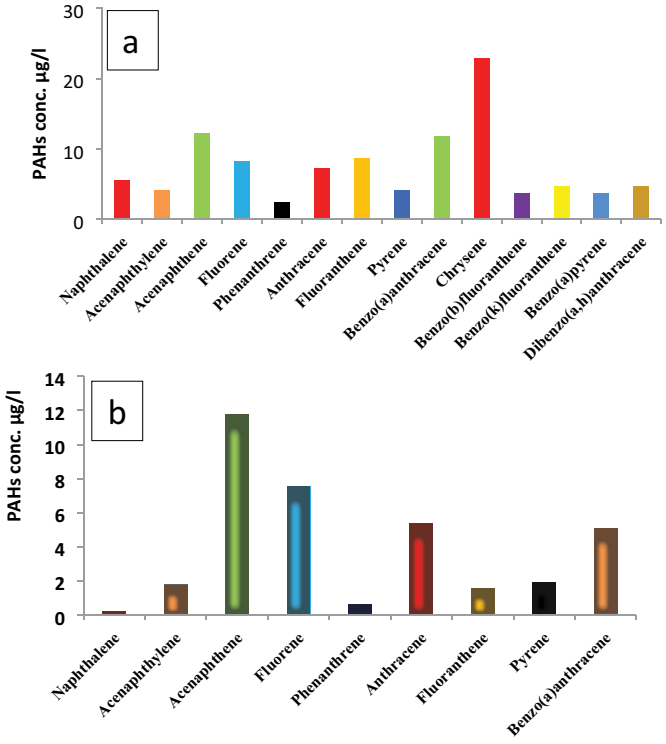


Fig. 5. Major peaks of Al-Daura Oil Refinery wastewater (a) before fixed-bed treatment and (b) after fixed-bed treatment.

Table 5 represents the quality of the treated PAHs samples and the percentage removal of the pollutants. The surface properties of adsorbents play an essential role, mainly when used for adsorption from wastewater by a continuous fixed-bed process. The active site on the surface of adsorbents could improve hydrophilicity, but it blocked the adsorption of hydrophobic contaminants in wastewater. Adsorbents cover with strong ion exchangeability were useful to the adsorption of organic pollutants.

3.5. COD reduction

The performance of the continuous fixed bed for COD removal is presented in Fig. 6. The influent COD sample was filtered using filter paper to obtain a soluble COD concentration. Although the soluble COD varied in range (32–63 mg/L) throughout the study, the effluent COD was essentially lower than 25 mg/L, with an average removal efficiency of 53%. This meets the standard limits for discharge (i.e., 50 mg/L). In general, the results indicated that the continuous fixed bed was effective in eliminating organic matter: although the influent varied, the COD removal efficiency was sustained at 40%–66%. This percentage of removal represents the total removal of aromatic and other substances. Other contaminants like BOD_5 and NH_3–N cannot be removed by adsorption; however, they can be removed by other techniques like activated sludge systems.

The removal efficiency of the adsorption (R%) was observed may be attributed to positive charge sites are created on the MCM-41 surface, and it has resulted in a considerably high electrostatic attraction between organic compounds (COD) and the positively charged surface of the MCM-41. This outcome is in good agreement with the results reported by El-Naas et al. [39] investigated the adsorption of wastewater contaminants from petroleum refineries by date-pit activated carbon and achieved 30% COD removal at 36°C. In contrast, at 60°C, 53% COD removal was reached.

Table 3
Characteristics of the secondary (biologically) treated wastewater

No.	Parameter	Unit	Value
1	BOD_5	mg/L	15–20
2	COD	mg/L	30–70
3	NH_3–N	mg/L	<5
4	pH	µg/L	7–7.5
5	Naphthalene	µg/L	5–21.3
6	Acenaphthylene	µg/L	4–17.1
7	Acenaphthene	µg/L	5–12
8	Fluorene	µg/L	8–9.1
9	Phenanthrene	µg/L	2–5.6
10	Anthracene	µg/L	7–9.5
11	Fluoranthene	µg/L	3–9
12	Pyrene	µg/L	3.0–5
13	Benzo(a)anthracene	µg/L	5–11
14	Chrysene	µg/L	2.3–23
15	Benzo(b)fluoranthene	µg/L	9
16	Benzo(k)fluoranthene	µg/L	6
17	Benzo(a)pyrene	µg/L	3–9
18	Dibenzo(a,h)anthracene	µg/L	4–135
19	Benzo(g,h,i)perylene	µg/L	0–70
20	Indeno(1,2,3-cd)pyrene	µg/L	0–19

