

New Insights on the Adsorption of Phenol Red Dyes from Synthesized Wastewater using Activated Carbon Prepared from the $\text{Fe}_2(\text{MoO}_4)_3$ -treated Mespilus Germanica Leaves: Equilibrium, Kinetic, and Thermodynamic Studies

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Abstract

Water shortage is considered as one of the main challenges of human life. A practical solution to this problem is the wastewater treatment. The removal of dyes from wastewaters has received considerable critical attention by researchers due to their high volume and toxicity. In the current research, the adsorption of phenol red dyes from synthetic wastewater using the activated carbon produced from *Mespilus Germanica* modified with $\text{Fe}_2(\text{MoO}_4)_3$ was studied. The proposed adsorbent was characterized by FTIR, XRD, SEM, EDX/Map, BET, and Raman techniques. The optimal adsorption operating parameters were pH = 3, stirring rate of 500 rpm, 25°C, the dosage of adsorbent of 1 g/lit, dye initial concentration of 10 mg/lit, and contact time of 60 min. Furthermore, the successful regeneration of the adsorbent for 3 times denoted its capability in performing adsorption and desorption processes. Equilibrium studies showed that the adsorption of phenol red dyes by AC/ $\text{Fe}_2(\text{MoO}_4)_3$ was desirable and physical and the experimental data were fitted well by Freundlich model. In addition, the kinetic behavior of the current adsorption process was well described by the pseudo-second order kinetic model, while thermodynamic calculations showed that the process was exothermic and spontaneous.

1. Introduction

Environmental drastic impacts of wastewaters containing dye pollutants have been considerably increasing as a result of development of industries. The presence of such pollutants not only reduces the visual quality of surface waters, but also disrupts the aquatic ecosystems [1, 2]. As an organic pollutant of natural water sources, chemical dye substances are considered as one of the most destructive ones, since they are produced by both industrial and household activities[3]. The discharge of such wastewaters to surface waters is dangerous because it results in blockage of light diffusion into deep waters and disrupting photosynthesis and other biological processes related to aquatic life [4, 5]. In addition, the presence of these pollutants in water causes dangerous human like cancer, genetic disorders and mutations [6]. As a consequence, the removal of these type of pollutants from wastewaters prior to their entrance into environment seems essential.

Various methods have been applied to treat the wastewaters containing dye pollutants like precipitation, chemical coagulation, sand filters, ion exchange, adsorption [7], chemical treatment by oxidants such as chlorine, ozone, and hydrogen peroxide [8], membrane filtration, reverse osmosis, and biological decomposition [9]. Although these methods are effective, they have some drawbacks; for example, membrane processes present acceptable removal efficiencies, however they produce concentrated sludge which is difficult to remove. Additionally, advanced chemical oxidation processes have high operating costs [10]. Moreover, Biological treatment methods are simple and low-cost, however they are ineffective for dye sludge; because these substances are non-biodegradable and toxic for microorganisms and the application of such processes results in bulking up of sludge [11, 12]. Among these methods, adsorption which is a low-cost and simple process, is considered effective for the removal of dye pollutants and its efficiency is strongly dependent on the adsorbent's features and the dye's chemical nature[13].

Several researches addressed the adsorption of dyes from aqueous solutions in recent years. Joseph et al. studied the removal of phenol red using kola nut (*Cola acuminata*) shell activated carbon and optimized the operating parameters by the response surface methodology [14]. In another work, Adlnasab et al. used amine rich functionalized mesoporous silica for the effective removal of alizarin yellow and phenol red dyes from waste waters and their results showed that the proposed adsorbent had acceptable maximum adsorption capacities [15]. Gautam et al. assessed the extract of waste tea for the modification of iron nanoparticles to remove phenol red from aqueous solution. Regarding their results, the uptake efficiency decreased with initial concentration of dyes and temperature [16]. Masoudian et al. used titanium oxide nanoparticles loaded onto activated carbon prepared from bio-waste watermelon rind for the efficient ultrasonic-assisted adsorption of congo red and phenol red dyes from wastewaters. They reported the optimal operating conditions for the removal of these two pollutants [17]. In another research, 99% of phenol red was removed by carbon-CUO nanocomposites in optimal conditions [18]. Jawad and Fairouz conducted a comparative study for adsorption phenol red dye using spinel $\text{Co}_{1-x}\text{MxFe}_2\text{O}_4$ nano composites and concluded that their proposed adsorbent was proper for the removal of phenol red dyes [19]. Linh et al. used modified bentonite for the phenol red removal from aqueous media which yielded high uptake efficiencies [20].

The purpose of this study is assessing the efficiency of phenol red dyes adsorption from aqueous solution by the activated carbon derived from *Mespilus Germanica* modified with $\text{Fe}_2(\text{MoO}_4)_3$. The modified adsorbent was characterized through several analyses and the operating conditions were optimized to yield the maximum phenol red removal efficiency. Moreover, the regeneration capability of the adsorbent was investigated beside the equilibrium, kinetic, and thermodynamic studies.

