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Reduction of oil and COD from produced water by activated carbon, zeolite, and mixed adsorbents in a fixed-bed column

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ABSTRACT

In this work, activated carbon, zeolite, silica gel, and mixed adsorbents (activated carbon and silica gel) were used for adsorption of oil and chemical oxygen demand (COD) from produced water by experiments of adsorption (continuous fixed-bed column). Two types of activated carbon (powdered and granular) were utilized. The effects of operational parameters, such as flow rate (1.25–3.15 mL/min), oil concentration (40–1,000 ppm), and COD concentration (1,350–28,500 ppm), on the performance of the column were studied. Also, two kinetics models (Thomas and Yoon–Nelson models) were applied to predict the breakthrough curve and calculate the distinguishing parameters of the column that are beneficial for a process design. The results reveal that Thomas kinetic model was suitable for the adsorption of oil and COD on all types of adsorbents. Also, the removal of pollutants increased with a decrease in flow rate and concentration. The highest removal of oil and COD were obtained (83.62% and 78.81%) by mixed adsorbents, (72.98% and 69.5%) by powdered activated carbon, (67.8% and 64.74%) by silica gel, (64.87% and 60.94%) by granular activated carbon, (58.58% and 52.49%) by zeolite at a flow rate (1.25 mL/min), adsorbent dose (0.5 g) oil concentration (40 ppm), and COD (1,350 ppm) bed height (2 cm); the highest adsorption capacity was 108.38 mg/g for oil and 96.74 mg/g for COD by mixed adsorbents. As well, the results illustrate that the highest removal of pollutants by mixed adsorbents, and least removal of pollutants by zeolite. Therefore, the results suggest that mixed adsorbents (activated carbon and silica gel) can be an effective adsorbent for the removal of pollutants from produced water.

Keywords: Activated carbon; Adsorption; COD; Fixed bed column; Mixed adsorbents; Oil; Produced water; Zeolite

1. Introduction

Water pollution is considered a significant problem in the Iraqi environment, it affects several aspects of our life and environment such as the effect on drinking water and groundwater resources, danger to aquatic life creates atmospheric pollution, affects crop production, and ultimately dangerous to human health. Industrialization and urbanization have contributed to the increase in pollution. Wastewater mostly discharges into rivers, wells, streams, and other water bodies either without treatment or with inappropriate treatment. Produced water is water trapped during the formation of subsurface and is brought along with gas or oil to the surface. It forms the largest volume of the stream of waste associated with gas and oil production. The amounts of produced water depend on the characteristics of the reservoir, extraction technology, and the oil extraction rate. Globally, 77 billion bbl of water are produced per year [1–3]. Produced water contains the organic and inorganic compounds, soluble and insoluble petroleum fractions (such as oil droplets not removed by physical separation), metals, salts, organic acids, phenols, and dissolved hydrocarbons, at different concentrations [4,5]. The discharge of produced water may cause severe pollution of surface water, soil water, and underground water; therefore, the treatment of produced water may need to meet regulatory

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limits. Oil is considered an important contaminant in PW since it can create potentially toxic effects near the discharge point, also can significantly contribute to biological oxygen demand (BOD), and hence affects the aquatic or marine ecosystem [6]. Therefore, the removal and measurement of oil in produced water is significant for control processes and for reporting to regulatory authorities. The conventional methods for dealing with wastewater are reinjection into wells, and direct discharge or reuse in case of a thermal loop. From these methods, the more effective method for treating produced water is to reinject it into wells [1,7]. The organic matter from petroleum and industrial wastewater can be treated by several chemicals, physical, and biological methods [8–11]. Involves advanced oxidation, activated sludge process, anaerobic reactors, trickling filters, and membrane bioreactors [12–14]. The physicochemical treatments, such as electrostatic separator, adsorption, are the most efficient for the removal of organic pollutants (oil and grease) from petrochemical wastewater [15,16]. All of these methods except adsorption have several restrictions and involve complex proceedings that are economically infeasible and have their own limitations such as high cost, generation of secondary pollutants, and poor removal efficiency [17].

The adsorption method is the cheaper, simpler, and more suitable method to remove pollutants from wastewater [18]. The adsorption process can be carried out in a batch system or a bed column under continuous conditions [19]. Actual adsorption processes are mostly associated with adsorption in a column. Fixed-bed columns are widely utilized in several chemical industries because of their easy operation [20,21]. The operation involving the use of a column is efficient for adsorption and desorption because it achieves a better utility for the concentration difference known to be a driving force of adsorption. This operation also allows the use of the more effective adsorbents and therefore obtains the best quality of effluent [22]. The advantages of utilizing a fixed-bed column in the treatment of wastewater involve a high-quality removal for inveterate production, easy operation, simplicity, and the possibility of regeneration in situ. Furthermore, it is appropriate for use in pollutants treatment [23,24]. Two models (Thomas model and Yoon–Nelson model) were used to analyze the column performance for the removal of oil and COD produced water by using different types of adsorbents.

The adsorption process uses either activated carbon, carbon nanotubes, fullerene [25] or other adsorbents, such as zeolite, activated alumina, or low-cost adsorbents, such as limestone, rice husk ash and peat [26,27]. Adsorption by activated carbon was found to be superior to other methods of water treatment owing to its design simplicity and its ability to adsorb a wide range of various kinds of adsorbate efficiently [28,29]. Activated carbon is acquired from materials with a high carbon content and a large capacity of adsorption, which is fundamentally determined by their porous structure [30]. It can be utilized as a powder called a powdered activated carbon (PAC), in which form it is mixed with the liquid to be treated and then removed by filtration. Further, it can be utilized as a granular form called a granular activated carbon (GAC), which is packed in adsorption columns [31,32]. Zeolite is an important class of aluminosilicates used as catalysts and adsorbents [33]. An important property of zeolite is its capacity to be easily regenerated while preserving its initial properties. Studies of zeolite adsorption of organic molecules from an aqueous solution are relatively rare [34,35]. Silica gel considers a low-cost adsorbent and has a high surface area and pore volume, it's a good adsorbent for the adsorption of pollutants due of it has mechanical, thermal, and chemical stability. In addition, there are two various types of functional groups; siloxane (Si–O–Si) and silanol (Si–OH) on the surface of silica gel [36]. Adsorption from an aqueous solution depends not only on the zeolite pore structure but also on the competition between the organic adsorbate and water for the adsorption site [37,38]. Although the use of low-cost adsorbents prepared from the waste materials for removal, the different pollutants from aqueous solutions extensively. However, the use of mixed adsorbents to remove oil and COD from produced water is still not fully understood.

The aims of this research are to investigate the possibility of PAC, GAC, zeolite, silica gel, and mixed adsorbents (activated carbon and silica gel) to remove oil and COD from produced water at South Oil Company in Iraq, to compare these types of adsorbents for pollutant removal, and to recommend the mathematical models for the dynamic adsorption of oil and COD onto adsorbents mentioned above from produced water.