3.6. Compression study

This work investigated the performance of the adsorption process for the removal of real wastewater from the Al-Daura Oil Refinery in Central Iraq, employing batch and continuous (fixed-bed column) adsorption systems. A functionalized mesoporous material with amine groups (NH_2-MCM-41) was used as a competent adsorbent for the removal of various types of polycyclic aromatic hydrocarbons (PAHs) compounds. A comparative study between this work and others was achieved, as shown in Table 6. It is obvious from Table 5 that NH_2-MCM-41 is a promising adsorbent to remove the PAHs and COD from oil refinery wastewater. Also, because NH_2-MCM-41 has a similar performance to adsorbents documented in the literature, the results of this study support the use of NH_2-MCM-41 as an adsorbent for the elimination of organics from industrial wastewater and surface water.

4. Conclusions

The adsorption process by batch and fixed-bed treatments showed parallel performance in removing PAHs compounds (85% and 74.24%, respectively), with COD removal ranging from 40%–66%. This was expected as the amount of MCM-41 in the batch and the fixed-bed process was a size that had worked under similar operating conditions. However, the research was conducted only at one wastewater processing unit (i.e., the fixed-bed method of the wastewater treatment facility at the Al-Daura Oil Refinery). The batch plus fixed-bed treatment was established to increase the efficiency of processing undesirable oil refinery wastewater. When evaluated in relation to the best-operating conditions obtained from kinetic and isotherm sorption in our previous study, the efficiency of the batch and fixed-bed treatments in this

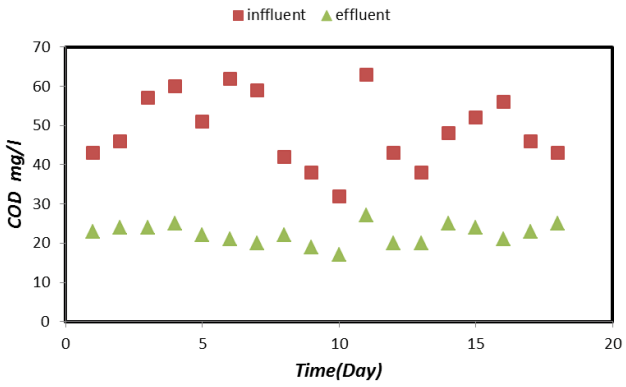


Fig. 6. Reduction of COD of Al-Daura Oil Refinery wastewater after treatment.

Table 4
Removal efficiency of PAHs by functionalized MCM-41 using batch adsorption

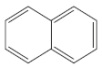
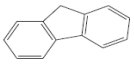
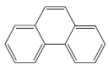
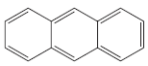
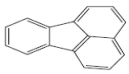
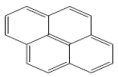
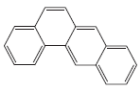
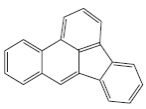
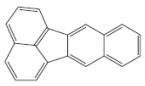
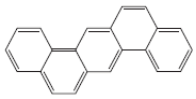
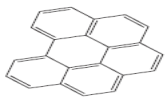
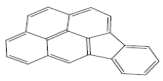
No.	PAHs compound	Molecular Formula	In (μg/L)	Out (μg/L)	Removal %
1	Naphthalene		21.3	11.4	46.28
2	Acenaphthylene		17.1	15.9	7.38
3	Acenaphthene		5.6	2.6	53.57
4	Fluorene		9.1	0.0	100
5	Phenanthrene		5.6	0.0	100
6	Anthracene		9.5	0.0	100
7	Fluoranthene		3.4	0.0	100
8	Pyrene		3.0	0.0	100
9	Benzo(a)anthracene		5.2	0.0	100
10	Chrysene		2.3	0.0	100
11	Benzo(b)fluoranthene		9.1	0.0	100
12	Benzo(k)fluoranthene		5.8	0.0	100
13	Benzo(a)pyrene		68.7	0.0	100
14	Dibenzo(a,h)anthracene		134.8	0.5	99
15	Benzo(g,h,i)perylene		65.6	8.9	86.5
16	Indeno(1,2,3-cd)pyrene		18.4	4.6	75