2. Material And Methods

2.1. Chemicals

In this study, *Mespilus Germanica* leaves were used as the feedstock of the adsorbent. The source of the leaves was Fars Province local gardens (South West Iran). Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), nitric acid (HNO_3), methanol (CH_3OH), sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol, and phenol red dyes were purchased from Sigma-Aldrich Co. (Germany) and were used without further purification. The stock solutions of phenol red dye with proper concentrations were prepared and then were diluted using deionized water and were utilized in adsorption experiments. Initial pH of the solutions prior to addition of the adsorbents were adjusted by NaCl (1M) and HCl (1M) solutions.

2.2. Apparatus

In the current work, a magnetic stirrer with heating (IKA, RH basic 2, Germany) was used for stirring of the samples and a digital scale with 0.0001g precision (Sartorius, Germany) was applied for weighting with high precision. pH measurement was carried out by Metrohm 744 digital pH meter and centrifuge

(Eppendorf Centrifuge 5425/5425 R, Germany) and mill (PerkinElmer Lab Mill 3610, Germany) sets were utilized for centrifuging and milling of the substances, respectively. In addition, a laboratory oven (Mettler, UP400, Germany) and a UV spectrophotometer (Shimadzu UV-1700 Pharma Spectrophotometer, Japan) were applied for drying the leaves and measuring the concentration of the residual phenol red dyes in aqueous solutions, respectively, while the carbonization was performed by an atmosphere furnace (ALARGE, ABF – 1400T, China). FTIR (Bruker Vector 22, Germany), XRD (Philips PW 1730, Netherlands), SEM (Tescan, Czech Republic), and EDX/Mapping (Tescan SAM), BET (Quantachrome Nova, Austria), and Raman (Takram p50C0R10 Iran) were used for investigating the adsorbent's surface functional groups, crystalline structure and distance between the planes, adsorbent surface variations before and after the adsorption of pollutants, the adsorbent surface elements and their distribution, the adsorbent specific surface area, and its structure respectively.

2.3. Synthesis of AC/Fe₂(MoO₄)₃ Adsorbent

In order to synthesize the adsorbent, dust and other probable impurities were initially removed from *Mespilus Germanica* leaves by washing them with deionized water for several times. Afterwards, they were dried completely for 180 min in the oven at 90°C. The dried leaves were grinded using the mill and were placed in the furnace for 3h at 500°C to become carbonized completely. The final step is powdering and sieving the carbonized leaves by no. 25 sieves (with the nominal sieve opening of 700 µm). Then they were stored in tightened cap bottles for further use. Afterwards, a mixture of 0.3269g of Fe(NO₃)₃·9H₂O with 50 ml of deionized water was prepared in a 100ml balloon, which was followed by the addition of 0.5g of the carbonized powder and the content of the balloon was stirred for 30 min. At the end of stirring, the mixture was heated to 80–90°C and the acidified ammonium molybdate tetrahydrate solution using HNO₃ (pH = 2) was added in a drop wise manner and then the achieved mixture was stirred for 3 h. Afterwards, it was centrifuged and dried at the rate of 3000 rpm for 24 h at 105°C. It is worthy to note that during the synthesis of the current adsorbent the ratio of molybdate to iron was 1.5 [21, 22].

3. Results And Discussion

In the current research, phenol red dyes were adsorbed from the synthesized solutions using the adsorbent produced from *Mespilus Germanica* leaves in the solution pH of 2 to 11, stirring rate of 0-700 rpm, temperature of 25–50°C, dosage of adsorbent range of 0.25-5 g/L, phenol red initial concentration between 10 and 100 mg/L, and contact time of 5-160 minutes. The samples were tested at the end of batch adsorption tests and the concentration of the residual dye was measured using the spectrophotometer apparatus.

The adsorption percentage (R) and the adsorption capacity of the adsorbed pollutants per the dry adsorbent mass (mg/g) (q_e) are calculated by equations 1 and 2, respectively:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1) \quad q_e = \frac{(C_o - C_e)}{w} \times V \quad (2)$$

where, C_0 (mg/ml), C_e (mg/ml), V (ml), and W (g) are phenol red dyes initial and final concentrations in solutions, solution volume, and adsorbent mass, respectively.

3.1. Characterization of the Adsorbent

As mentioned before, in the current research the structure and surface of the adsorbent and the effect of adsorption of pollutants on the adsorbent's structure were analyzed through FTIR, XRD, SEM and EDX/Map, BET, and Raman techniques.