2. Materials and experiment

2.1. Adsorbents

Activated carbon (powdered and granular), zeolite, and silica gel that were utilized in this study were obtained from chemical companies in Baghdad/Iraq. The properties of adsorbents were determined by the Brunauer–Emmet–Teller method, and the results are shown in Table 1. The study involved the use of PAC and its conversion to mixed activated carbon with silica gel. Silica gel is the colloidal form of silica (SiO_2) and usually resembles coarse white sand. A mixture of a homogeneous proportion (1:1) wt.% of the PAC and silica gel was prepared for the mixed adsorbents.

2.2. Preparation of synthetic produced water

Samples of the produced water were prepared by the homogenous mixing of water, oil, clay (bentonite), and salt food (NaCl). The synthetic produced water (SPW) was found on the chemical properties of samples collected from Iraqi natural oil fields (South Oil Company in Basra, Iraq) (composition of chemical materials: salt, 100 g; clay, 0.4 g; oil, 0.04 g, 0.1 g, 0.5 g, and 1 g (for deriving various concentrations) in 1 L of distilled water). The mixture was blended at a speed of 2,000 rpm for 20 min to obtain a regular diffusion of additive chemical materials. SPW samples have been prepared at the required concentrations. Table 2 summarizes the SPW characteristics used in this research.

The pollutants in the water were analyzed by using special analytical instruments. Oil content analyzer HORIBA instrument model OCMA-350 to measure the concentration of oil content in SPW, and COD instrument model Lovibond SN11/25370 to measure the concentration of COD in SPW.

Table 1
Properties of the adsorbents

Properties	Powder activated carbon (PAC)	Zeolite	Granular activated carbon (GAC)	Silica gel
Real density (g/cm^3)	0.423	2.430	1.563	0.784
Surface area (m^2/g)	824.34	303.45	504.35	615.61
Pore volume (cm^3/g)	0.753	0.503	0.632	0.693
Pore diameter (nm)	3.12	3.01	3.07	3.10

Table 2
Characteristics of synthetic produced water

Parameter	Range
Oil (ppm)	40–1,000
COD (ppm)	1,250–28,500
Turbidity (NTU)	320
TDS (ppm)	100,000
pH	7

2.3. Continuous adsorption experiments

The continuous adsorption process was studied in a fixed-bed column made of a pyrex glass tube having an internal diameter of 1 cm and a height of 50 cm. A layer of glass wool was placed at the bottom of the column to prohibit the loss of adsorbents. In fixed-bed adsorption, a sample of produced water was pumped up from a container to the top of the column by a peristaltic pump to avoid channeling due to gravity [39], and the samples were taken at intervals from the bottom of the column. Fig. 1 demonstrates the schematic diagram of the process. To obtain the conditions that are best suited to the hydrodynamic parameters for the adsorption column, adsorption experiments were conducted at different flow rates (1.25, 2.25, and 3.15 mL/min), different oil concentrations (40; 100; 500; and 1,000 ppm), different COD concentrations (1,350; 2,500; 13,500; and 28,500 ppm) pH = 7, and ambient temperature.

2.4. Fixed-bed-column data analysis for oil and COD adsorption on adsorbents

From the analysis of the pollutant removal from the produced water, the shape of the breakthrough curve was obtained, that is, the shape that determines the performance of the column studied by plotting curves. The maximum capacity of the column, q_{total} (mg), for a specific flow rate and feed concentration is equal to the area under the plot of the adsorbed of oil and COD concentration. This can be expressed as $(1 - C/C_0)$ ppm, vs. effluent time t (min) and is obtained from Eq. (1):

$$q_{total} = \frac{QC_0}{1{,}000}\int_{t=0}^{t=t_{total}}\left(1-\frac{C}{C_0}\right)dt \quad (1)$$

where C is the effluent concentration, C_0 is the influent concentration, and Q is the volumetric flow rate (mL/min), which can be determined by dividing the volume of effluent (V_{eff}, mL) by the total time (t_{total}, min) as in Eq. (2):

$$Q = \frac{V_{eff}}{t_{total}} \quad (2)$$

where q_{exp} (mg/g) is the equilibrium uptake, can be determined from Eq. (3):

$$q_{exp} = \frac{q_{total}}{m} \quad (3)$$

where m (g) is the total amount of adsorbent in the column.

where m_{total} is the total amount of pollutants sent to the column, which is determined from Eq. (4):

$$m_{total} = \frac{C_0 Q_{total}}{1{,}000} \quad (4)$$

The percentage removal of the total amount of pollutants can be calculated from Eq. (5) [40]:

$$R = \frac{q_{total}}{m_{total}} \times 100 \quad (5)$$

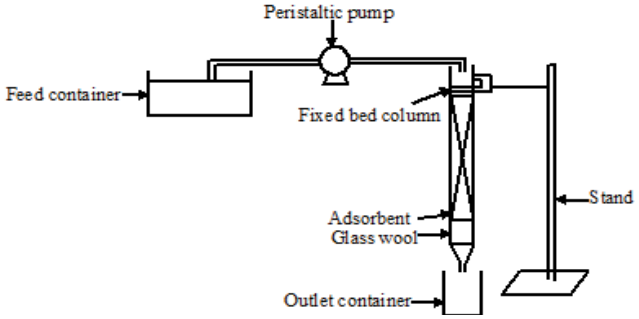

Fig. 1. Schematic diagram of a continuous fixed bed process.

3. Results and discussion

3.1. Effect of flow rates

Fig. 2 demonstrate the breakthrough curves for the adsorption of oil and COD by activated carbons, zeolite, and silica gel at various flow rates (1.25, 2.25, and 3.15 mL/min) with a bed depth of 2 cm, an initial concentration of oil of 40 ppm, and a COD concentration of 1,350 ppm.

The results showed that the removal efficiency and adsorbed quantity decreased with the increase of the flow rate for all types of adsorbents. This behavior can be