Table 5
Removal efficiency of PAHs by continuous process adsorption

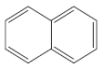
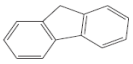
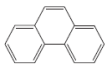
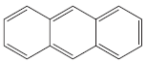
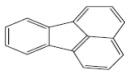
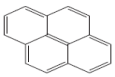
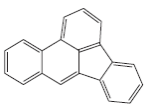
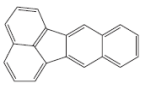
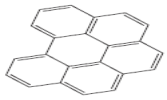
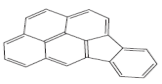
No.	PAHs compound	Molecular formula	In (μg/L)	Out (μg/L)	Removal %
1	Naphthalene		5.5	0.2	96.63
2	Acenaphthylene		4.1	1.7	58.53
3	Acenaphthene		12.2	11.8	3.278
4	Fluorene		8.2	7.5	8.536
5	Phenanthrene		2.4	0.6	75
6	Anthracene		7.3	5.3	27.4
7	Fluoranthene		8.7	1.5	78.16
8	Pyrene		4.2	1.9	82.75
9	Benzo(a)anthracene		11.8	5.0	57.62
10	Chrysene		22.9	0.0	100
11	Benzo(b)fluoranthene		3.6	0.0	100
12	Benzo(k)fluoranthene		4.8	0.0	100
13	Benzo(a)pyrene		3.6	0.0	100
14	Dibenzo(a,h)anthracene		4.8	0.0	100
15	Benzo(g,h,i)perylene		0.0	0.0	100
16	Indeno(1,2,3-cd)pyrene		0.0	0.0	100

Table 6
Removal efficiency of PAHs by batch and continuous process adsorption

No.	Process applied	Pollutants	Removal (%)	References
1	Adsorption by periodic mesoporous organosilica	PAHs	60	[40]
2	Adsorption by porous carbons	PAHs	84.5	[41]
3	Adsorption by different mesoporous molecular sieves of MCM-41	PAHs	74.5	[42]
4	Adsorption by Si–MCM-41	PAHs	91.5	[43]
5	Adsorption by different low-cost adsorbents	PAHs	69	[44]
6	Adsorption by PABA-MCM-41	PAHs	93.8	[45]
7	Adsorption by organoclay	COD	62	[25]
8	Adsorption by activated carbon	COD	60	[46]
9	Adsorption columns filled with granular biologically activated carbon	COD	99	[47]
10	Adsorption by activated carbon prepared from date palm waste	COD	95.4	[48]
11	Adsorption column filled granular activated carbon	COD	90	[9]
12	Adsorption by NH_2-MCM-41 (batch)	PAHs/COD	85/45	This work
13	Adsorption by NH_2-MCM-41 (fixed-bed column)	PAHs/COD	74/60	This work

study was comparable. In summary, full elimination of PAHs was always accomplished when using this method for 12 h of the continuous process. This technique can be employed to remove different types of PAHs from secondary treated industrial wastewater, while also reducing processing and operational costs. The degradation of the PAHs pollutants of the secondary treated wastewater was certified to the combined effects of the Si–O–Si bonds in its frame-work and hydroxyl groups (OH) and amino groups (NH_2) at the pore surface. Maximum COD removal from wastewater was achieved and sustained at 40%–66% at the optimum conditions. This is recognized for their remarkable high surface area and high electrostatic attraction between organic compounds (COD) and the positively charged surface of the MCM-41.

