



Experimental evaluation of Farashband gas refinery wastewater treatment through activated carbon and natural zeolite adsorption process

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ABSTRACT

The treatment of oily wastewater produced from Farashband gas refinery through adsorption process has been presented using activated carbon (AC) and natural zeolite (NA). For the purpose of identifying the characteristics of the adsorbents, scanning electron microscopy, X-ray diffraction, and Brunauer–Emmett–Teller analysis were performed. According to the results, since the specific surface area of AC was around 897 m²/g which was much greater than 19.87 m²/g of NA, AC had considerably better performance than NA for oily wastewater treatment. The comparison between the adsorptive capacity of adsorbents revealed that using 30 g/L of activated carbon at 300 rpm reduced the amount of chemical oxygen demand (COD) from 848 to less than 60 ppm (93% removal) while within the examined dosage range of NA (5–40 g/L), the COD decreased only from 848 to 756 ppm (10% removal). Moreover, the modification of AC with phosphoric acid improved the adsorption efficiency significantly in terms of adsorbent consumption. The removal percentage which was acquired by applying 20 g/L of the modified AC (33% reduction in AC consumption) was equivalent to that attained by 30 g/L of unmodified AC. Kinetic analysis signified that the adsorption for both adsorbents followed the pseudo-first-order kinetic model equation.

Keywords: Oily wastewater treatment; Adsorption process; Activated carbon; Natural zeolite

1. Introduction

Nowadays, regarding the explosive growth of cities and population along with the expansion of industries, environmental issues such as air and water pollutions have caused global concerns. Discharge of industrial wastewaters into the environment is one of the main reasons for such pollutions which is essentially required to be addressed by treatment and recovery. The presence of various petroleum and oil compounds such as emulsions containing crude oils and gas condensates in the water is regarded as serious threats for not only humans but also many animal and plant species. These pollutions are mainly caused by the release

of effluent from different chemical plants including oil and gas drilling, refinery, petrochemical, metallurgical, food, transportation, textile, and leather industries [1,2].

Researchers in the field of petroleum wastewater treatment have been constantly looking for new solutions to develop existing wastewater treatment methods. Several factors involving the content of oily contaminants in the wastewater, the permissible limit of contaminants in the treated water, economical factors, environmental factors, and the type of application of the treated water have been taken into account to select the proper treatment method. In this regard, various physical methods (e.g., adsorption, floatation, and gravity separation, centrifugation, and membrane

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methods), chemical methods (e.g., coagulation and clotting, advanced oxidation, and precipitation), biological methods, or a combination of such methods have been employed [3–6].

One of the most well-established treatment methods is adsorption, which has extensively been studied by many scientists considering its numerous advantages over its counterparts. The superior quality of the treated water, no need for chemical additives, smaller equipment size, simpler automatic maintenance and control of the unit, and lower operational costs are some advantages of the adsorption process [7–10]. It should be noted that the adsorption process is comparatively economical and effective on the presumption that there is a uniform impurity content with low concentration in the wastewater.

Zeolite and carbon-based adsorbents are the most widely used materials in adsorption processes. To illustrate, activated carbon (AC) is of paramount significance owing to its unique characteristics including high specific surface area, highly porous structure, high adsorption capacity, regeneration ability, as well as its low cost compared to inorganic adsorbents such as artificial zeolites. Also, for the desorption process and regeneration of adsorbents, elution with different solvents and thermal methods are commercial processes.

The use of natural zeolites (NAs) are also economically justifiable for wastewater treatment regarding the existence of vast zeolite-rich minefields in Iran [10–12]. There are a number of studies confirming the appropriateness of AC and NA for industrial wastewater treatment [13–16].

In a study conducted by Movahedian and Ebrahimi [17], the performance of natural zeolites (NAs) and synthetic resins in the removal of nickel, copper, and zinc ions from industrial wastewater was assessed. The range of NA dosage, pH, contact time was 20–50 g/L, 3–7, 1–3.5 h, correspondingly, and three different ranges for the grain size including 297–420 μm ; 420–1,180 μm ; and larger than 1,180 μm were selected to be examined. Results showed that the optimum pH range for zeolite was 4–7, and with increasing the contact time and zeolite content, and also reducing the grain size the removal efficiency improved. Gholikandi et al. [18] used natural zeolites (natrolite) as a stable adsorbent to remove heavy metals from drinking water. Results indicated that natrolite can remove around 80% of calcium, 95% of magnesium, and 100% of iron. They also realized that it was more effective for hard waters, and its ability to remove permanent hardness was greater than temporary. In 2012, Mortula and Shabani [19] studied total dissolved solids (TDS) removal from an artificial wastewater sample (TDS = 1,150 mg/L) using activated alumina, activated carbon, steel slag, and limestone as adsorbents. Limestone reduced TDS in water to about 270 mg/L, while the others reduced TDS to 600 mg/L. Asgari et al. [20] investigated chromium adsorption using Iranian zeolite modified with hexacetyl trimethyl ammonium bromide (HDTMA-Br) as the surfactant. In their study, the effects of various variables such as contact time and solution pH were measured. Accordingly, the highest chromium removal efficiency of 91% was obtained at the pH of 7. Anbukumar et al. [21] studied industrial wastewater treatment using a set of filters containing activated carbon and zeolite layers. The diameter of the filter set was 2.4 m with a height of 1.8 m, where the height of activated carbon and zeolite was 45 cm each.

The wastewater sample was allowed to flow for 12 d in the filter set at the loading rate of 440 g d/m², yielding 69%, 80%, and 70% TDS, biochemical oxygen demand (BOD), and chemical oxygen demand (COD) removal, respectively. In another work, Hamed et al. [22] assessed the removal of metals using natural zeolite and modified zeolite (NaCl and NH₄Cl as the modifiers) from the water produced by the Hegel oil field in Sudan. They understood that the best removal efficiency corresponded to the pH of 4.5 which was obtained to be 94.9%, 97%, and 98% for magnesium, calcium, and iron ions, respectively. Khatmode and Thakare [23] evaluated TDS and dye removal from textile wastewater using sawdust as the adsorbent. In their work, the sawdust was first passed through a filter with a pore size of 0.5 mm, then washed with distilled water to remove particles adhering to the surface. They could obtain the dye and TDS removal of around 65% and 27%, respectively. Okiel et al. [24] dealt with the separation of oil and water emulsion using activated carbon, bentonite, and carbon precipitate. They found out that bentonite and carbon deposition have higher capacities than activated carbon. Moazerd and Viraraghavan [25] focused on the treatment of petroleum wastewater using modified bentonite in a discontinuous system revealing that bentonite could be an appropriate adsorbent for the removal of petroleum effluents. Aliyu et al. [26] examined the removal of petroleum effluents using banana peel in a packed tower, and the experimental results confirmed the suitability of the adsorbent. They also applied bed depth service time (BDST) model to predict the adsorption efficiency, which was well-matched with the experimental data. Mowl et al. [27] worked on the modeling of the break-through curve of oil effluent from saline water through a modified clay adsorbent. They also estimated the mass transfer coefficient through optimization methods.