In Fig. 1, FTIR spectra of the produced activated carbon samples, $AC/Fe_2(MoO_4)_3$ composite prior to and after the adsorption of phenol red dyes are illustrated. As it can be seen in Fig. 1a, there are three peaks in 3834 cm^{-1} , 3743 cm^{-1} , 3429 cm^{-1} which are attributed to O-H free and hydrogen bonds in activated carbon structure [23–25]. Additionally, there is also an intense adsorption peak in 1428 cm^{-1} which is attributed to C = C bonds of aromatic content and alkene of the activated carbon [26]. There is a shift in the adsorptive peaks of $AC/Fe_2(MoO_4)_3$ composite which were appeared in the activated carbon structure (Fig. 1b); the adsorptive peaks seen in 3834 cm^{-1} , 3743 cm^{-1} , and 3429 cm^{-1} were moved to 3850 cm^{-1} , 3742 cm^{-1} , and 3389 cm^{-1} . It should be mentioned that these peaks were associated to O-H stretching vibrations [27]. Additionally, there are other adsorptive peaks in 1618 cm^{-1} and 1689 cm^{-1} which are the result of $\delta(H_2O)$ and C = O vibrations of oxalate groups present in this composite structure [28]. Moreover, there are some other peaks in 1743 cm^{-1} and 1390 cm^{-1} which are attributed to tension vibrations of C = O and C-O bonds, respectively [27, 29]. The intense adsorptive peaks seen in 800 cm^{-1} and 430 cm^{-1} are related to Mo(VI)-O and Fe(III)-O in $AC/Fe_2(MoO_4)_3$ structure [27, 30, 31]. The FTIR spectra of the composite after the adsorption of phenol red dyes is also shown in Fig. 1c. As it can be observed, the intensity and location of the $AC/Fe_2(MoO_4)_3$ composite peaks prior to adsorption changed as the result of adsorption of phenol red dyes on this composite.

The XRD patterns of the activated carbon and $AC/Fe_2(MoO_4)_3$ composite in the 2Θ range of $5-80^\circ$ are presented in Fig. 2. The peaks which are appeared in the two structures with different intensities approve the crystalline and semi-crystalline phases in their structures; as a result, it can be concluded that both of materials have crystalline structures. The peaks seen in 23.12° and 43.16° in the activated carbon's XRD pattern are attributed to graphite structure's (002) and (001) crystalline phases [32–34]. Additionally, there are other peaks in 29.40° (220), 36.04° (311), 39.44° (222), and 64.8° (440) [32, 35]. In the XRD pattern of $AC/Fe_2(MoO_4)_3$ composite, there are some peaks in 18.68° , 58.76° , 31.28° , 34.32° , 39.36° , and 45.44° which are associated to (112), (202), (222), (116), (511), and (225) crystalline phases of $Fe_2(MoO_4)_3$ structure, respectively [27, 28]. There are some other peaks in 2Θ values of 47.08° , 49.32° , 54.04° , 58.04° , and 59.84° which are attributed to (312), (012), (226), (211), and (137) crystalline phases, respectively [36].

In order to study the surface properties of the *Mespilus Germanica* leaves derived activated carbon and their variations after modification by $Fe_2(MoO_4)_3$ and also the surface morphology of $AC/Fe_2(MoO_4)_3$

composite before and after the adsorption of phenol red dyes SEM and EDX/Map analyses were used and the results are presented in Fig. 3. SEM micrographs show the produced activated carbon from *Mespilus Germanica* leaves has a porous structure which increases its capability in the adsorption of pollutants (Fig. 3a). Besides, the results of EDX/Map of the activated carbon showed that carbon (74.26%) and oxygen (25.74%) are its major constituents (Fig. 3b and c). Comparing the SEM image of AC/Fe₂(MoO₄)₃ composite (Fig. 3d) with the SEM of the activated carbon (Fig. 3a), it can be observed that iron molybdate particles were properly located on the activated carbon surface and the synthesis process was fulfilled properly. Additionally, EDX/Map results approve the presence of iron and molybdenum in the synthesized adsorbent structure (Fig. 3e and f).

The comparison between the SEM micrographs of AC/Fe₂(MoO₄)₃ composite before (Fig. 3e) and after (Fig. 3g) the adsorption of phenol red dyes shows that the accumulation of particles increased and the pores and porosity on the surface of the adsorbent decreased, which can be the result of diffusion of dye molecules into the pores and layers of the composite. In addition, the increase of carbon percentage in AC/Fe₂(MoO₄)₃ composite after the adsorption of phenol red dyes can be seen in results of EDX/Map analysis (Fig. 3h and i). General, the results of SEM and EDX/Map techniques of AC/Fe₂(MoO₄)₃ composite approved its proper synthesis and ability for the adsorption of phenol red dyes from aqueous solution.

The result of BET analysis of the activated carbon and AC/Fe₂(MoO₄)₃ composite is reported in Table 1. As it can be seen, the particle size of the composite adsorbent is approximately equal to the size of the activated carbon particles. However, the surface area of the composite is 45.978 m²/g which is higher than the surface area of the activated carbon (39.706 m²/g) which leads to its higher adsorption efficiency. Moreover, the composite's pore volume (0.0199 cm³/g) is higher than that of activated carbon (0.0172 cm³/g). These parameters affect the adsorption efficiency of the adsorbents directly and their higher values for the AC/Fe₂(MoO₄)₃ composite approves its proper synthesis and capability in adsorption of pollutants from aqueous media.