Acknowledgments

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References

[1] T.M. Albayati, K.R. Kalash, Polycyclic aromatic hydrocarbons adsorption from wastewater using different types of prepared mesoporous materials MCM-41 in batch and fixed bed column, Process Saf. Environ. Prot., 133 (2020) 124–136.
[2] S.A. Younis, N.S. El-Gendy, W.I. El-Azab, Y.M. Moustafa, Kinetic, isotherm, and thermodynamic studies of polycyclic aromatic hydrocarbons biosorption from petroleum refinery wastewater using spent waste biomass, Desal. Water Treat., 56 (2015) 3013–3023.
[3] K.R. Kalash, M.H. Al-Furaiji, B.I. Waisi, R.A. Ali, Evaluation of adsorption performance of phenol using non-calcined Mobil composition of matter no. 41 particles, Desal. Water Treat., 198 (2020) 232–240.
[4] Y.A. Abd Al-Khodor, T.M. Albayati, Employing sodium hydroxide in desulfurization of the actual heavy crude oil: theoretical optimization and experimental evaluation, Process Saf. Environ. Prot., 136 (2020) 334–342.
[5] H.I. Abdel-Shafy, M.S.M. Mansour, A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation, Egypt. J. Pet., 25 (2015) 107–123.
[6] USEPA Environmental Protection Agency, Polycyclcic Aromatic Hydrocarbons (PAHs) United States Office of Solid Waste, Washington D.C., 2008.
[7] F. Benyahia, M. Abdulkarim, A. Embaby, M. Rao, Refinery Wastewater Treatment: A True Technological Challenge, The Seventh Annual U.A.E. University Research Conference, U.A.E., 2006.
[8] R.A. Geyer, Polycyclic aromatic hydrocarbons in the aquatic environment, Mar. Chem., 10 (1981) 167–168.
[9] M.H. El-Naas, R. Surkatti, S. Al-Zuhair, Petroleum refinery wastewater treatment: a pilot scale study, J. Water Process Eng., 14 (2016) 71–76.
[10] T.M. Albayati, A.A. Sabri, D.B. Abed, Functionalized SBA-15 by amine group for removal of Ni(II) heavy metal ion in the batch adsorption system, Desal. Water Treat., 174 (2020) 301–310.
[11] T.M. Albayati, A.M. Doyle, Purification of aniline and nitro-substituted aniline contaminants from aqueous solution using beta zeolite, Chem.: Bulgarian J. Sci. Educ., 23 (2014) 105–114.
[12] J. Guo, F. Ma, C.-C. Chang, D. Cui, L. Wang, J. Yang, L. Wang, Start-up of a two-stage bioaugmented anoxic–oxic (A/O) biofilm process treating petrochemical wastewater under different DO concentrations, Bioresour. Technol., 100 (2009) 3483–3488.
[13] D.T. Sponza, R. Oztekin, Removals of PAHs and acute toxicity via sonication in a petrochemical industry wastewater, Chem. Eng., 162 (2010) 142–150.
[14] A.M. Alkafajy, T.M. Albayati, High performance of magnetic mesoporous modification for loading and release of meloxicam in drug delivery implementation, Mater. Today Commun., 23 (2020) 100890, https://doi.org/10.1016/j.mtcomm.2019.100890.
[15] M.H. Al-Furaiji, J.T. Arena, M. Chowdhury, N. Benes, A. Nijmeijer, J.R. McCutcheon, Use of forward osmosis in treatment of hyper-saline water, Desal. Water Treat., 133 (2018) 1–9.
[16] K.R. Kalash, H.A. Alalwan, M.H. Al-Furaiji, A.H. Alminshid, B.I. Waisi, Isothermal and kinetic studies of the adsorption removal of Pb(II), Cu(II), and Ni(II) ions from aqueous solutions using modified *Chara* sp. algae, Korean Chem. Eng. Res., 58 (2020) 301–306.
[17] H. Alalwan, A. Alminshid, An in-situ DRIFTS study of acetone adsorption mechanism on TiO_2 nanoparticles, Spectrochim. Acta, Part A, 229 (2020) 117–990.
[18] K.R. Kalash, M.A. Kadhom, M.H. Al-Furaiji, Short-cut nitrification of Iraqi municipal wastewater for nitrogen removal in a single reactor, Mater. Sci. Eng., 518 (2019) 22–24.