Wastewater analysis conducted by API (American Petroleum Institute) oil–water separator revealed that the COD concentration of oily wastewater taken from Farashband gas refinery was around 848 ppm. However, this exceeds the permitted value of Iran's environmental standard (i.e., lower than 60 ppm) to be discharged into surface and groundwater sources. To the best of our knowledge, there is no research in the literature dealing with the employment of modified natural zeolite and activated carbon for the treatment of a real wastewater on a pilot scale. Therefore, in this study, the use of modified activated carbon (AC) and natural zeolite (NA) is pioneered for the treatment of oily wastewater of Farashband gas refinery on a pilot scale. Besides, the kinetics of the adsorption process and its corresponding models are evaluated. It is worth mentioning that regarding the low cost of such materials as well as the high efficiency of the proposed method, the adsorption process can practically be applied for industrial-scale treatment processes.

2. Materials and methods

2.1. Characteristics of the adsorbents and oily wastewater

2.1.1. Wastewater sample

In all the experiments performed in this study, the wastewater discharged from the Farashband gas refinery has

been selected to be examined. The refinery plant is located on the southern outskirts of Fars province, near Farashband city. In this case, the oily wastewater originates from washing areas contaminated with oil or other hydrocarbons as well as rainwater runoff which are all directed to the gravity pool of the API through existing canals. The results of wastewater analyses are listed in Table 1.

2.1.2. Adsorbents

Natural zeolite (NA) was provided from Semnan, Iran and activated carbon with ash content lower than 2% and pH_{zpc} equal to 7 [13] was purchased from a company in Iran. Typically, the chemical composition of the used zeolite is represented in Table 2. Accordingly, loss on ignition (L.O.I) of natural zeolite (NA) is about 10%–12%.

2.1.3. Adsorbent modifiers

In order to modify the adsorbents (i.e., AC), sulfuric acid, phosphoric, and nitric acid with the purity of 98, 85, and 65 wt.%, respectively, were used, all made by the Merck Company (Germany). To measure the COD of wastewater before and after adsorption process, DR200 reactor (US Hack Company, USA) was used to prepare samples, and DR900 photometer was applied to measure the amount of COD according to international standards.

2.1.4. Characterization of the adsorbents

Also, to accurately characterize the surface morphology, structure, and cavities of the adsorbents, scanning electron microscopy (SEM) analysis was performed by TESCAN, Czech Republic, X-ray diffraction (XRD) by Philips device made in the Netherlands and Brunauer–Emmett–Teller (BET) by Micromeritics, USA.

2.2. Experimental method for the wastewater treatment through adsorption

All adsorption experiments were conducted in a batch mode, and the effects of the mixer speed, adsorbent dose, adsorbent type, and adsorbent contact time with the

wastewater sample were examined. For all the tests, the adsorbent was immersed and rotated through a mixer in a fixed volume of the industrial wastewater (10 L). Based on results of similar researches in the literature [12–14], the mixing speed, contact time, and adsorbent dose were chosen to be in the range of 150–350 rpm, and 10–70 min, and 5–40 g/L, correspondingly. For the simplicity and reduction in costs, for each level of adsorbent dose, a specific mixer speed was considered, and then the effect of contact time over the adsorption process was evaluated. Therefore, the mixer speed of 150, 200, 250, 300, and 350 rpm were specified for the adsorbent dose of 5, 10, 20, 30, and 40 g/L, respectively [16,20,21].

It should be noted that to check the accuracy of results, some tests were performed for two times, revealing a difference of less than 2%.

2.3. Adsorbent modification

In order to modify the adsorbents, three substances were used including sulfuric acid, phosphoric acid, and nitric acid. For this purpose, first, a specific amount of the adsorbent was separated, and then the modifiers (in an amount twice of the separated adsorbent) were added separately to the distilled water (with the water to acid ratio of 10/1). Following that, the separated pieces of the adsorbents were added to the dilute acid solution and then allowed to stand for 24 h at room temperature on a magnetic heater stirrer with the speed of 300 rpm. Afterward, the adsorbents were separated from the acid solution by passing through a filter paper and placed in an oven at 80°C. After the drying process was completed, the samples were placed in a nitrogen furnace at 400°C for 2 h. Next, the samples were thoroughly washed to remove the acid contents and again dried at 80°C in the oven [13].

2.4. Adsorption kinetics

In this regard, the kinetic equations of zero, first, and second-order were examined, as Eqs. (1)–(3):

$$C_0 - C = Kt \quad (1)$$

$$\ln\left(\frac{C}{C_0}\right) = Kt \quad (2)$$

$$\left(\frac{1}{C}\right) - \left(\frac{1}{C_0}\right) = Kt \quad (3)$$

Table 1
Analyses results of the wastewater from the Farashband gas refinery

Analysis	Value
EC ($\mu\text{s}/\text{cm}$)	1,935
Total dissolved solids (TDS) (ppm)	984
COD (ppm)	805
Cl (ppm)	602
NaCl (ppm)	993
TSS (ppm)	4.5
Free oil content (ppm)	10
pH	5.88
Turbidity (NTU)	85
Hardness (mg/L)	458

Table 2
Chemical composition of natural zeolite (NA)

Component	Percentage (%)
SiO_2	68.5
Al_2O_3	11
Na_2O	3.8
K_2O	4.4
CaO	0.6
Fe_2O_3	0.2–0.9
Loss on ignition	10–12

where C_0 is equal to the initial COD of the wastewater in ppm, C is the COD of the treated wastewater at different times (t), and K is the constant reaction rate.

3. Results and discussion

3.1. Characterization of natural zeolite and activated carbon adsorbents

Figs. 1 and 2 represent the electron microscopy images (SEM) of the surface of AC and NA, respectively. It is clearly discernible that the structure of AC is more porous than that of NA, and also the cavity size on AC surface is around 1–5 μm , while for NA, this is around one μm .

In order to confirm the purity of AC, and determine the structure of NA and its constituent minerals, XRD analysis is carried out, as shown in Figs. 3 and 4. The results obviously indicate the purity of AC as the carbon peak can distinguishably be observed in the range of 20° to 30° , while other peaks are insignificant. These results are fairly similar to those conducted by previous studies [10]. According to Fig. 4, four different phases can be identified for NA including clinoptilolite, quartz, feldspars, and mordenite, which are marked as C, Q, F, and M. In addition, based on the literature, the NA samples extracted from Semnan mines are mainly comprised of the clinoptilolite phase [9].