Table 1
BET analysis data

Parameter	AC	AC/Fe ₂ (MoO ₄) ₃
BET surface area	39.706 m ² /g	45.978 m ² /g
micropore volume	0.0172 cm ³ /g	0.0199 cm ³ /g
Adsorption average pore diameter	5.454 nm	5.529 nm

Raman spectroscopy which is based on the intensity and measurement of surface bonds [37] is used for the characterization of activated carbon produced from *Mespilus Germanica* leaves and AC/Fe₂(MoO₄)₃ composite (Fig. 4). There is a characteristic bond in 1600 cm⁻¹ (G bond) of the Raman spectrum of the activated carbon which is attributed to sp² vibrations of carbon atoms present in its hexagonal structure

and the sp^3 which is related to irregularities in the carbon atom structure [38, 39]. The mentioned peak is also observed in the composite's spectrum with a slight variation which approves the presence of carbon in its structure. Additionally, the lower intensity can be related to location of iron, molybdenum, and oxygen particles on the activated carbon's surface [40, 41].

3.2. Effect of Solution pH

One of the most critical parameters of adsorption process is solution pH. This parameter plays a key role in promotion of adsorption by changing the status of the adsorbent's active sites [42–45]. The effect of solution pH on the removal of phenol red dyes from aqueous solutions was investigated in the range of 2–11 and the results are illustrated in Fig. 5. Considering this diagram, by decrease of pH from 11 to 3 the electrostatic adsorption between the positive tails of amine group and hydroxyl and the negative ions of dyes happen as the result of protonation of amine and hydroxyl groups of the adsorbent which leads to higher adsorption efficiencies [46, 47]. By further decrease of pH, the competition between H^+ ions of the solution and the protonated amine groups of the adsorbent for the electrostatic adsorption of anionic ions increased which is followed by lower adsorption efficiencies [48]. In high pH values, due to presence of OH^- ions, the number of protonated amine groups on the adsorbent surface decreased; as a result, the total charge of the adsorbent surface becomes negative due to the presence of hydroxyl groups which lowers the adsorption power of the adsorbent due to repulsion between the negative charged surface and dye ions [46, 49]. Considering these data, the optimal pH value for the adsorption of phenol red dyes by $AC/Fe_2(MoO_4)_3$ composite is equal to 3.

3.3 Stirring Rate Effect

Stirring rate effect (0–700 rpm) on the adsorption of phenol red dyes by $AC/Fe_2(MoO_4)_3$ composite was investigated in the optimal pH = 3, 30°C, dosage of adsorbent of 1 g/L, initial concentration of 10 mg/L, and in 60 min (Fig. 6). A positive relationship between the stirring rate and adsorption efficiency was observed; because the probability of collisions between the dye molecules and the adsorbent surface increases in higher stirring rates from 0 to 500 rpm. However, there is not any sensible change in the adsorption efficiency between 500 to 700 rpm, while the process cost increases dramatically. A similar behavior was reported by Modirshahla et al. [50]. Considering these data, the optimal stirring rate for the adsorption of phenol red dyes by $AC/Fe_2(MoO_4)_3$ composite is 500 rpm.

3.4. Effect of Temperature

In adsorption processes, the highest operating temperature is substantially 50°C in order to prevent the degradation and corruption of the adsorbent [51]. Regarding this fact, in this research the maximum temperature in adsorption of phenol red by $AC/Fe_2(MoO_4)_3$ composite was considered equal to 50°C.

Temperature supplies the required energy in the form of heat and its effect on adsorption efficiency depends of endothermic/exothermic nature of the system [52]. The effect of temperature was investigated in this work in the range of 25–50°C and the results are illustrated in Fig. 7. It can be observed that the current adsorption process is temperature dependent and the adsorption efficiency

dropped from 94.31–85.32% in the range of 25–50°C; as a result, the process is exothermic. Such a falling trend of adsorption percentage with temperature can be attributed to the increase of the dye molecules tendency for leaving the adsorbent surface (solid phase) and moving freely in the solution [53, 54] or degradation of the adsorbent active sites in high temperatures [55]. On the other hand, the solubility of the phenol red dyes may be increased by temperature which results in lower adsorption efficiencies [56]. General, 25°C is the optimal temperature for the current adsorption process by AC/Fe₂(MoO₄)₃ composite.

3.5. Effect of Adsorbent Dosage

As a significant parameter of adsorption, the adsorbent dosage is used to determine the adsorbent capacity [57]. In this research, the adsorbent dosage effect was investigated between 0.25 mg/L and 5 mg/L (Fig. 8). It can be observed that by increasing the adsorbent dosage from 0.25 g/L to 1 g/L, the efficiency saw a rise from 28.76–99.23% and became approximately constant for dosages values higher than 1 g/L. Such a trend can be attributed to the higher contact area and higher number of active sites [58]. Moreover, the constant efficiency for the adsorbent dosage values higher than 1 g/L can be the result of low number of the remained dye molecules in the solution. Such a trend was observed in other adsorption processes [56, 59]. Considering the achieved results, the optimal adsorbent dosage was 1 g/L.