[19] S.M. Alardhi, J.M. Alrubaye, T.M. Albayati, Adsorption of methyl green dye onto MCM-41: equilibrium, kinetics and thermodynamic studies, Desal. Water Treat., 179 (2020) 323–331.
[20] S.T. Kadhum, G.Y. Alkindi, T.M. Albayati, Eco friendly adsorbents for removal of phenol from aqueous solution employing nanoparticle zero-valent iron synthesized from modified green tea bio-waste and supported on silty clay, Chin. J. Chem. Eng., (2020), (In Press), https://doi.org/10.1016/j.cjche.2020.07.031.
[21] S.M. Alardhi, T.M. Albayati, J.M. Alrubaye, A hybrid adsorption membrane process for removal of dye from synthetic and actual wastewater, Chem. Eng. Process. Process Intensif., 157 (2020) 108113, https://doi.org/10.1016/j.cep.2020.108113.
[22] M. Kadhom, N. Albayati, S. Salih, M. Al-Furaiji, M. Bayati, B. Deng, Role of cellulose micro and nano crystals in thin film and support layer of nanocomposite membranes for brackish water desalination, Membranes, 9 (2019) 101, https://doi.org/ 10.3390/membranes9080101.
[23] M.N. Abbas, T.H. Nussrat, A statistical analysis of experimental data for the adsorption process of cadmium by watermelon rinds in a continuous packed bed column, Int. J. Innovation Creativity Change, 13 (2020) 124–138.
[24] D.A. Aljuboury, H.B. Abdul Aziz, S. Feroz, Treatment of petroleum wastewater by conventional and new technologies – a review, Global Nest J., 19 (2017) 439–452.
[25] V.F.L. Cavalcanti, C.A.M. Abreu, M.N. Carvalho, M.A. Motta Sobrinho, M. Benachour, O.S. Baraúna, Removal of effluent from petrochemical wastewater by adsorption using organoclay, Petrochemicals, (2012), doi: 10.5772/37200.
[26] S. Sathian, M. Rajasimman, C.S. Rathnasabapathy, C. Karthikeyan, Performance evaluation of SBR for the treatment of dyeing wastewater by simultaneous biological and adsorption processes, Water Process Eng., 4 (2014) 82–90.
[27] M.H. Muhamad, S.R. Sheikh Abdullah, A.B. Mohamad, R. Abdul Rahman, A.A. Hasan Kadhum, Application of response surface methodology (RSM) for optimisation of COD, NH_3–N and 2,4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR), Environ. Manage., 121 (2013) 179–190.
[28] W.H.W. Osman, S.R.S. Abdullah, A.B. Mohamad, A.A.H. Kadhum, R.A. Rahman, Simultaneous removal of AOX and COD from real recycled paper wastewater using GAC-SBBR, J. Environ. Manage., 121 (2013) 80–86.
[29] A. Balati, A. Shahbazi, M.M. Amini, S.H. Hashemi, K. Jadidi, Comparison of the efficiency of mesoporous silicas as absorbents for removing naphthalene from contaminated water, Eur. J. Environ. Sci., 4 (2011) 69–76.
[30] M. Anbia, S.E. Moradi, Removal of naphthalene from petrochemical wastewater streams using carbon nanoporous adsorbent, Appl. Surf. Sci., 255 (2009) 5041–5047.
[31] S.M. Alardhi, T.M. Albayati, J.M. Alrubaye, Adsorption of the methyl green dye pollutant from aqueous solution using mesoporous materials MCM-41 in a fixed-bed column, Heliyon. 6 (2020) e03253, https://doi.org/10.1016/j.heliyon.2020.e03253.
[32] APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C., 1980.
[33] HACH, Water Analysis Handbook, HACH Company, Color, USA, 2002.
[34] WHO, Polynuclear Aromatic Hydrocarbons in Drinking Water, World Health Organization, Geneva, 2003.
[35] J.K. Al-Saad, S.M. Shamshoom, J.K. Abaychi, Seasonal distribution of dissolved and particulate hydrocarbons in Shatt Al-Arab Estuary and North-West Arabian Gulf, Mar. Pollut. Bull., 36 (1998) 850–855.
[36] S.M. Al-Saad, J.K. Abaychi, S.M. Shamshoom, Hydro-carbons in the waters and sediments of Shatt Al-Arab Estuary and NW-Arabian Gulf, Mar. Mesopotamica, 11 (1995) 135–148.
[37] A. Al-Timari, Oil pollution in Shatt Al-Arab water studying the monthly variation of polycyclic aromatic hydrocarbons (PAHs), Mar. Mesopotamica, 15 (2000) 535–548.
[38] S. Nasher, L.Y. Heng, Z. Zakaria, S. Surif, Concentrations and sources of polycyclic aromatic hydrocarbons in the seawater around Langkawi Island, Malaysia, Chemistry (Easton), 2013 (2013) 975781, https://doi.org/10.1155/2013/975781.
[39] M.H. El-Naas, S. Al-Zuhair, M.A. Alhaija, Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon, J. Hazard. Mater., 173 (2009) 750–757.
[40] C.B. Vidal, A.L. Barros, C.P. Moura, A.C.A. de Lima, F.S. Dias, L.C.G. Vasconcellos, P.B.A. Fechine, R.F. Nascimento, Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica, J. Colloid Interface Sci., 357 (2011) 466–473.
[41] M. Yuan, S. Tong, S. Zhao, C.Q. Jia, Adsorption of polycyclic aromatic hydrocarbons from water using petroleum coke-derived porous carbon, J. Hazard. Mater., 181 (2010) 1115–1120.
[42] R.S. Araújo, D.C.S. Azevedo, C.L. Cavalcante, A. Jiménez-López, E. Rodríguez-Castellón, Adsorption of polycyclic aromatic hydrocarbons (PAHs) from isooctane solutions by mesoporous molecular sieves: influence of the surface acidity, Microporous Mesoporous Mater., 108 (2008) 213–222.
[43] J.A. Costa, R. Anjos, C.M.P. da Silva, L.P.C. Romão, Efficient adsorption of a mixture of polycyclic aromatic hydrocarbons (PAHs) by Si–MCM–41 mesoporous molecular sieve, Powder Technol., 308 (2017) 434–441.
[44] R. Crisafully, M.A.L. Milhome, R.M. Cavalcante, E.R. Silveira, D. De Keukeleire, R.F. Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin, Bioresour. Technol., 99 (2008) 4515–4519.
[45] J.A.S. Costa, V.H.V. Sarmento, L.P.C. Romão, C.M. Paranhos, Performance of the MCM-41-NH_2 functionalized mesoporous material synthetized from the rice husk ash on the removal of the polycyclic aromatic hydrocarbons, Silicon, 12 (2020) 1913–1923.
[46] M.H. El-Naas, M.A. Alhaija, S. Al-Zuhair, Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater, Environ. Sci. Pollut. Res., 24 (2017) 7511–7520.
[47] D. Miskovic, B. Dalmacija, Z. Zivanov, An investigation of the treatment and recycling of oil refinery wastewater, Water Sci. Technol., 18 (1986) 105–114.
[48] A.E.A. Nayl, R.A. Elkhashab, T. El Malah, S.M. Yakout, M.A. El-Khateeb, M.M.S. Ali, H.M. Ali, Adsorption studies on the removal of COD and BOD from treated sewage using activated carbon prepared from date palm waste, Environ. Sci. Pollut. Res., 24 (2017) 22284–22293.