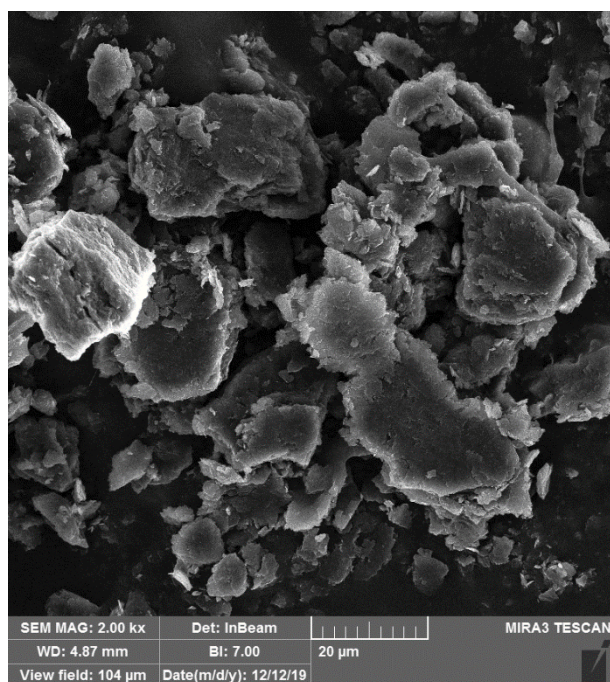
Figs. 5 and 6 illustrate the BET analysis for the measurement of the specific surface area of AC and NA adsorbents, respectively. Obviously, a substantial proportion of AC pores are smaller than 10 nm (pore diameter), while for NA, they are mostly greater than 10 nm. In Table 3, the specific surface area, average pore diameter, and the specific pore

volume for both adsorbents are listed. Accordingly, the specific surface area of AC is $897 \text{ m}^2/\text{g}$, which is much higher than $19.87 \text{ m}^2/\text{g}$ of NA. This is most presumably owing to the fact that the used NA is a raw mineral extracted from the mines, whereas AC is prepared by a process at which its special surface area has automatically been increased. However, it should be noted that the average pore diameter in the structure of AC is about 2.0 nm, which is much smaller than 11.7 of NA, and correspondingly the specific pore volume of AC is around 10 times greater than that of NA.

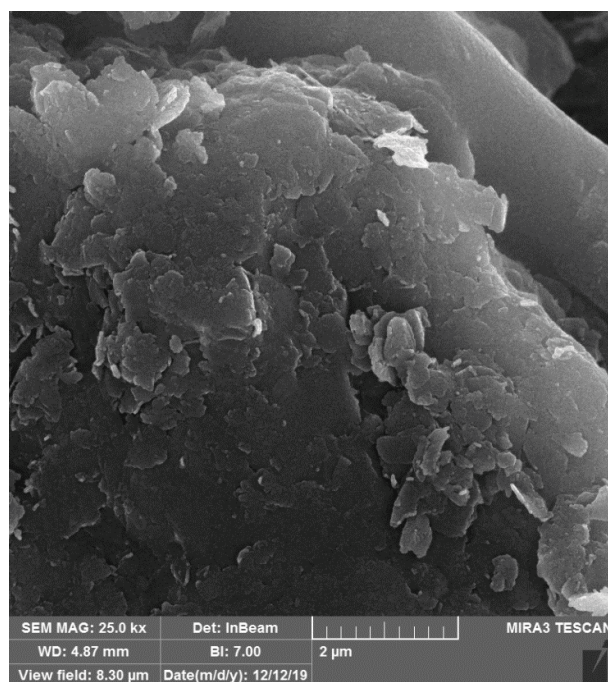
In addition, Fig. 7 represents the FTIR analysis of the modified activated carbon. This Fig. 7 presents the values of surface functional groups of AC and alternation of the spectrum peaks that are influenced by the modification process. The sharp peak and large difference of bonds due to the stretching vibration of C–O–C and O–H bonds confirm that the physical adsorption happens successfully [13].

3.2. Wastewater treatment through adsorption using AC and NA

Fig. 8 depicts the alternation of COD vs. time for AC with the dosage of 5–40 g/L and the mixer speed of 150–350 rpm, according to the experimental method in section 2.2 (Experimental method for the wastewater treatment through adsorption). The first clear observation is that as the adsorption time increases from 10 to 70 min, the COD declines for all adsorbent doses, and this reduction is much sharper within the first 10 min of operation due to the existence of enough active sites and lack of saturated sites [28]. Another obvious observation is that the simultaneous increase in mixer speed and adsorbent does can strongly affect the COD as it can lead to an increase in dynamism [28].



(a)



(b)

Fig. 1. SEM image of the activated carbon (AC) surface with magnification of (a) 2 kx and (b) 25 kx.

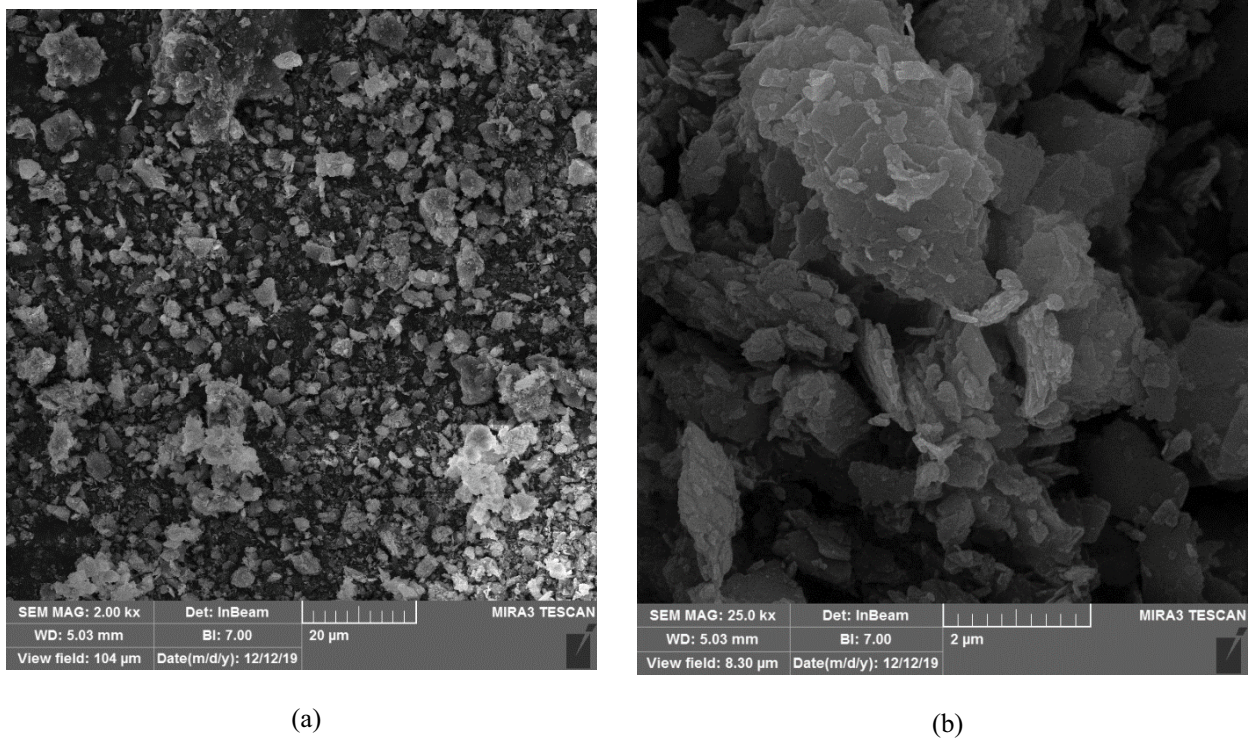


Fig. 2. SEM image of the natural zeolite (NA) surface with magnification of (a) 2 kx and (b) 25 kx.