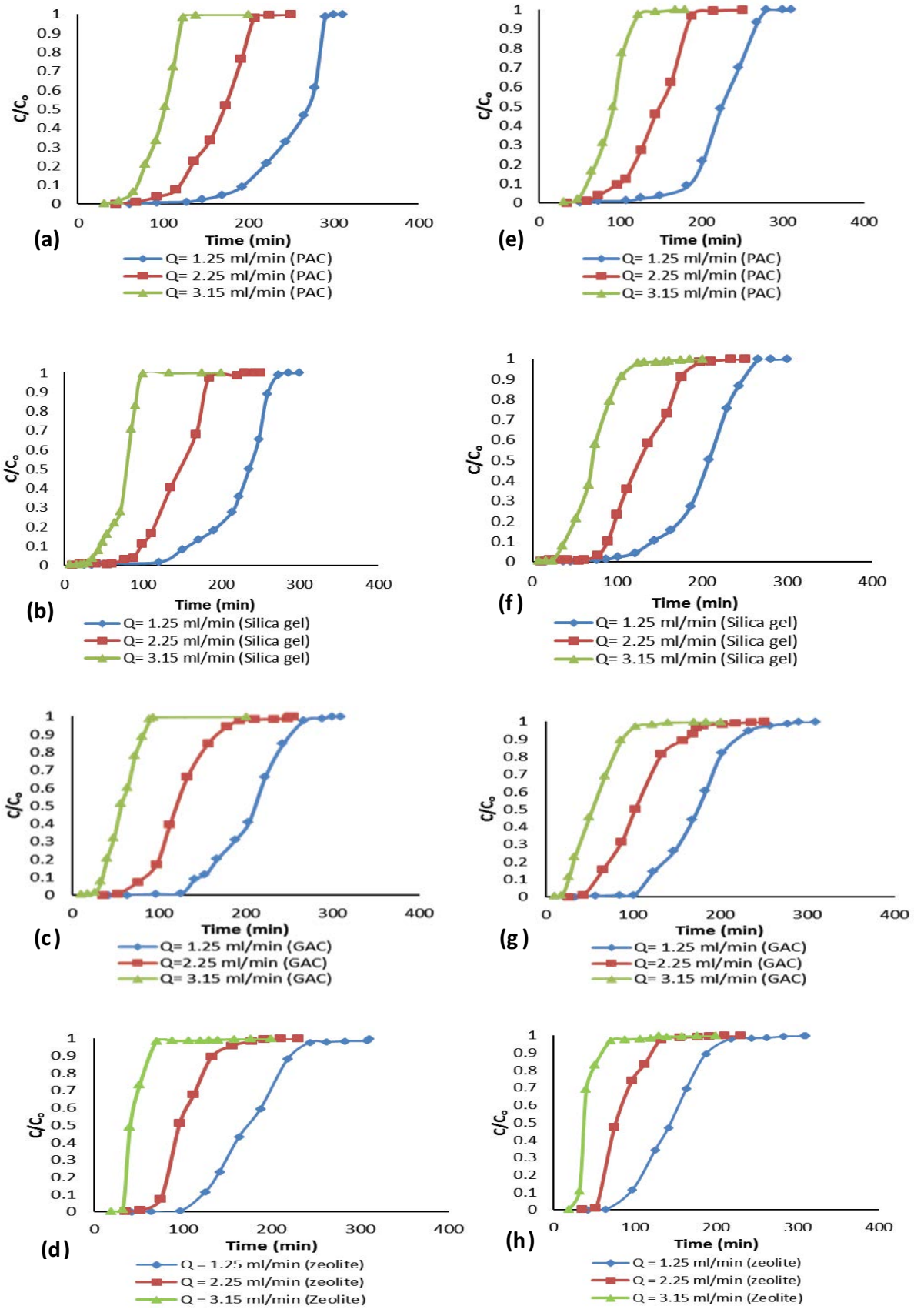

Fig. 2. Breakthrough curves of (a–d) oil adsorption and (e–h) COD by using different adsorbents.

explained by the insufficient residence time of the solute in the fixed-bed column and the diffusion of the solute into the pores of the adsorbent (rapid saturation of the filter bed) causes to decrease in the exchange speed between the adsorbent and pollutants. Therefore, the solute left the column before equilibrium was reached and the breakthrough curves became steeper and reached the breakthrough point more quickly when the flow rate is increased. This means that the contact time between the adsorbate and the adsorbent was minimized, thus leading to a decrease adsorption efficiency. These results agree with those obtained by Fathy et al. [41], El-Sayed et al. [42], and El Mouhri et al. [43].

On the other hand, the best performance of the column appeared when the flow rate was low and noted a longer breakthrough and exhaustion time (sufficient time for adsorption), cause the increase of speed exchange between sorbent and sorbed, therefore leads to an increase in the capacity adsorption and removal efficiency of oil and COD with decreased flow rate.

The maximum adsorption capacity of oil and COD was 85.78 and 71.83 mg/g, respectively, by PAC, while the minimum adsorption capacity by zeolite, this result due to the large surface area of PAC and small surface area of zeolite. The porous nature and the high internal surface area of PAC are favorable characteristics for the adsorption process, the adsorption capacity of the activated carbon is associated with a very high surface area per unit volume [44]. Whilst the adsorption capacity of pollutants by silica gel was higher than the adsorption capacity of pollutants by GAC for the same reason previous. As shown in Fig. 2, the highest efficiency removal of oil and COD was at the lowest flow rate (1.15 mL/min) by PAC; therefore, it was considered the best adsorbent for the adsorption of organic pollutants.

3.2. Effect of initial oil and COD concentrations

Fig. 3 shows the effect of oil and COD concentration on the breakthrough curves at the flow rate of 1.15 mL/min and bed depth of 2 cm. It observed the decrease in breakthrough and exhaustion times upon the oil concentration increased from 40 to 1,000 ppm and COD from 1,350 to 28,500 ppm.

At a high concentration, the availability of the molecules for the adsorption sites was greater, which led to a higher uptake of oil and COD at a higher concentration, although the breakthrough time was shorter than that of lower concentrations. Besides, at a high concentration, the isotherm gradient was smaller, yielding a high driving force for the adsorbent. Thus, the equilibrium was attained faster for a high concentration of COD and oil, which leads to increased adsorption capacity [45].

On the other hand at low concentration, the decreased adsorption capacity of the fixed-bed column, due to a negative effect on the mass transfer rate between adsorbent and pollutants (lower mass transfer flux from the bulk solution to the particle surface) owing to weak driving force [46].

The maximum adsorption capacity of oil and COD were 377.82 and 275.4 mg/g by GAC, 410.54 and 344.8 mg/g by silica gel, 282.36 and 196.2 mg/g when zeolite was used, 551.846 and 434.962 mg/g by PAC, respectively. Therefore, PAC performed better adsorption properties than other adsorbents in the adsorption of oil and COD. These results align with those obtained by Mohammed et al. [47].

3.3. Mixed adsorbents for removal of oil and COD from produced water

The behavior of the oil and COD adsorption process onto mixed adsorbents (activated carbon and silica gel) was investigated at 40 ppm and 1,350 ppm initial oil and COD concentrations, the flow rate of 1.25 mL/min, and a bed height of 2 cm. In Fig. 4 depicts, the results of the breakthrough and exhausting times for oil and COD were 321 and 338 min; the removal percentage of oil and COD reached 83.63% and 78.81%, respectively, and the equilibrium adsorption capacity for oil and COD was 108.38 and 96.74 mg/g, respectively.

Moreover, a mixed adsorbent was more efficient to remove pollutants from produced water in comparison with a single adsorbent (activated carbon, silica gel, and zeolite) and the adsorption capacity is greater due to the presence of a number of surface sites of various structure. This result can be explained due to the mixed adsorbents (PAC and silica gel) have a higher surface area and pore volume compared with other adsorbents as shown in Table 1, therefore, mixed adsorbents have more effective surface area for adsorption of oil and COD and the diffusion will be much easy, and thus the adsorption kinetics will be higher so, the removal efficiency and adsorption capacity were higher [48].

3.4. Column dynamics models

Both the Thomas model and the Yoon–Nelson model were applied. The linear form of the Thomas model for adsorption column is expressed as Eq. (6) [49]:

$$\ln\left(\frac{C}{C_0}-1\right)=\frac{K_{TH}q_{TH}M}{Q}-\frac{K_{TH}C_0V}{Q} \tag{6}$$

where C (mg/L) is the effluent concentration, C_0 (mg/L) is the initial concentration, K_{TH} (mL/min mg) is the constant of the Thomas model, q_{TH} (mg/g) is the predicted adsorption capacity, M (g) the mass of adsorbent, Q (mL/min) the flow rate, and V (mL) is the volume of the bed.