Supporting information

S1. Preparation of MCM-41

MCM-41 were prepared using sol–gel process [1]. The silica source was tetraethoxysilane, and the construction directing tool was cetyltrimethylammonium bromide (CTAB). Mesoporous material was made by adding TEOS (5.78 g) to a solution including CTAB (1.01 g) and NaOH (0.34 g) in 30 mL of deionized water and was mixed using a magnetic mixer for 60 min at 298 K. The produced mix was formed at 383 K using an autoclave for 4 d. The product (solid) was filtered and washed several times by the deionized water to remove the incomplete surfactant, and the prepared MCM-41 was dried thoroughly at 313 K for 6–24 h in order to get the non-calcined MCM-41. The powder was then calcined at 823 K for 360 min to separate the surfactant, then the powder with white color of MCM-41 was prepared.

S2. Functionalization

The functionalized MCM-41 was accomplished by the reaction between the silanol groups and the silylating agent onto the MCM-41 surface. 25 g from MCM-41 was suspended in dry toluene (200 mL) after that 3-aminopropyltriethoxysilane (10 mL) was added to the mixture. The mixture was agitated and refluxed for 720 min at atmospheric conditions. The resulted output was separated and frequently rinsed with ethanol and toluene, then evaporated for 360 min at 298 K [1].

S3. Characteristics of the adsorbent material

The characterizations of the functionalized mesoporous material MCM-41 were accomplished according to the traditional method and had been achieved in our previous work [1]. The prepared adsorbent was characterized using X-ray diffraction (XRD) Fig. S3a, scanning electron microscopy (SEM) Fig. S2, Fourier-transform infrared spectroscopy (FTIR) Fig. S3c, thermal gravimetric analysis Fig. S3d, energy-dispersive analysis of X-ray (EDAX) Fig. S1 and zeta potential (ζ) Fig. S4, as. A Brunauer–Emmett–Teller (BET) surface area with N_2 adsorption–desorption was achieved as well Fig. S3b.