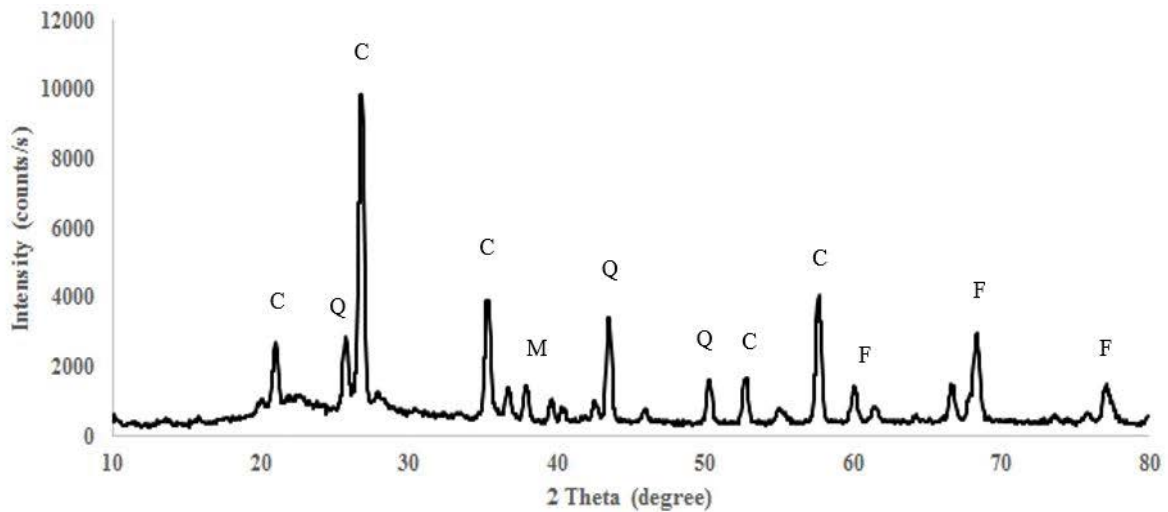


Fig. 3. XRD analysis of natural zeolite (NA). Q: Quartz; M: Mordenite; C: Clinoptilolite; F: Feldspar.

By way of illustration, using 5 g/L of AC and the mixer speed of 150 rpm, the COD decreases to 281 ppm after 70 min of operation, while using 40 g/L and 350 rpm, the COD declines to 57 ppm. However, the optimum adsorbent dose and mixer speeds are 30 g/L and 300 rpm, respectively, as the COD reaches 54 ppm for the contact time of over 60 min.

According to environmental standards of Iran, for discharging wastewaters to surface and groundwater resources the safe COD value must be less than 60 ppm. Thus, here to reach the permissible limit of COD, considering the removal efficiency of COD and the amount of adsorbent

consumption, the adsorption process of Farashband refinery wastewater using AC is needed to be conducted over 60 min at the adsorbent dose of 30 g/L, and the mixer speed of higher than 300 rpm. Then, the treated wastewater can be reutilized for irrigation or to be discharged to surface and ground waters without causing environmental problems.

In order to draw a more detailed comparison, the effect of adsorbent dose in terms of COD removal percentage is represented in Fig. 9. It is obvious that the greatest COD removal percentage (i.e., 94%) corresponds to the highest adsorbent dose (40 g/L), while the least removal

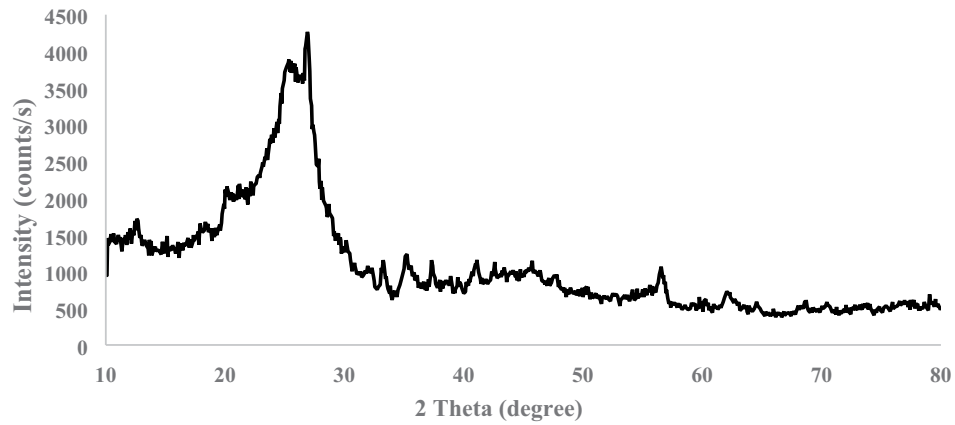


Fig. 4. XRD analysis of activated carbon (AC).

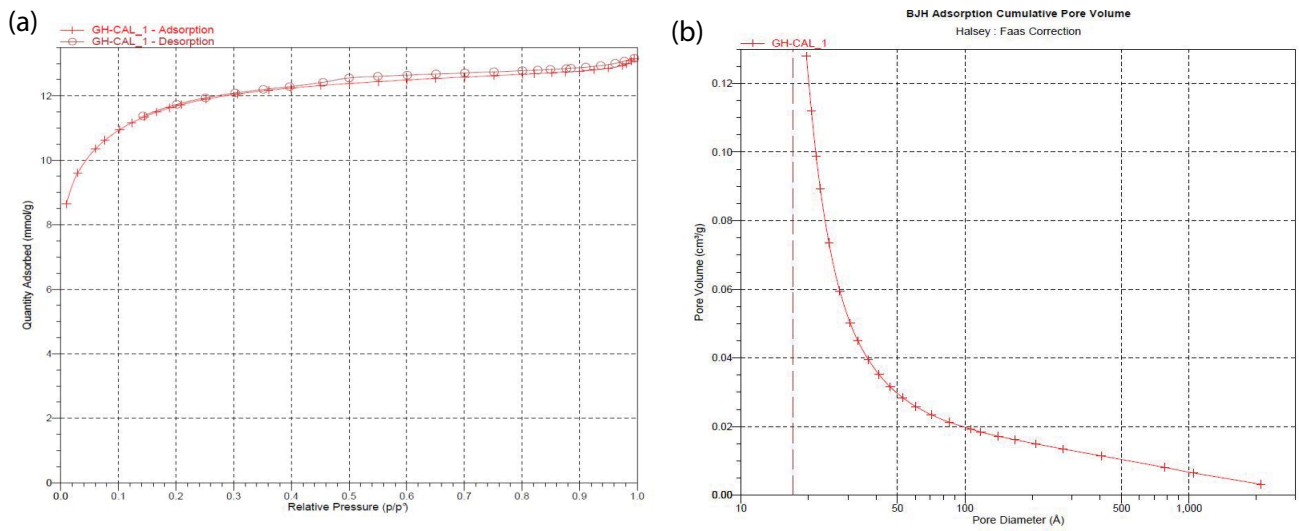


Fig. 5. BET analysis for AC surface: (a) adsorption/desorption curve and (b) cumulative pore volume curve.