The Yoon–Nelson linearized model for a single component system is given as Eq. (7) [50,22]:

$$\ln\left(\frac{C}{C_0-C}\right)=K_{YN}t-K_{YN}\tau \tag{7}$$

where τ (min) is the time required for 50% adsorbate breakthrough, t (min) is the breakthrough (sampling) time, and K_{YN} (min^{-1}) is the constant rate. The breakthrough curves were plotted for the adsorbate by the Eqs. (6) and (7) for two models (Thomas and Yoon–Nelson) at different concentrations and flow rates. Thomas and Yoon–Nelson parameters are listed in Tables 3–7. From Tables 3–7, it can be observed that correlation coefficients (R^2) for the Thomas model are higher than those from the Yan model, and the experimental adsorption capacity of oil and COD has fitted

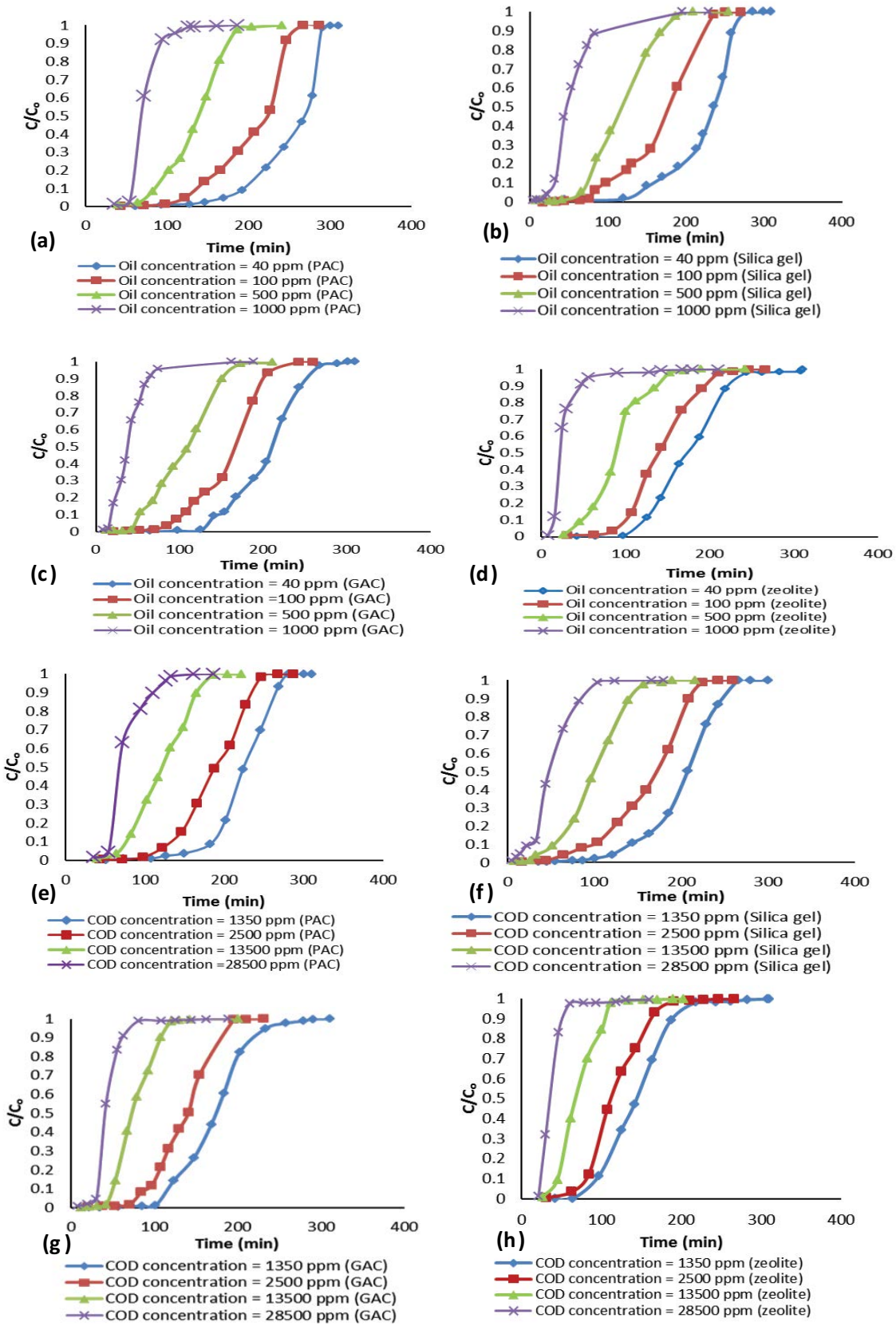

Fig. 3. Breakthrough curves of (a–d) oil adsorption and (e–h) COD adsorption on different concentration (flow rate = 1.25 mL/min, L = 2 cm, and pH = 7) by using different adsorbents.

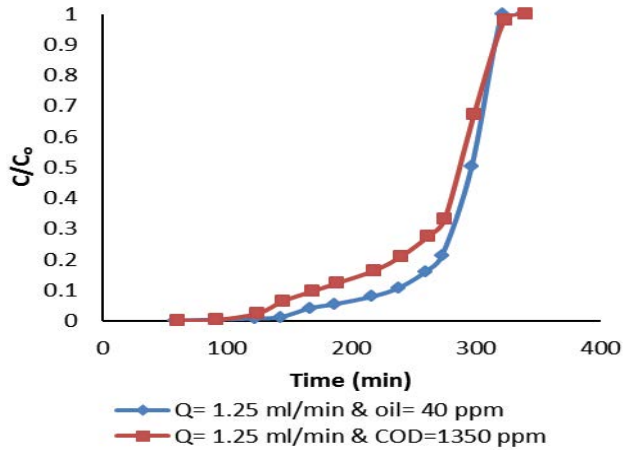

Fig. 4. Breakthrough curves of oil and COD adsorption by using mixed adsorbents adsorbent (flow rate = 1.25 mL/min, L = 2 cm, and pH = 7).

the Thomas model well. Therefore, the Thomas model can be considered as a more suitable kinetic model for describing oil and COD adsorption in a fixed-bed column of activated carbon, silica gel, zeolite, and mixed adsorbents. The mechanism of this model that when the molecules of oil and COD are adsorbed, they moved and fixed on the surface of the adsorbents. If a molecule has an affinity for adsorbents, it will be attracted to the adsorbents, until it reaches equilibrium [51].

According to Tables 3–7, it can be concluded that all of the parameters (the inlet oil and COD concentration as well as the flow rate) influenced the Thomas model constants (K_{TH}) and (q_{TH}) and the Yan model constants (K_{YN}) and (q_Y). As the flow rate increased from 1.25 to 3.15 mL/min, the values of K_{TH} increased, and the values of q_{TH} decreased. The reason is that the driving force for adsorption is the concentration difference between the oil and COD on the adsorbents in the produced water. However, when the inlet oil and COD concentration increased from 40 to 1,000 ppm, q_{TH} increased because of the driving force for adsorption, although the K_{TH} value decreased because of the rise in the driving force for adsorption stemming from the higher oil and COD concentration.