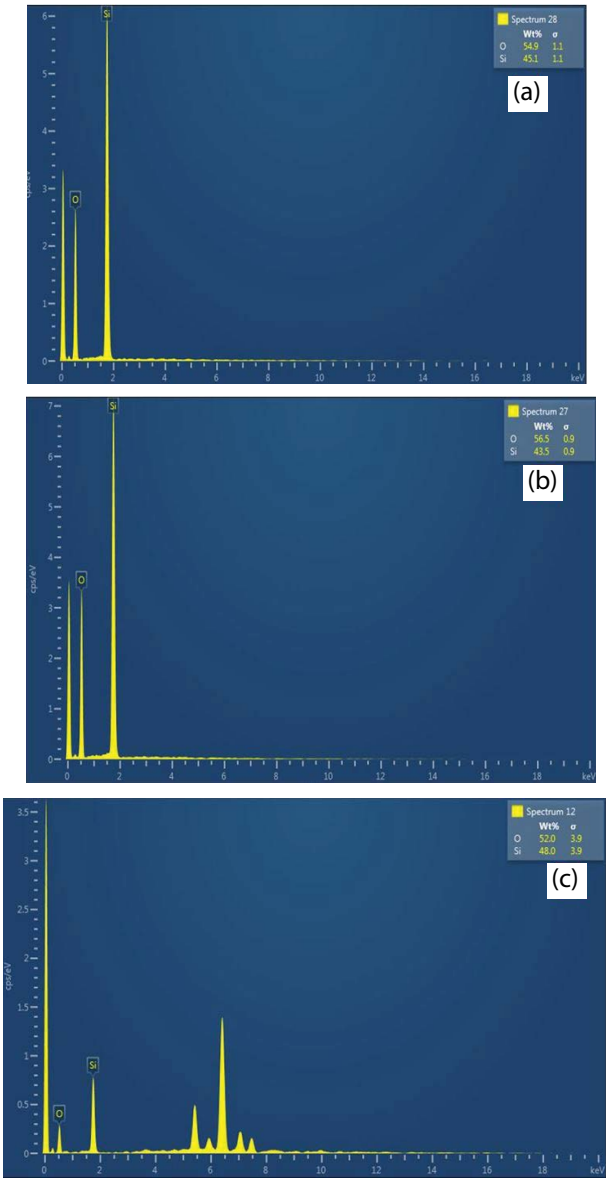

Fig. S1. Typical EDAX image for MCM-41 (a) uncalcined, (b) calcined, and (c) functionalized.

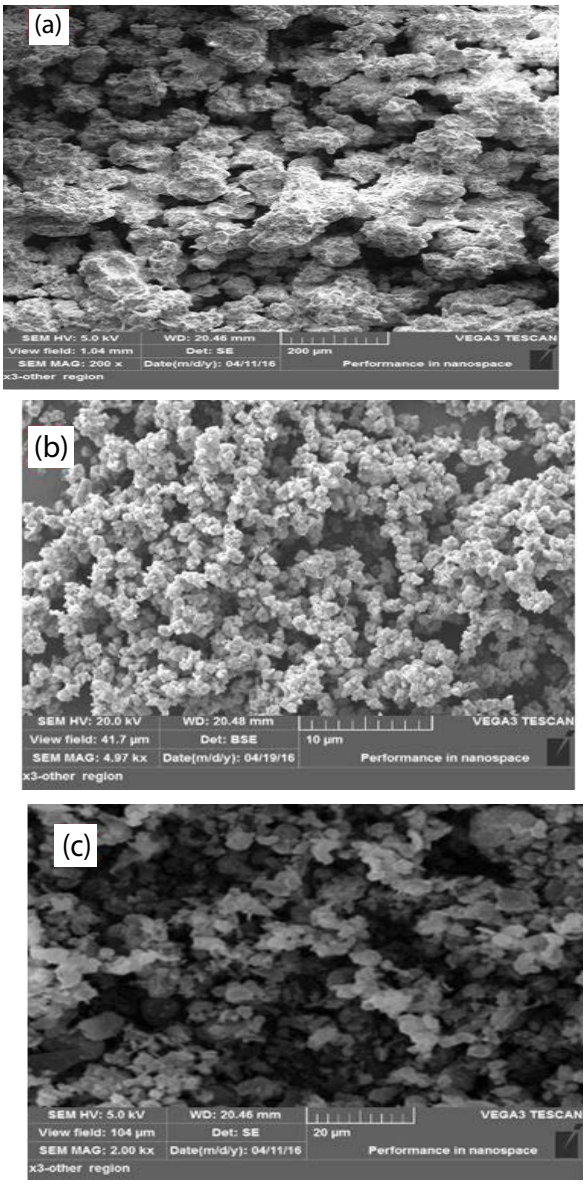

Fig. S2. Typical SEM image for MCM-41 (a) uncalcined, (b) calcined, and (c) functionalized.