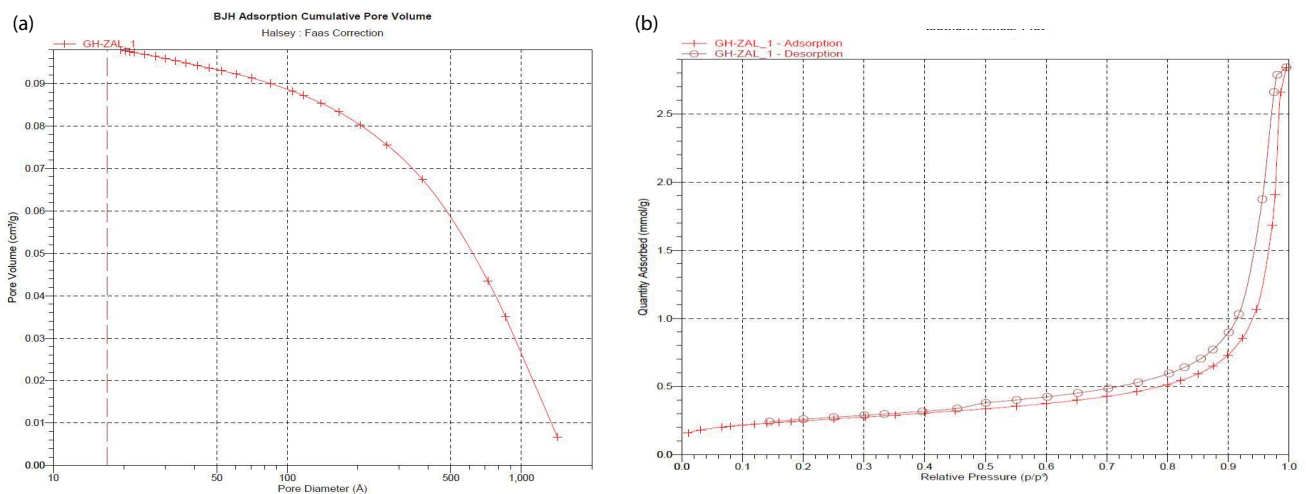


Fig. 6. BET analysis for NA surface (a) adsorption/desorption curve and (b) cumulative pore volume curve.

Table 3
Specific surface area, average pore diameter, and specific pore volume for both adsorbents

Parameter	Specific pore volume (cm ³ /g)	Average pore diameter (nm)	Specific surface area (m ² /g)
Activate carbon (AC)	0.128	2	897.5
Natural zeolite (NA)	0.098	11.7	19.87

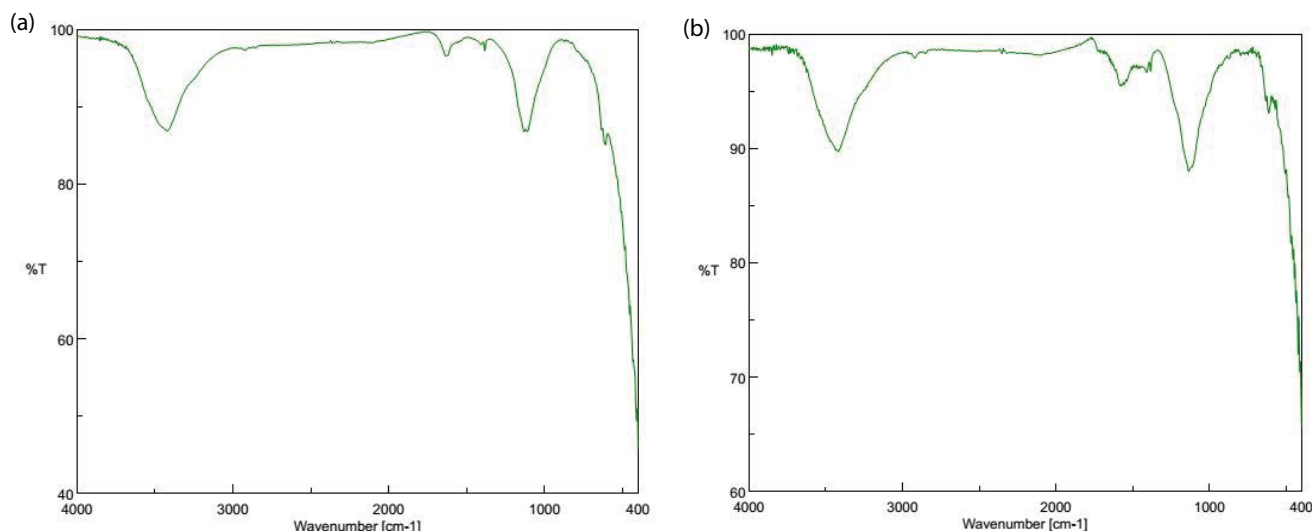


Fig. 7. FTIR spectra of activated carbon, before (a) and after modification with phosphoric acid (b).

percentage (67%) is related to the lowest dose (5 g/L), that is to say, the presence of unsaturated active sites promotes the interaction of adsorbent with molecules [13–28].

Fig. 10 indicates the COD reduction vs. time for three different doses of NA. It is clearly discernible that the COD reduction is virtually the same for different doses of NA. However, contrary to the promising results observed for the AC adsorbent, the performance of NA is fairly disappointing for the treatment of wastewater samples in this study. To illustrate, within the whole examined the range of NA dose (i.e., 5–40 g/L), the largest COD reduction is around 92 ppm (i.e., the reduction from 848 to 756 ppm), which is related to the highest NA dose (40 g/L) and mixer speed (350 rpm). Thus, the maximum obtainable COD removal using NA is about 10% which is considerably lower than that obtained by AC (94%) at the same operating conditions (Fig. 11). This result can be attributed to various reasons including the types of pollutants, the relatively low specific surface area of NA, the low adsorption capacity of pollutants on the active surface of NA, and the presence of repulsive forces between the pollutants and NA surface.

Due to the weak performance of NA in high doses (i.e., COD removal of around 10%), lower ones (20% and 30%) are not evaluated in terms of COD reduction, as it is inevitably known that higher adsorbent doses can adsorb a greater amount of pollutants because of the existence of more unsaturated active sites on the adsorbent surface [13–28]. As it can be seen, after 50 min, there is no considerable change in the removal percentage due to saturation of active sites by molecules in the wastewater [28].

3.3. Wastewater treatment through adsorption using the modified AC

In this respect, as mentioned before, sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and nitric acid (HNO₃) were used separately to modify the AC adsorbent. Taking into account the fairly weak performance of NA (section 3.2 (Wastewater treatment through adsorption using AC and NA)) relative to AC to meet the environmental standards, here only AC is modified. In Fig. 12, the effects of different modifiers over the COD reduction is compared, revealing the superiority of phosphoric acid over others. Actually, by modifying AC using phosphoric acid, with the AC dose of 20 g/L, the COD reduces to 58 ppm, reaching the acceptable environmental standards (i.e., 60 ppm). This result suggests that giving equal COD reduction, 20 g/L of modified AC using phosphoric acid can be substituted for 30 g/L of unmodified AC in the adsorption process, which reduces the consumed amount of AC by 33%. Fig. 13 compares the effect of three different modifiers over the performance of AC in terms of COD removal percentage. Accordingly, the best removal percentage of 92% is related to the phosphoric acid. This is mainly due to the considerable improvement provided by phosphoric acid in active surface area, specific surface area, and the number of pores as well as a substantial decrease in repulsive forces between the AC surface and pollutants. Nevertheless, modification of AC through sulfuric acid and nitric acid leads to a weaker performance in comparison with the unmodified sample. These results highlight the importance of choosing suitable acids as the modifier.