The results also show that the rate constants, K_{YN} and q_Y, increased with an increased flow rate and initial oil and COD concentration. This is due to the increased rivalry between the molecules of the adsorbate at the site of adsorption and by the high concentration of oil and COD a fact that is obvious in the state of increasing the uptake rate [39]. This observation is in agreement with that made by Fathy et al. [41].

3.5. Modeling the behavior of oil and COD in a fixed-bed column adsorption

The performance of adsorption onto an adsorbent was evaluated by the mathematical model for the simulation of adsorption processes to predict adsorption behavior [52]. The Thomas model was chosen to fit the data of the experiments.

Fig. 5 presents the experimental breakthrough curves obtained for each activated carbon, silica gel, zeolite, and mixed adsorbent at a flow rate of 1.25 mL/min, inlet oil concentration of 40 ppm, COD of 1,350 ppm, and a bed height of 2 cm. The theoretical curves calculated according to the proposed model are also shown in Fig. 5. It can be seen that the theoretical curve is in agreement with the experimental curve.

3.6. Comparison between different adsorbents for oil and COD removal

Fig. 6 shows a comparison between mixed adsorbents and other adsorbents (PAC, GAC, silica gel, and zeolite) for exploring the ability of these adsorbents of COD and oil adsorption. Fig. 6 also shows that mixed adsorbents were more efficient in removing oil (R% = 83.63) and COD (R% = 78.81) while the percentage removal of oil (R% = 58.58) and COD (R% = 52.49) decreased when zeolite was utilized. Fig. 6 further reveals that when GAC is used as an adsorbent for removal pollutant, we obtained the percentage removal of oil as R% = 64.87, and COD as R% = 60.94, but when PAC was utilized, the removal of oil reached 72.98% and COD reached 69.5%. Where the percentages removal of pollutants by different adsorbents were arranged as follows: (Re% mixed adsorbents > Re% PAC > Re% silica gel > Re% GAC > Re% zeolite). This arranged can be related to the characteristics (surface area, pore volume) of the adsorbents that were used, where the surface area was 824.34, 615.61, 504.35, and 303.45 m^2/g and pore volume was 0.753, 0.693, 0.632, and 0.503 cm^3/g for PAC, silica gel, GAC, zeolite, respectively. This can be explained when the surface area (large pore size) of the adsorbent is increased the amount of adsorption capacity increases due to a decrease in the diameter of the adsorbent particles, because of increasing the active sites and the activity of adsorption kinetic for adsorbent to adsorb oil and COD from produces water and therefore the increased removal efficiency of organic pollutants [53]. On the other hand, the smaller particle sizes reduce the internal diffusion and mass transfer limitation to penetrate the adsorbate inside the adsorbent. As a result, the removal efficiency of organic pollutants was low for adsorbents that possess small particle sizes (small surface area) [54]. Moreover, these results illustrate the higher removal of pollutants was by mixed adsorbents and the lower removal was by zeolite. As well as, the results show the possibility of using mixed adsorbents as an adsorbent for the removal of pollutants as by so doing, an efficient removal percentage can be attained.

4. Conclusion

The present study deals with the investigation of removing oil and COD from synthetic produced water by fixed-bed adsorption using different adsorbents (PAC, GAC, zeolite, silica gel, and mixed adsorbent), and comparison between them. Also, the effects of flow rate 1.25, 2.25, and 3.15 mL/min and concentration of oil 40; 100; 500; and 1,000 mg/L and COD 1,350; 2,500; 13,500; 28,500 mg/L were studied on pollutants removal. The results illustrated the uptake capacity of adsorbents decreased when the flow rate increased and concentration decreased. The Thomas and Yoon–Nelson models were applied in the experiments, but the former turned out to be the better model for describing

Table 3
Kinetic parameters for adsorption of oil and COD on powdered activated carbon in a fixed bed column

Kinetic model	Flow rates			Oil concentration		
	1.25 mL/min	2.25 mL/min	3.15 mL/min	100 ppm	500 ppm	1,000 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	0.098	0.13	0.215	5.41	2.98	0.67
$q_{TH} \times 10^{-2}$ (mg/g)	34.7	29.5	28.9	4.53	17.8	27.8
R^2	0.900	0.958	0.971	0.933	0.975	0.978
Yoon–Nelson						
K_{YN} (min^{-1})	7.82	7.98	8.10	5.54	6.29	6.87
$q_Y \times 10^{-2}$ (mg/g)	3.75	6.88	9.87	7.56	46.4	78.7
R^2	0.869	0.897	0.892	0.872	0.917	0.958
				COD concentration		
				2,500 ppm	13,500 ppm	28,500 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	0.034	0.043	0.215	0.19	0.048	0.028
$q_{TH} \times 10^{-3}$ (mg/g)	90.3	77.7	76.5	110.7	374.7	586.2
R^2	0.941	0.912	0.943	0.949	0.958	0.964
Yoon–Nelson						
K_{YN} (min^{-1})	6.41	6.6	8.08	6.51	6.54	6.77
$q_Y \times 10^{-2}$ (mg/g)	3.76	6.90	9.90	191.1	105.0	225.7
R^2	0.883	0.803	0.837	0.831	0.900	0.959

Table 4
Kinetic parameters for adsorption of oil and COD on zeolite in a fixed bed column

Kinetic model	Flow rates			Oil concentration		
	1.25 mL/min	2.25 mL/min	3.15 mL/min	100 ppm	500 ppm	1,000 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	9.60	10.6	19. 90	5.2	1.03	0.87
$q_{TH} \times 10^{-2}$ (mg/g)	30.5	25.9	24.4	34.7	129.3	148.6
R^2	0.985	0.934	0.964	0.941	0.976	0.978
Yoon–Nelson						
K_{YN} (min^{-1})	6.93	7.12	7.44	5.27	5.34	5.87
$q_Y \times 10^{-2}$ (mg/g)	3.87	6.81	9.95	7.7	47.3	80.7
R^2	0.923	0.912	0.954	0.80	0.952	0.961
				COD concentration		
				2,500 ppm	13,500 ppm	28,500 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	0.28	0.43	0.61	0.21	0.04	0.02
$q_{TH} \times 10^{-2}$ (mg/g)	706.2	643.2	620.1	808.8	2,840	3,521
R^2	0.977	0.964	0.978	0.981	0.972	0.975
Yoon–Nelson						
K_{YN} (min^{-1})	5.87	6.36	6.80	5.65	6.29	6.87
$q_Y \times 10^{-2}$ (mg/g)	3.88	7.16	9.61	194.1	1,068	2,328
R^2	0.933	0.957	0.965	0.902	0.944	0.956

Table 5
Kinetic parameters for adsorption of oil and COD on silica gel in a fixed bed column