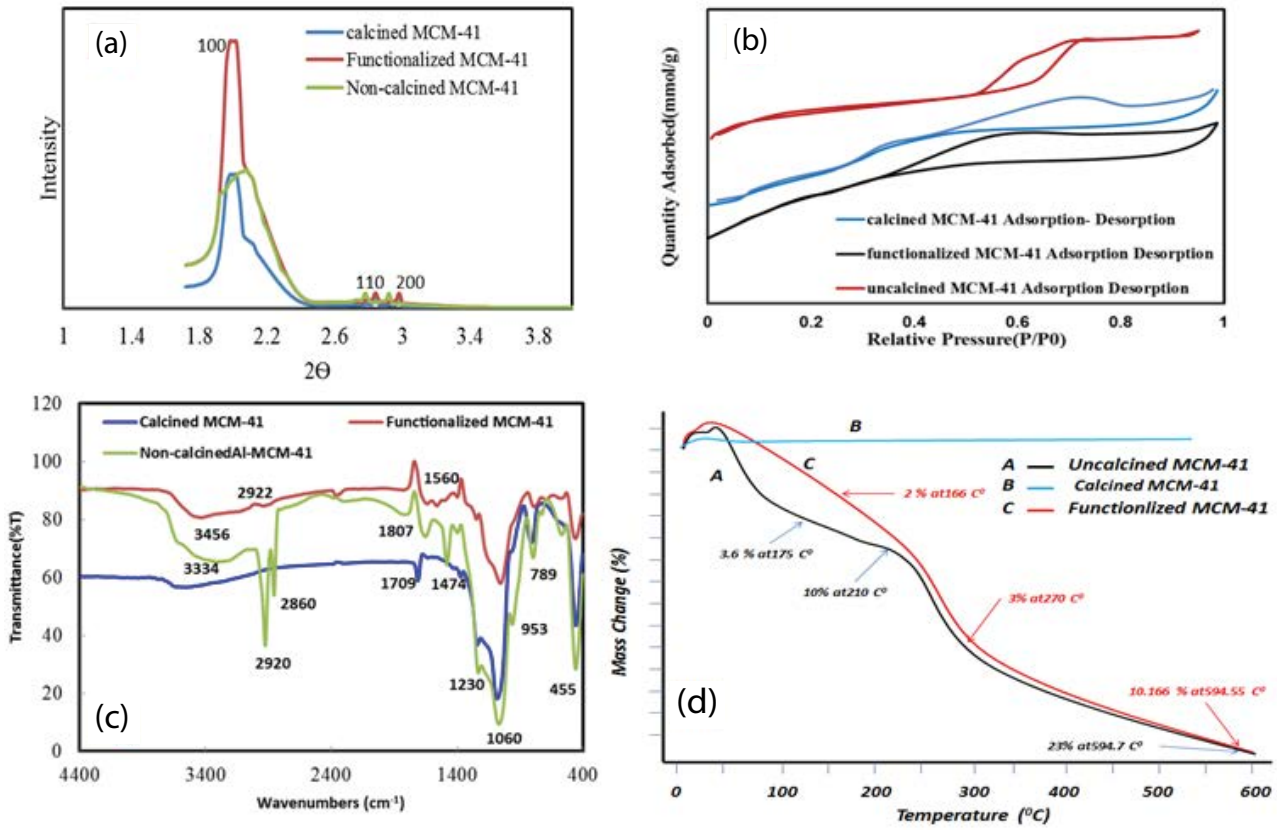

Fig. S3. (a) XRD patterns, (b) isotherms of nitrogen sorption–desorption, (c) FTIR spectra of the organic containing silica material, and (d) thermal gravimetric analysis.

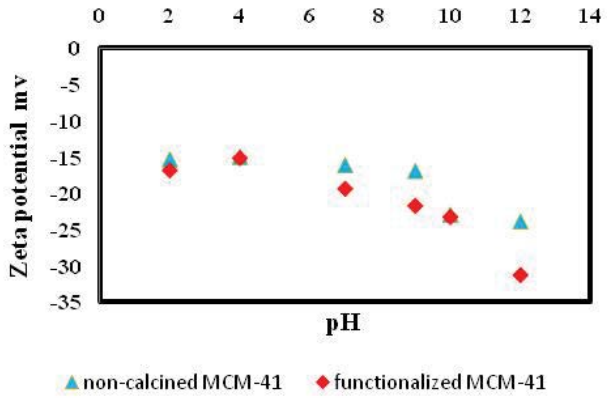

Fig. S4. Zeta potential for non-calcined and functionalize MCM-41 at different pH.