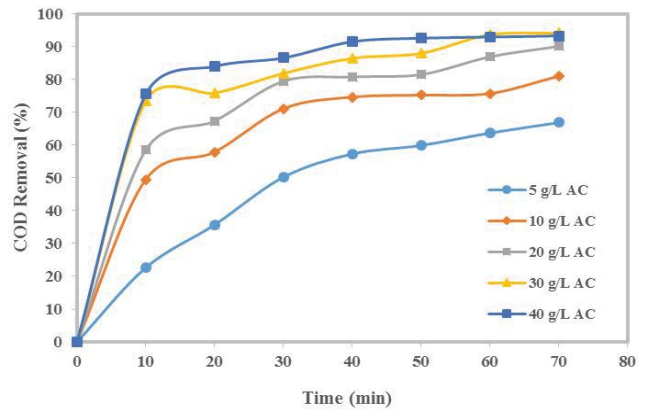
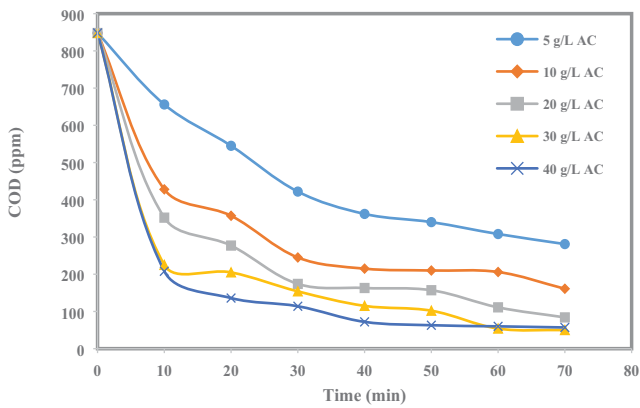


Fig. 8. COD alternation vs. contact time using AC for different adsorbent doses.

Fig. 9. COD removal percentage vs. contact time using AC for different adsorbent doses.

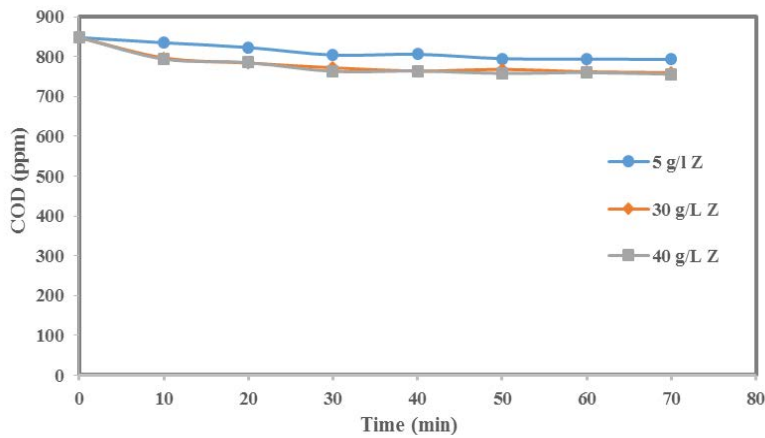


Fig. 10. COD removal percentage vs. contact time using NA for different adsorbent doses.

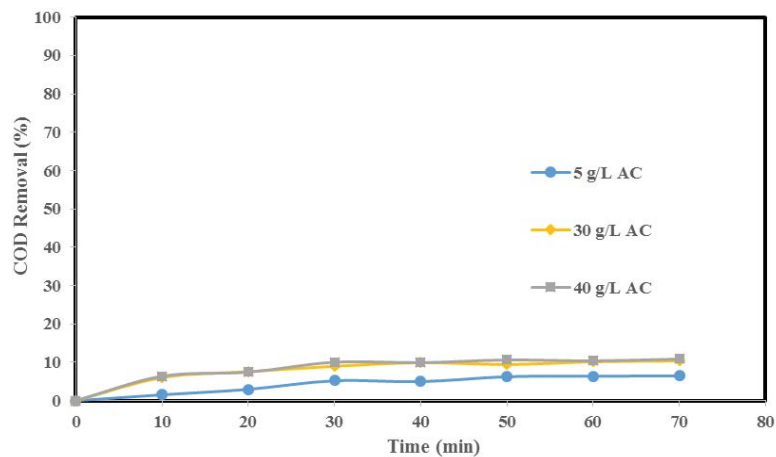


Fig. 11. COD alternation vs. contact time using NA for different adsorbent dose.

Finally, it should be noted that one of the main factors which influence the rate of adsorption is the pH of wastewater. It is found that with an increase in the pH value, the amount of H⁺ ions decreases, leading to a rise in the comparative attraction between the adsorbate and adsorbent.

Conversely, the comparative attraction between the adsorbate and solvent phase declines [13]. In addition, about the effect of ionic strength on the removal of COD based on our previous research, according to the removal percentage of COD at the different dosages of adsorbents, it is

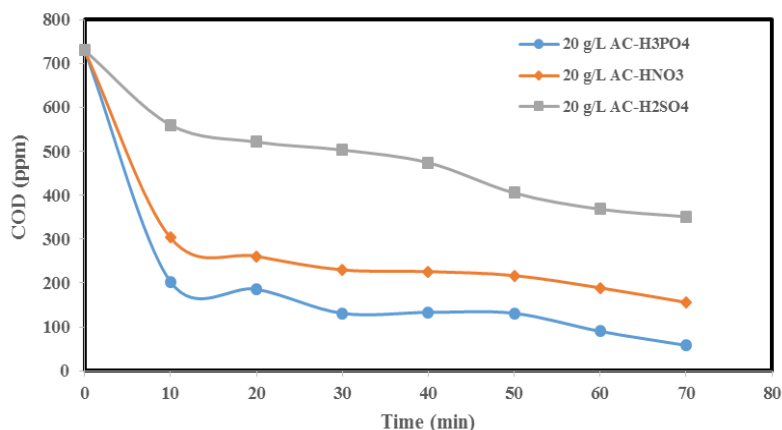


Fig. 12. Effects of different modifiers over AC performance in terms of COD reduction.

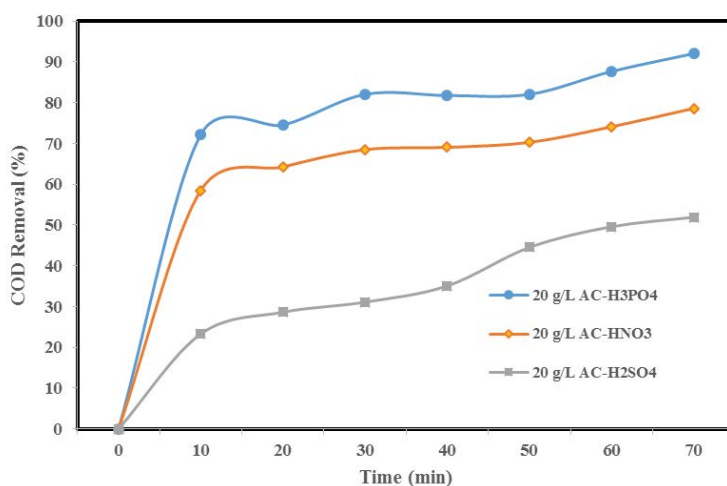


Fig. 13. Effects of different modifiers over AC performance in terms of COD removal percentage.

deduced that the presence of ions in the wastewater functions as an electrostatic shield between opposite charges at the surface of adsorbent and molecules in wastewater, resulting in a reduction in the adsorption efficiency [13].