Kinetic model	Flow rates			Oil concentration		
	1.25 mL/min	2.25 mL/min	3.15 mL/min	100 ppm	500 ppm	1,000 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	10.64	12.76	19.02	4.85	2.67	1.23
$q_{TH} \times 10^{-2}$ (mg/g)	17.53	14.31	11.56	20.37	78.92	104.1
R^2	0.943	0.926	0.914	0.954	0.934	0.928
Yoon–Nelson						
K_{YN} (min^{-1})	3.86	4.02	5.03	1.99	2.67	3.65
$q_Y \times 10^{-2}$ (mg/g)	2.07	3.27	7.88	39.03	68.09	75.95
R^2	0.887	0.904	0.896	0.876	0.846	0.887
				COD concentration		
				2,500 ppm	13,500 ppm	28,500 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	0.27	0.34	0.51	0.37	0.21	0.17
$q_{TH} \times 10^{-2}$ (mg/g)	462.8	407.3	378.2	189.2	223.6	605.3
R^2	0.916	0.908	0.930	0.926	0.935	0.906
Yoon–Nelson						
K_{YN} (min^{-1})	2.08	3.0	3.93	2.06	2.95	3.21
$q_Y \times 10^{-2}$ (mg/g)	87.9	173.8	264.8	171.01	1,017	2,203
R^2	0.876	0.888	0.907	0.887	0.895	0.867

Table 6
Kinetic parameters for adsorption of oil and COD on granular activated carbon in a fixed bed column

Kinetic model	Flow rates			Oil concentration		
	1.25 mL/min	2.25 mL/min	3.15 mL/min	100 ppm	500 ppm	1,000 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	13.28	15.66	22.82	7.96	4.12	1.23
$q_{TH} \times 10^{-2}$ (mg/g)	20.6	17.7	15.5	27.04	89.68	104.1
R^2	0.882	0.903	0.944	0.931	0.908	0.967
Yoon–Nelson						
K_{YN} (min^{-1})	5.17	5.29	8.48	3.39	4.27	5.98
$q_Y \times 10^{-2}$ (mg/g)	3.82	7.07	10.18	48.17	77.80	84.47
R^2	0.739	0.895	0.846	0.881	0.827	0.907
				COD concentration		
				2,500 ppm	13,500 ppm	28,500 ppm
Thomas						
$K_{TH} \times 10^4$ (mL/min/mg)	0.44	0.56	0.72	0.5	0.35	0.26
$q_{TH} \times 10^{-2}$ (mg/g)	515.0	459.6	403.8	213.4	242.4	634.9
R^2	0.912	0.881	0.899	0.926	0.935	0.962
Yoon–Nelson						
K_{YN} (min^{-1})	3.87	4.19	5.36	3.75	4.28	5.97
$q_Y \times 10^{-2}$ (mg/g)	106.6	196.0	282.4	196.15	1,092	2,426
R^2	0.878	0.794	0.781	0.854	0.865	0.917

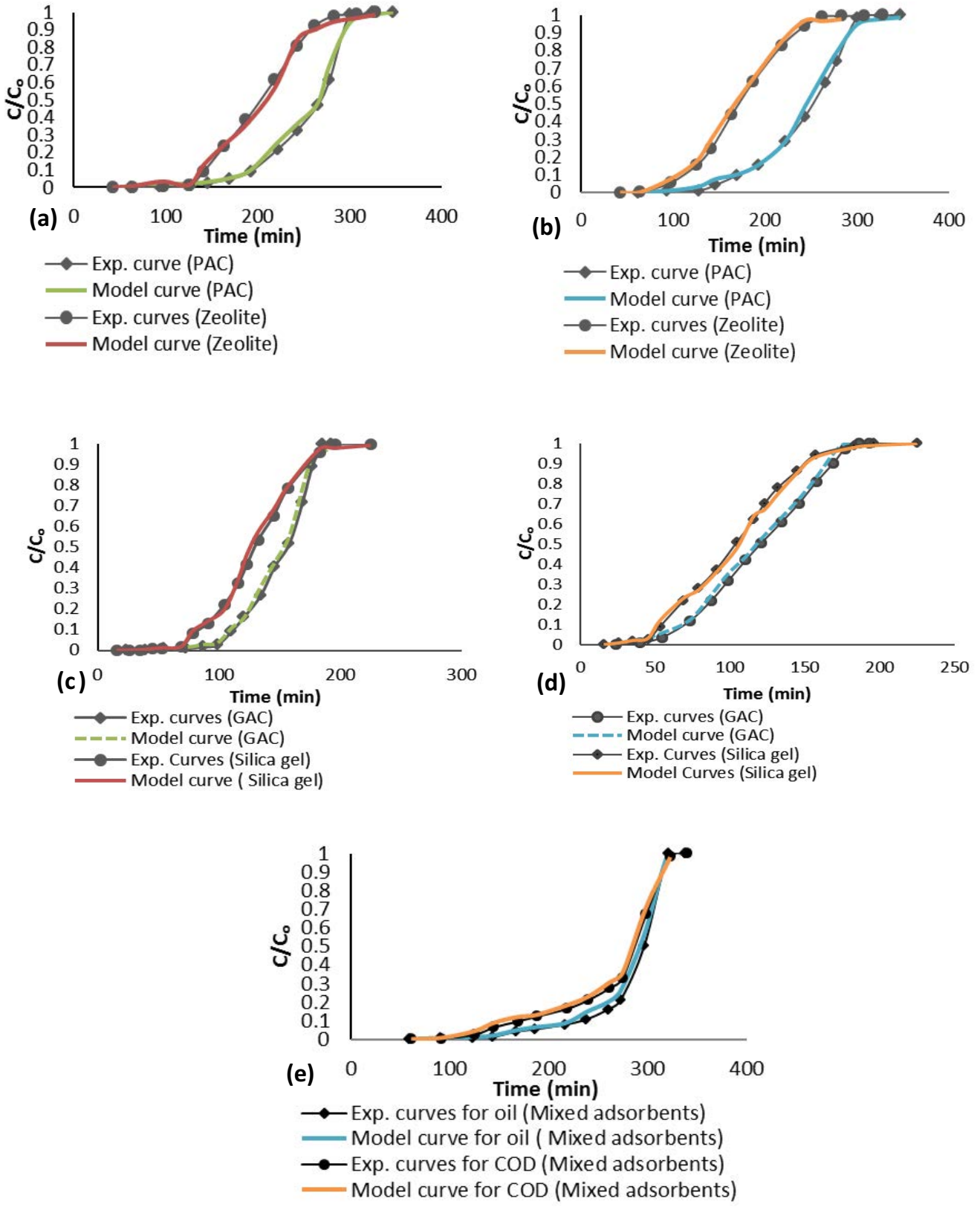

Fig. 5. Comparison of predicted and experimental curves for the adsorption of oil and COD (a and b) by PAC and zeolite (c) by GAC (d) by mixed adsorbents.