3.6. Effect of Dye Initial Concentration and Contact Time

Initial concentration of the pollutant acts as a major role in description of the adsorption mechanism [60]. Figure 9 shows the effect of dye initial concentration (10–100 mg/L). It can be clearly seen that the removal efficiency in 10 mg/L was higher than the other concentrations in all of the contact times. The fall of the efficiency with the increase in the phenol red dye concentration can be the result of attachment of all of the dye molecules on the adsorbent surface in low concentrations, while in higher concentrations the active sites are filled and saturated completely by dye molecules; therefore, the adsorption of the remained molecules is impossible [61].

Contact time affects the adsorption efficiency and determines the kinetic nature of the process [62]. In this research, the effect of contact time on the adsorption of phenol red dyes were investigated between 5 and 160 min and the results are illustrated in Fig. 9. There is a linear initial raising phase (fastest phase of adsorption) in which the pollutant particles diffuse into the surface of the adsorbent. The second phase is the inter-particle diffusion, and the third one is the diffusion of the particles into the small pores of the adsorbent and achievement of the equilibrium time. The rapid adsorption of pollutants in initial phase is the result of the high number of unsaturated active sites on the surface of the adsorbent. Additionally, the concentration gradient of phenol red in the solution in initial moments is high and then decreases gradually with time [63]. Consequently, the concentration gradient and the number of unsaturated active sites on the adsorbent surface decrease with time which results in a constant adsorption efficiency. Overall, 60 min is the optimal contact time for the removal of phenol red dyes from aqueous solutions by AC/Fe₂(MoO₄)₃ composite since the adsorption efficiency is constant behind this point in all concentration values.

3.7. Regeneration Experiments

Regeneration capability of an adsorbent is significant from the economic viewpoint[64]. Reusability studies on the $\text{AC/Fe}_2(\text{MoO}_4)_3$ composite adsorbent after the adsorption of phenol red dyes from the synthetic wastewater was carried out for 5 cycles in the optimal experimental conditions determined in this work and the results are depicted in Fig. 10. For this purpose, prior to washing by methanol and drying in the oven at 120°C , the recovery of the used adsorbent was done by vacuum filtration. Regarding Fig. 10, the removal efficiency of the regenerated adsorbent declined gradually in the first three adsorption/desorption cycles, after which the decline was considerable. This trend is the result of deposition of dye molecules on the surface of the adsorbent and the probable blockage of the active sites [65]. Considering these data, it is possible to use $\text{AC/Fe}_2(\text{MoO}_4)_3$ adsorbent for 3 adsorption/desorption stages of phenol red dyes from the synthesized wastewater and can be considered as an appropriate one for the removal of such pollutants.

3.8. Comparison with similar works

Table 2 summarizes a comparison between the removal percentage of phenol red dyes using $\text{AC/Fe}_2(\text{MoO}_4)_3$ composite adsorbent which was achieved in the optimal operating conditions of the present work and the values in the adsorption studies published earlier. Considering these data, the current adsorption efficiency is in an acceptable agreement with others.

Table 2
Comparison of the current adsorption efficiency with similar works

Adsorbent	Dye	Removal (%)	Ref.
Kola Nut (Cola acuminata) Shell Activated Carbon	Phenol red	89.95%	[14]
Iron Nanoparticle	Phenol red	94.9%	[16]
titanium oxide (TiO ₂) + activated carbon (AC)	Congo red and phenol red	100.24%	[17]
Carbon-CuO nanocomposite	Phenol red	99.98%	[18]
GO-Fe ₃ O ₄ hybrids	Phenol red	68%	[66]
Spinel Co _{1-x} M _x Fe ₂ O ₄ Nano Composites (M = Cd, Ag)	Phenol red	84.2% of Cd and 75.2% of Ag	[19]
TiN-WN composite particles	Methylene blue	90%	[67]
Tea waste/Fe ₃ O ₄ magnetic composite (TWMC)	Crystal violet	98.7%	[68]
Carbon composite lignin-based	Azo dyes congo red and Eriochrome blue black R	99%	[69]
Modified nitrate intercalated MgAl LDH adsorbent	Methyl orange	98.22%	[70]
Hollow mesoporous manganese dioxide nanoadsorbents with strong negative charge and their ultra-efficient adsorption	Crystal violet and methylene blue	95%	[71]
A novel adsorbent (PA-β-CD)	Methylene blue, basic green 4, astrazon pink, and crystal violet	90%	[72]
Current adsorbent	Phenol red	95.1%	This work

3.9. Kinetic Study

In order to evaluate the adsorption progress with respect to time, the kinetic behavior of the process is studied which determines the diffusion of adsorbate into the adsorbent's pores [66]. In addition, it focuses on the rate of the chemical process which is characterized by the parameters affect the rate of the reactions [67]. Kinetics of adsorption process includes the precise investigation of the experimental conditions of the chemical reactions which finally helps finding the appropriate equilibrium time.