3.4. Kinetics of adsorption process in wastewater treatment

In order to examine the rate controlling step and reactions occurring during process which rely on the physical and/or chemical properties of the adsorbent, some kinetic models are applied [13–28].

The COD reduction vs. contact time is modeled and represented in Figs. 14–16 for the AC, NA, and modified AC, respectively. The kinetic equations (Eqs. (1)–(3)) are linearized, and the degree of proximity to the linear state is determined by R^2 . Accordingly, the adsorption kinetics are mainly consistent with the first-order kinetic equations because the R^2 of the first-order equation is closer to 1.0 than that of zero-degree and second-order ones. These results indicate that the filling rate of adsorbent sites is proportional to the number of vacant adsorbent sites and chemical

reaction, controlling the adsorption process to reduce the COD of the wastewater.

4. Conclusion

In this study, the possibility of treating the API wastewater of the Farashband refinery through the adsorption process was explored where AC and NA were selected as the adsorbents. SEM, XRD, and BET analyses were performed to characterize the structure of adsorbents as well as their surface properties. Results indicated that the structure of AC was more porous than NA, and also it was understood that the specific surface area of AC was $897 \text{ m}^2/\text{g}$, being significantly larger than that $19.87 \text{ m}^2/\text{g}$ of NA. The experiments were conducted by varying the adsorbent dose and mixer speed for a fixed volume of the wastewater sample (10 L) and a contact time of 70 min. Results demonstrated that using 30 g/L of AC and the mixing speed of 300 rpm, the COD of the treated sample reached 54 ppm for the contact time of over 60 min, meeting the environmental standards (i.e., <60 ppm). In contrast, for

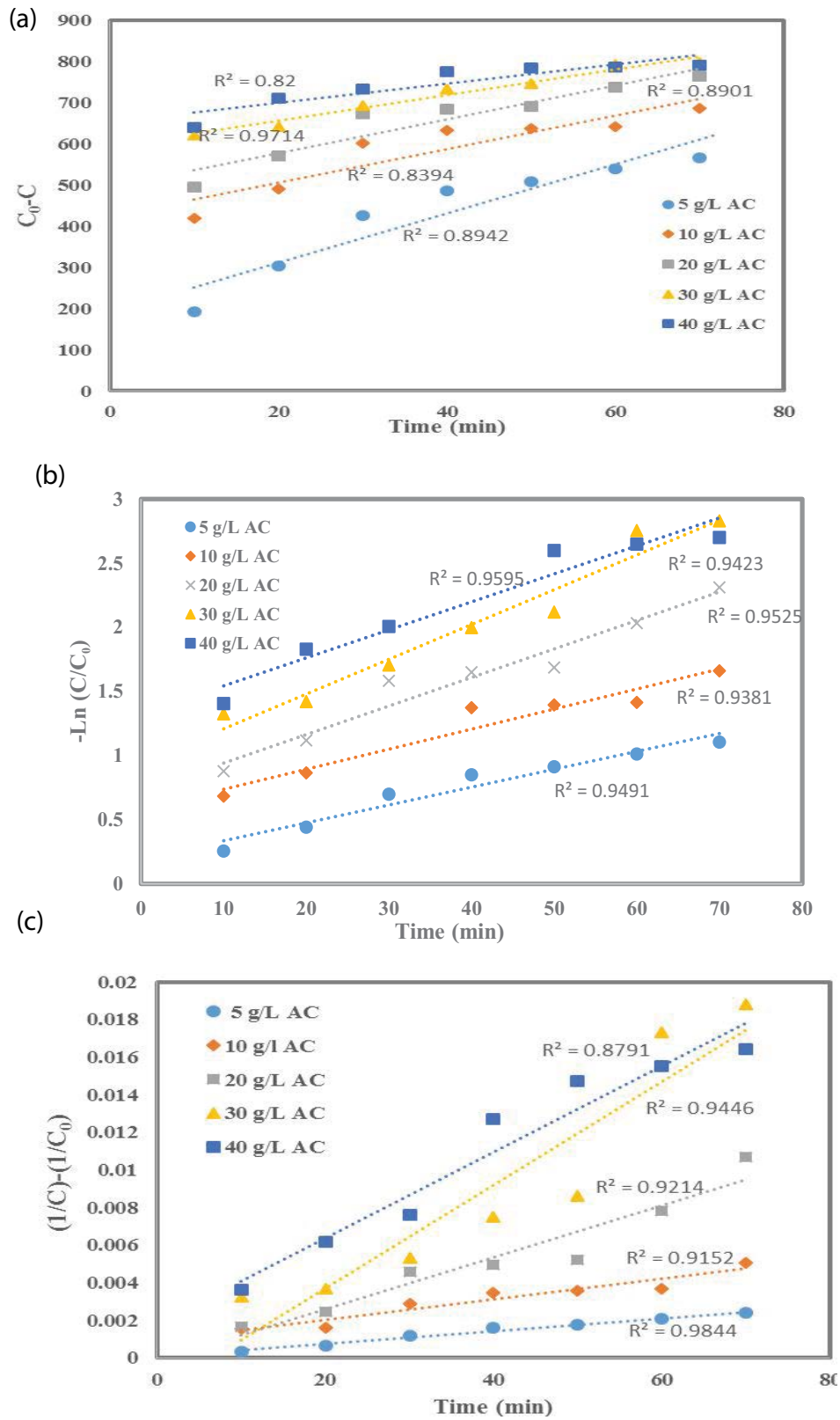


Fig. 14. Adsorption kinetics for different doses of AC using (a) zero-order, (b) first-order, and (c) second-order equations.