Table 7
Kinetic parameters for adsorption of oil and COD on mixed adsorbents in a fixed bed column

Pollutants	Kinetic model					
	Thomas			Yoon–Nelson		
	$K_{TH} \times 10^4$ (mL/min mg)	$q_{TH} \times 10^{-2}$ (mg/g)	R^2	K_{YN} (min^{-1})	$q_Y \times 10^{-2}$ (mg/g)	R^2
Oil	8.8	32.38	0.984	7.08	3.74	0.868
COD	0.029	1,503.2	0.958	6.80	103.25	0.814

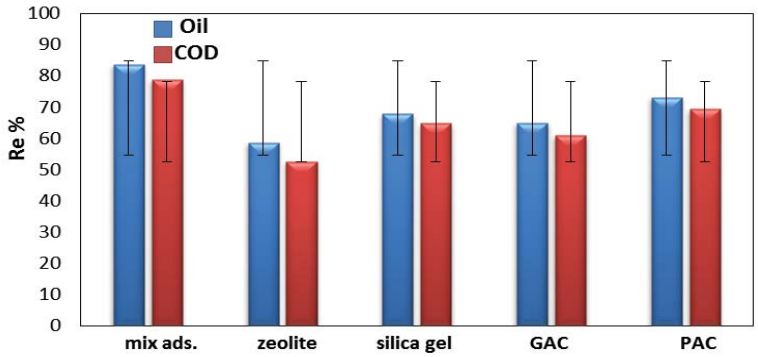

Fig. 6. Comparison between adsorbents in fixed bed for removal of oil and COD from produced water.

the kinetic experimental data. Finally, the highest removal of oil and COD (83.62% and 78.81%) was attained at a flow rate = 1.25 mL/min, oil concentration = 40 mg/L, and COD concentration = 1,350 mg/L by utilizing mixed adsorbents prepared from activated carbon and silica gel compared with the other types of adsorbents were utilized in this study (Re% by mixed adsorbents > Re% by PAC > Re% by silica gel > Re% by GAC > Re% by zeolite). Therefore, it appears to be the more attractive alternative and better for produced-water treatment. While when compared the single adsorbents, the present study proved the best adsorption efficiency of oil and COD was by PAC (72.98% and 69.5%) comparing with GAC, silica gel, and zeolite because it has the highest surface area for adsorption of pollutants.

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References

[1] R.T. Duraisamy, A.H. Beni, A. Henni, In: W. Elshorbagy, State of the Art Treatment of Produced Water, Water Treatment, Intechopen Publication, UAE, 2013, pp. 199–222.
[2] A.Z. Rodriguez, H. Wang, L. Hu, Y. Zhang, P. Xu, Treatment of produced water in the Permian basin for hydraulic fracturing: comparison of different coagulation processes and innovative filter media, Water, 12 (2020) 770–786, doi: 10.3390/w12030770.
[3] M.S. Kuyukina, A.V. Krivoruchko, I.B. Ivshina, Advanced bioreactor treatments of hydrocarbon-containing wastewater, Appl. Sci., 10 (2020) 831–850, doi: 10.3390/app10030831.
[4] A.A. Olajire, Recent advances on the treatment technology of oil and gas produced water for sustainable energy industry–mechanistic aspects and process chemistry perspectives, Chem. Eng. J. Adv., 4 (2020) 100049–100074, doi: 10.1016/j.ceja.2020.100049.
[5] A.N. Ernawan, A. Fachrizal, A. Wijaya, B. Syahreza, M.R. Alkhandi, M. Firdaus, M. Dyatmahendri, R. Ananda, W. Rustam, M.K. Afdhol, T. Erfando, Review of absorption oil content in water injection, Preprints, 1 (2020) 1–13, doi: 10.20944/preprints202001.0079.v1.
[6] E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, Int. J. Low-Carbon Technol., 9 (2014) 157–177.
[7] U.W. Siagian, S. Widodo, A.K. Wardani, I.G. Wenten, Oilfield produced water reuse and reinjection with membrane, MATEC Web Conf., 156 (2018) 08005–08015, doi: 10.1051/matecconf/201815608005.
[8] A. Pallavi, K. Sunil, K. Kavita, A review on research for industrial wastewater treatment with special Emphasis on distillery effluent, Int. J. Ethics Eng. Manage. Educ., 1 (2014) 1–4.
[9] D. Aljuboury, P. Palaniandy, H.B. Abdul Aziz, S. Feroz, Treatment of petroleum wastewater by conventional and new technologies–A review, Global Nest J., 19 (2017) 439–452.
[10] D.G. Rao, R. Senthilkumar, J.A. Byrne, S. Feroz, Eds., Wastewater Treatment: Advanced Processes and Technologies, CRC Press, London, 2012.
[11] T.M. Albayati, Application of nanoporous material MCM-41 in a membrane adsorption reactor (MAR) as a hybrid process for removal of methyl orange, Desal. Water Treat., 151 (2019) 138–144.
[12] J. Jyoti, D. Alka, S.J. Kumar, Application of membrane-bioreactor in waste-water treatment: a review, Int. J. Chem. Chem. Eng., 3 (2013) 115–122.
[13] S.R. Dhokpande, S.J. Kulkarni, D.J.P. Kaware, A review on research on application of trickling filters in removal of various pollutants from effluent, Int. J. Eng. Sci. Res. Technol., 3 (2014) 359–365.
[14] H.A. Gasim, S.R.M. Kutty, M.H. Isa, L.T. Alemu, Optimization of anaerobic treatment of petroleum refinery wastewater using artificial neural networks, Res. J. Appl. Sci. Eng. Technol., 6 (2013) 2077–2082.
[15] H.D. Basheer, M. Wan, A. Abdul, Treatment technologies for petroleum refinery effluents: a review, Process Saf. Environ. Prot., 89 (2011) 95–105.