In order to investigate the kinetic behavior of phenol red dyes adsorption using AC/Fe₂(MoO₄)₃ composite adsorbent, pseudo first order and pseudo second order kinetic models [68] (Table 3) were applied and the

results and kinetic parameters are reported in Figs. 11 and Table 4.

Table 3
Pseudo-first-order and pseudo-second-order kinetic models equations

Kinetic Model	Equation
Pseudo-first-order linear form	$\ln (q_e - q_t) = \ln q_e - K_1 t$ (3)
Pseudo-second-order linear form	$t/q_t = 1/K_2 + t/q_e$ (4)

Table 4
Pseudo first-order and pseudo second-order kinetic parameters for the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent

Kinetic model	Parameters	Concentration (mg/L)					
		10	20	30	50	70	100
Pseudo-first-Order	q _{e, Cal} (mg/g)	8.22	19.652	28.617	41.650	74.829	127.753
	k ₁ (1/min)	0.047	0.050	0.044	0.034	0.042	0.0453
	R ²	0.972	0.982	0.992	0.99	0.966	0.957
Pseudo-second-order	q _{e, Cal} (mg/g)	10.661	20.964	31.348	52.631	72.993	99.010
	k ₂ (g/mg.min)	0.087	0.0781	0.061	0.048	0.036	0.029
	R ²	0.997	0.997	0.995	0.992	0.983	0.986
	q _{e, exp} (mg/g)	9.781	19.074	27.852	45.465	60.228	78.96

Where q_t, K₁, and K₂ are the adsorbed molecule mass per gram of the adsorbent at given time t (mg/g), pseudo-first-order (1.min⁻¹), and pseudo-second-order (g.mg⁻¹ g⁻¹) constants, respectively. It should be noted that K₁ and q_e values are determined from the slope and intercept of ln(q_e-q_t) versus t diagram and K₂ can be found from the slope and intercept of t/q_t versus t linear diagram.

Considering the reported data, pseudo second order model performed better in description of the kinetic behavior of the process compared to pseudo first order model in all the studied concentrations since the former had higher correlation coefficient than the latter. Additionally, the calculated adsorption capacities achieved by the pseudo-first order kinetic model was lower than the values achieved by the pseudo second order model. In addition, these calculated capacities are in accordance with the data reported in the literature [74].

3.10. Adsorption Equilibrium

Adsorption equilibrium study is carried out using the experimental data and various models. An isotherm model with its unique constants give valuable information about the surface properties and the adsorption capacity of the adsorbents [69]. These isotherms describe the interactions between the adsorbent surface and adsorbates [65]. In the current study, Langmuir [70], Freundlich [71], and Dubinin-Radushkevich [72] isotherm models were used to investigate the equilibrium behavior of the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent in the concentration range of 10–100 mg/L and the results are presented in Fig. 12 and Table 6. The equations of these models are presented in Table 5. Langmuir isotherm is based on the hypothesis that a monolayer adsorption occurs on the active sites of a homogeneous adsorbent, while Freundlich model, as an empirical one, is assumed on the adsorption on a heterogeneous surface [73]. Additionally, Dubinin-Radushkevich model determines the physical or chemical nature of the adsorption processes [74].

Table 5
Equations of Langmuir, Freundlich, and Dubinin-Radushkevich isotherms

Isotherm Model	Definition	Equation	
Langmuir	Linear Form	$\frac{1}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m C_e}$	(5)
	Adsorption Intensity	$R_L = \frac{1}{1 + K_L C_i}$	(6)
Freundlich	Linear Form	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	(7)
Dubinin-Radushkevich	Linear Form	$\ln q_e = \ln q_m - \beta \epsilon^2$	(8)
	Polanyi potential	$\epsilon = RT \ln \left(1 + \frac{q_e}{q_m} \right)$	(9)
	Adsorption Mean Free Energy	$E = \frac{1}{\sqrt{2\beta}}$	(10)

Table 6
The parameters of Langmuir, Freundlich, and Dubinin-Radushkevich isotherms in the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent

Models	Parameters	Value
Langmuir	q_m (mg/g)	78.740
	K_L (L/mg)	0.164
	R^2	0.984
	R_L	0.057–0.378
Freundlich	n	2.046
	K_f (mg/g (L/mg) ^{1/n})	13.705
	R^2	0.988
Dubinin–Radushkevich (D-R)	E (kJ/mol)	1.389
	q_m (mg/g)	42.679
	$\beta \times 10^{-6}$ (mol ² /J ²)	0.259
	R^2	0.763