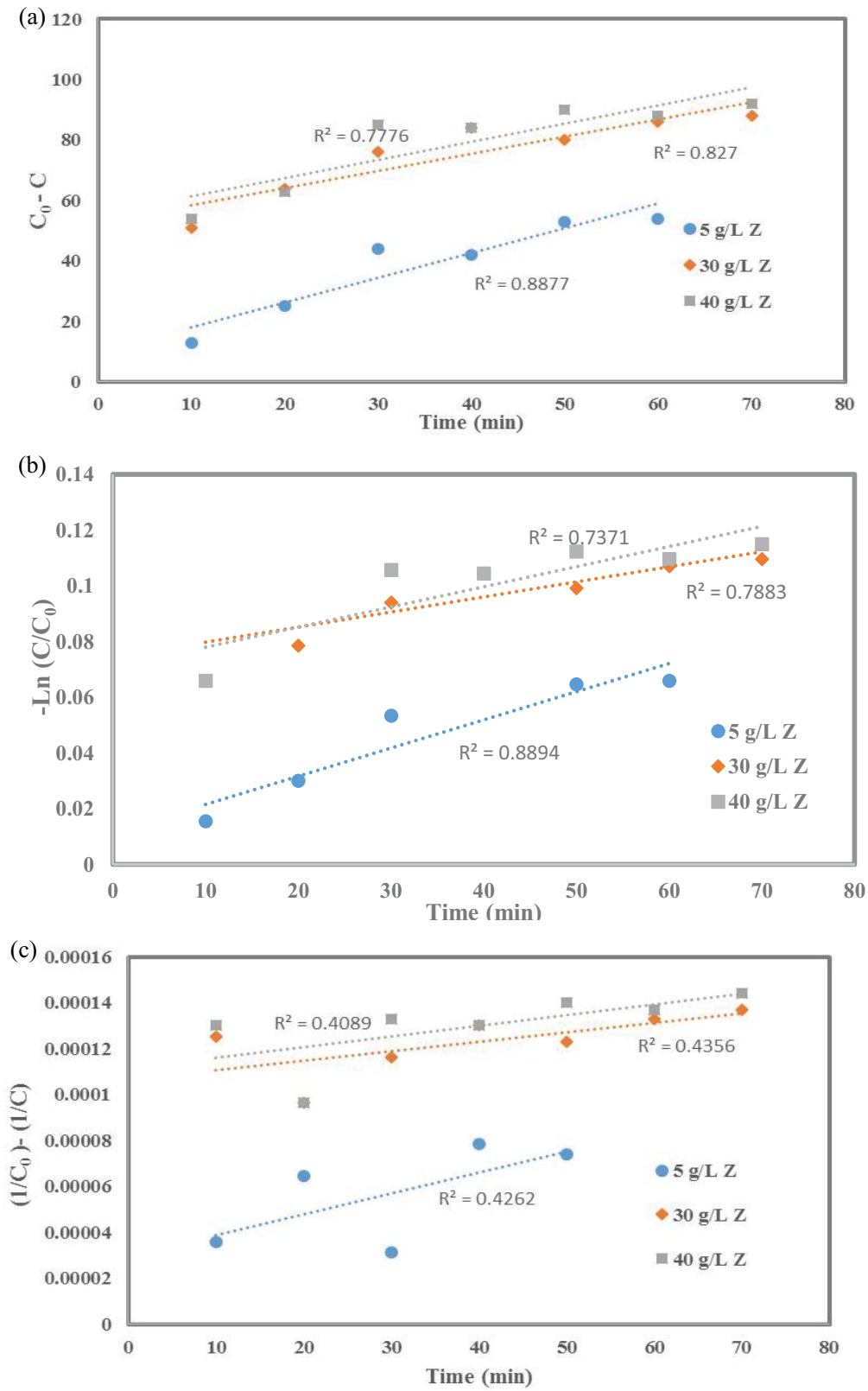


Fig. 15. Adsorption kinetics for different doses of NA using (a) zero-order, (b) first-order, and (c) second-order equations.

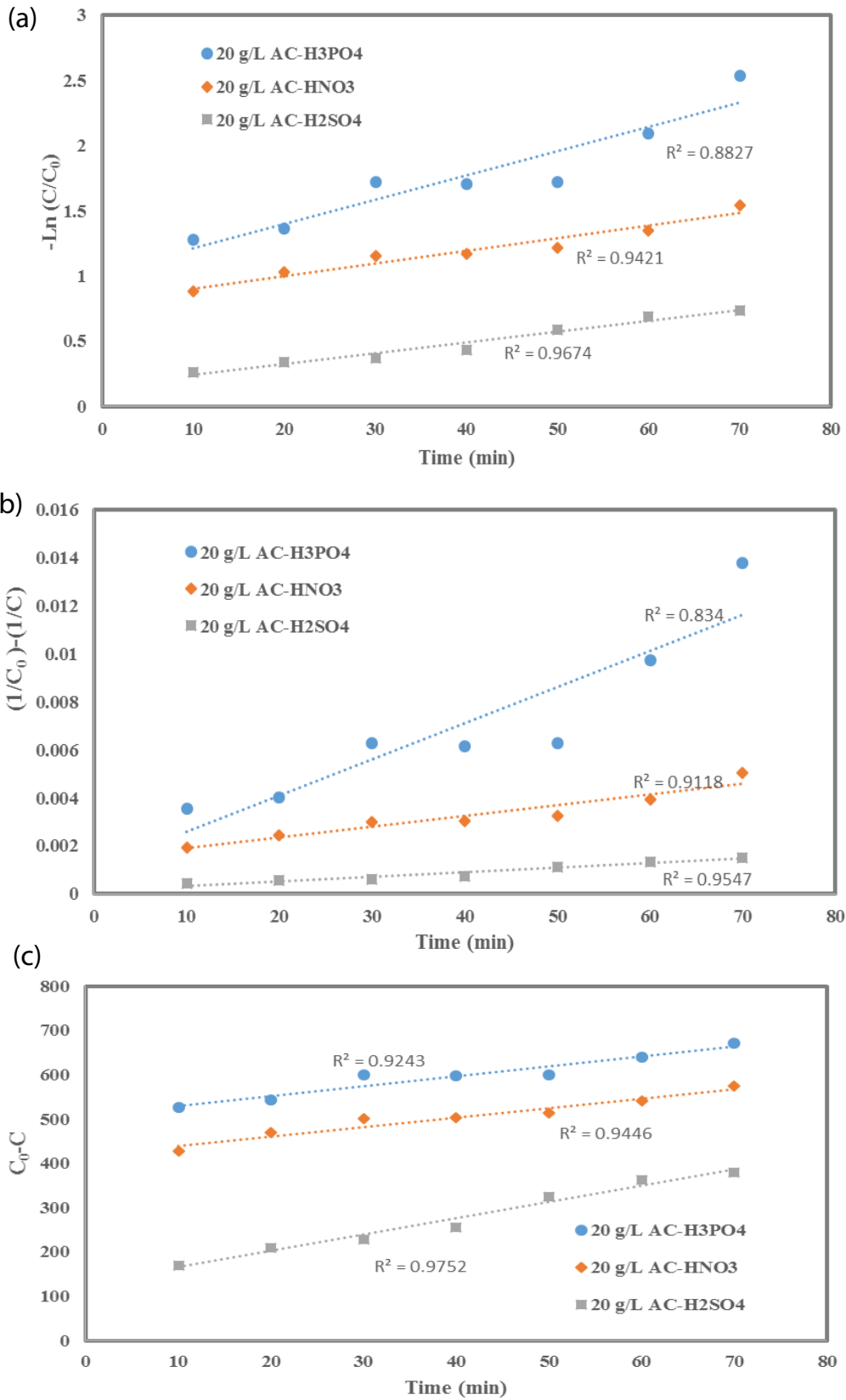


Fig. 16. Adsorption kinetics for different doses of modified AC using (a) zero-order, (b) first-order, and (c) second-order equations.

the NA adsorbent, the results were disappointing as within the evaluated range of adsorbent dose, the maximum COD reduction was around 92 ppm (from 848 to 756 ppm). In addition, by modifying the AC adsorbent with phosphoric acid, with the adsorbent dose of 20 g/L, the COD of the treated water reached 58 ppm, which was acceptable according to environmental standards (<60 ppm), which means 33% reduction in the required amount of AC. On the contrary, sulfuric acid and nitric acid modifiers exerted adverse effects over the adsorption performance when added to AC, suggesting that selecting the proper modifiers are of vital significance. Besides, the kinetic analysis revealed that the kinetics of the adsorption process through AC and NA were generally based on the first-order kinetic equations.

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