[16] G. Kamińska, M. Dudziak, E. Kudlek, J. Bohdziewicz, Preparation, characterization and adsorption potential of grainy halloysite–CNT composites for anthracene removal from aqueous solution, Nanomaterials, 9 (2019) 890–913, doi: 10.3390/nano9060890.
[17] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch and bulk removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv., 2 (2012) 8381–8389.
[18] T.M. Albayati, A.A. Sabri, R.A. Alazawi, Separation of methylene blue as pollutant of water by SBA-15 in a fixed-bed column, Arabian J. Sci. Eng., 41 (2016) 2409–2415.
[19] G. Kamińska, J. Bohdziewicz, Potential of various materials for adsorption of micropollutants from wastewater, Environ. Prot. Eng., 42 (2016) 161–178.
[20] 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) 1–7, doi: 10.1016/j.heliyon.2020.e03253.
[21] H. Patel, Fixed-bed column adsorption study: a comprehensive review, Appl. Water Sci., 9 (2019) 1–17.
[22] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochem., 39 (2004) 599–613.
[23] T.M. Albayati, K.R. Kalash, Polycyclic aromatic hydrocarbons adsorption from wastewater using different types of prepared mesoporous materials MCM-41in batch and fixed bed column, Process Saf. Environ. Prot., 133 (2020) 124–136.
[24] G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett., 17 (2019) 145–155.
[25] G. Kamińska, Removal of organic micropollutants by grainy bentonite-activated carbon adsorbent in a fixed bed column, Water, 10 (2018) 1791, doi: 10.3390/w10121791.
[26] Z. Daud, M.A. Rosli, A.A. Abdul Latiff, M.B. Ridzuan, H. Awang, A. Abdul Halim, Micro-Peat as a Potential Low-Cost Adsorbent Material for COD and NH_3–N Removal, T. Ohashi, M. Yahaya, Eds., Defect and Diffusion Forum, Vol. 382, Trans Tech Publications Ltd., Switzerland, 2018, pp. 297–301.
[27] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination, 262 (2010) 31–35.
[28] N. Elhadiri, M. Benchanaa, R. Chikri, Activated carbon for dyes removal: modeling and understanding the adsorption process, J. Chem., 2020 (2020) 2096834–2096843, doi: 10.1155/2020/2096834.
[29] Y. Kuang, X. Zhang, S. Zhou, Adsorption of methylene blue in water onto activated carbon by surfactant modification, Water, 12 (2020) 587–606, doi: 10.3390/w12020587.
[30] G. Özsin, M. Kılıç, E. Apaydın-Varol, A.E. Pütün, Chemically activated carbon production from agricultural waste of chickpea and its application for heavy metal adsorption: equilibrium, kinetic, and thermodynamic studies, Appl. Water Sci., 9 (2019) 1–14.
[31] L. San-Pedro, R. Méndez-Novelo, E. Hernández-Núñez, M. Flota-Bañuelos, J. Medina, G.Giacomán-Vallejos, Selection of the activated carbon type for the treatment of landfill leachate by Fenton-adsorption process, Molecules, 25 (2020) 3023–3039, doi: 10.3390/molecules25133023.
[32] V.K. Gupta, Suhas, Application of low cost adsorbents for dye removal - a review, J. Environ. Manage., 90 (2009) 2313–2342.
[33] E. Nyankson, J.K. Efavi, A. Yaya, G. Manu, K. Asare, J. Daafuor, R.Y. Abrokwah, Synthesis and characterisation of zeolite-A and Zn-exchanged zeolite-A based on natural aluminosilicates and their potential applications, Cogent Eng., 5 (2018) 1440480–1440504, doi: 10.1080/23311916.2018.1440480.
[34] I. Vera-Puerto, M. Saravia, J. Olave, C. Arias, E. Alarcon, H. Valdes, Potential application of chilean natural zeolite as a support medium in treatment wetlands for removing ammonium and phosphate from wastewater, Water, 12 (2020) 1156–1171, doi: 10.3390/w12041156.
[35] H.T. Shu, D. Li, A.A. Scala, Y.H. Ma, Adsorption of small organic pollutants from aqueous streams by aluminosilicate-based microporous materials, Sep. Purif. Technol., 11 (1997) 27–36.
[36] A. Bilgiç, A. Çimen, Removal of chromium(VI) from polluted wastewater by chemical modification of silica gel with 4-acetyl-3-hydroxyaniline, RSC Adv., 9 (2019) 37403–37414.
[37] H. Ramezani, S.N. Azizi, G. Cravotto, Improved removal of methylene blue on modified hierarchical zeolite Y: achieved by a "destructive-constructive" method, Green Process. Synth., 8 (2019) 730–741.
[38] M. Khalid, G. Joly, A. Renaud, P. Magnoux, Removal of phenol from water by adsorption using zeolites, Ind. Eng. Chem. Res., 43 (2004) 5275–5280.
[39] M. Fathy, T.A. Moghny, M.A. Mousa, A.A. El-Bellihi, A.E. Awadallah, Synthesis of transparent amorphous carbon thin films from cellulose powder in rice straw, Arabian J. Sci. Eng., 42 (2017) 225–233.
[40] S. De, A. Maiti, Arsenic Removal from Contaminated Groundwater, Energy and Resources Institute (TERI), 2012.
[41] M. Fathy, M. El-Sayed, M. Ramzi, O.H. Abdelraheem, Adsorption separation of condensate oil from produced water using ACTF prepared of oil palm leaves by batch and fixed bed techniques, Egypt. J. Pet., 27 (2018) 319–326.
[42] M. El-Sayed, M. Ramzi, R. Hosny, M. Fathy, T.A. Moghny, Breakthrough curves of oil adsorption on novel amorphous carbon thin film, Water Sci. Technol., 73 (2016) 2361–2369.
[43] G. El Mouhri, M. Merzouki, H. Belhassan, Y. Miyah, H. Amakdouf, R. Elmountassir, A. Lahrichi, Continuous adsorption modeling and fixed bed column studies: adsorption of tannery wastewater pollutants using beach sand, J. Chem., 2020 (2020) 7613484–7613493, doi: 10.1155/2020/7613484.
[44] C. Zheng, L. Zhao, X. Zhou, Z. Fu, A. Li, Treatment technologies for organic wastewater, Water Treat., 11 (2013) 250–286.
[45] S.H. Nekoo, S. Fatemi, Experimental study and adsorption modeling of COD reduction by activated carbon for wastewater treatment of oil refinery, Iran. J. Chem. Chem. Eng., 32 (2013) 81–89.
[46] J. Abdi, H. Abedini, MOF-based polymeric nanocomposite beads as an efficient adsorbent for wastewater treatment in batch and continuous systems: modelling and experiment, Chem. Eng. J., 400 (2020) 125862–125914, doi: 10.1016/j.cej.2020.125862.
[47] S.A. Mohammed, I. Faisal, M.M. Alwan, Oily wastewater treatment using expanded beds of activated carbon and zeolite, Iraqi J. Chem. Pet. Eng., 12 (2011) 1–12.
[48] C. Patawat, K. Silakate, S. Chuan-Udom, N. Supanchaiyamat, A.J. Hunt, Y. Ngernyen, Preparation of activated carbon from *Dipterocarpus alatus* fruit and its application for methylene blue adsorption, RSC Adv., 10 (2020) 21082–21091.
[49] H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc., 66 (1944) 1664–1666.
[50] Y.H. Yoon, J.H. Nelson, Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life, Am. Ind. Hyg. Assoc. J., 45 (1984) 509–516.
[51] M.H. El-Naas, M.A. Alhaija, In: C.R. Brennan, Modeling of Adsorption Processes, Mathematical Modelling, Nova Publishers, Inc., New York, 2013, pp. 579–600.
[52] J.T. Nwabanne, P.K. Igbokwe, Adsorption performance of packed bed column for the removal of lead(II) using oil palm fibre, Int. J. Appl. Sci. Technol., 2 (2012) 106–115.
[53] R. Bhaumik, N.K. Mondal, B. Das, P. Roy, K.C. Pal, C. Das, A. Baneerjee, Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies, E-J. Chem., 9 (2012) 1457–1480.
[54] A.A.A. Mohammed, Thermodynamics Approach in the Adsorption of Heavy Metals, J.C. Moreno-Pirajan, Ed., Thermodynamics–InteractionStudies–Solids,LiquidsandGases, IntechOpen, 2011. Available at: https://www.intechopen.com/books/thermodynamics-interaction-studies-solids-liquids-and-gases/thermodynamics-approach-in-the-adsorption-of-heavy-metals