In equations 5 and 6, q_m and K_L are Langmuir constants and denote the maximum adsorption capacity (mg/g) and adsorption energy (L/mg), respectively. Moreover, R_L is the adsorption intensity factor and for $0 < R_L < 1$ and $R_L > 1$ the process is favorable (and reversible) and unfavorable, respectively, while it is considered favorable (and linear) and reversible for $R_L = 1$ and $R_L = 0$, respectively [68]. It should be noted that using the slope and intercept of $1/q_e$ versus $1/C_e$ linear plot, the values of q_m and K_L are calculated. Additionally, n and K_f are Freundlich model constants and denote the rate of adsorption and the process nonlinearity [75]. The slope and intercept of the $\ln q_e$ vs. $\ln C_e$ diagram is used to calculate K_f and $1/n$. In Dubinin–Radushkevich isotherm model (equations (8–10)) β (mol²/kJ²) and ϵ are Dubinin–Radushkevich isotherm constant and Polanyi potential, respectively, while T is temperature (K), R is the universal gas constant, and E is the adsorption mean free energy (kJ/mol). While the process is considered chemical for $E > 8$ kJ/mol, it is physical in other E values [68]. In order to determine β and q_m , $\ln q_e$ versus ϵ^2 diagram is plotted

Considering the values reported in Table 6 and Fig. 12a, Langmuir maximum adsorption capacity, q_m , was 78.74 mg/g which might be considered a notable value for the maximum adsorption capacity [68, 75]. Additionally, the correlation coefficient of this isotherm model was equal to 0.984 which reflects this model's capability in description of the equilibrium of phenol red dyes using AC/Fe₂(MoO₄)₃ composite

adsorbent. Moreover, the calculated R_L values were between zero and one; as a result, the current adsorption process was favorable and reversible.

Figure 12b shows that Freundlich isotherm model parameter n is equal to 2.046 which denotes the physical nature of the current adsorption process. Moreover, the higher R^2 (0.988) of this model in comparison with the correlation coefficient of Langmuir model approves the higher capability of Freundlich model in description of the equilibrium behavior of phenol red dyes and these dyes were adsorbed on a heterogeneous surface.

Dubinin–Radushkevich adsorption isotherm model was used to evaluate the adsorption energy and the type of the reaction through the calculation of Polanyi Potential (Fig. 12c). Considering the data reported in Table 6, q_m , β and R^2 , are 42.679 mg/g, 0.259 mol²/J², and 0.763 respectively. In addition, the adsorption energy, E , was lower than 8 kJ/mol. Therefore, the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent is physical. General, in the current research Freundlich isotherm model performed better than Langmuir and Dubinin–Radushkevich adsorption isotherms in investigation of the equilibrium behavior of adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent.

3.10. Adsorption Thermodynamics

Thermodynamic nature of the adsorption process can be investigated through the calculation of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) is applied to investigate the spontaneous nature of the process. The required equations for the thermodynamic study of the adsorption process are presented in Table 7. As it can be seen in Eq. 13 (van’t Hoff equation), equilibrium constant is a function of temperature, standard enthalpy change, and standard entropy change [65].

Table 7
Thermodynamic parameters equations

Definition	Equation
Equilibrium constant	$K_e = \frac{q}{C_e}$ (11)
Gibbs free energy	$\Delta G^0 = -RT \ln K_e$ (12)
van't Hoff equation	$\ln K_e = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ (13)

The values of ΔH° and ΔS° is determined from the slope and intercept of $\ln K_e$ versus $1/T$ [75]. Figure 13 and Table 8 illustrate the thermodynamic parameters of the current adsorption process. According to the reported values, Gibbs free energy for the adsorption of phenol red dyes in the range of 25–50°C was negative; therefore, this adsorption process is spontaneous and thermodynamically desirable. It should be mentioned that Gibbs free energy increased with temperature which denotes that the spontaneity of the phenol red dyes adsorption decreased with temperature. Moreover, the negative ΔH° value of the

process shows that the current adsorption process was exothermic. Finally, the entropy (ΔS°) of the process was negative; consequently, the random collisions on the adsorbent surface and in the solution decreased during the adsorption process [76].

Table 8. Thermodynamic parameters for the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent

T(°C)	ΔG°(kJ/molL)	ΔH°(kJ/molL)	ΔS°(J/molL.K)
25	-6.635	-3.764	-9.963
30	-6.098		
35	-5.629		
40	-5.573		
45	-5.038		
50	-4.376		

4. Conclusion

In the current study phenol red dyes were removed from aqueous solutions using AC/Fe₂(MoO₄)₃ composite adsorbent. The result of FTIR, XRD, SEM, EDX/Map, BET, and Raman analyses showed that the applied composite was synthesized well and also performed appropriately in adsorption of phenol red dyes from aqueous solutions. Additionally, the optimal values of solution pH, stirring rate, temperature, adsorbent dosage, initial concentration of the phenol red dyes, and contact time, were 3, 500rpm, 25°C, 1 g/L, 10 mg/L, and 60 min, respectively. The adsorption experiment in the achieved optimal parameters yielded the removal efficiency of 95.1%. In addition, the adsorption percentage decreased with temperature which shows that the process was spontaneous. Furthermore, reusability experiments on the used composite adsorbent showed that it had an acceptable adsorption efficiency after 3 cycles of adsorption/desorption of dyes. Kinetic studies showed that the pseudo-second-order kinetic model performed well in description of the kinetics of the process in comparison with pseudo-first-order model. Additionally, the results of equilibrium studies indicated that Freundlich isotherm model was better in description of the adsorption process in comparison with Langmuir and Dubinin–Radushkevich adsorption isotherm models and the current adsorption process was desirable and physical. Finally, based on the calculated thermodynamic parameters the adsorption of phenol red dyes on AC/Fe₂(MoO₄)₃ composite adsorbent was exothermic and spontaneous.

Declarations

Data Availability

The data used to support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions

Author 1: Alireza Nobakht

- Discussed the results and contributed to the final manuscript
- Carried out the experiments

Author 2: Dariush Jafari

- Conceived of the presented idea
- Developed the theory and performed the computations
- Verified the analytical methods
- Discussed the results and contributed to the final manuscript

Author 2: Morteza Esfandyari

- Performed the analytic calculations
- Wrote the manuscript
- Helped to write the manuscript

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Figures

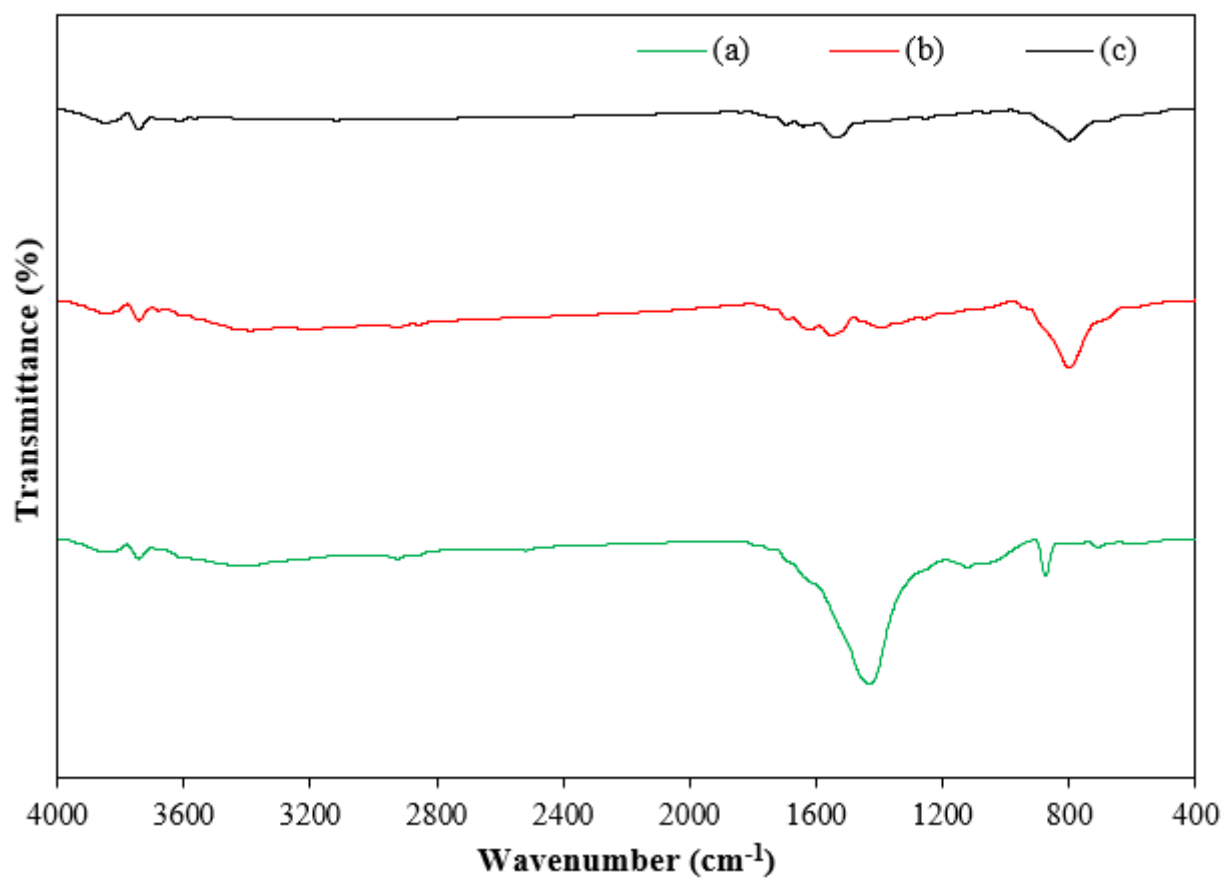


Figure 1

FTIR spectra of a) activated carbon produced from *Mespilus Germanica* leaves, b) AC/Fe₂(MoO₄)₃ composite prior to and c) after the adsorption of phenol red dyes

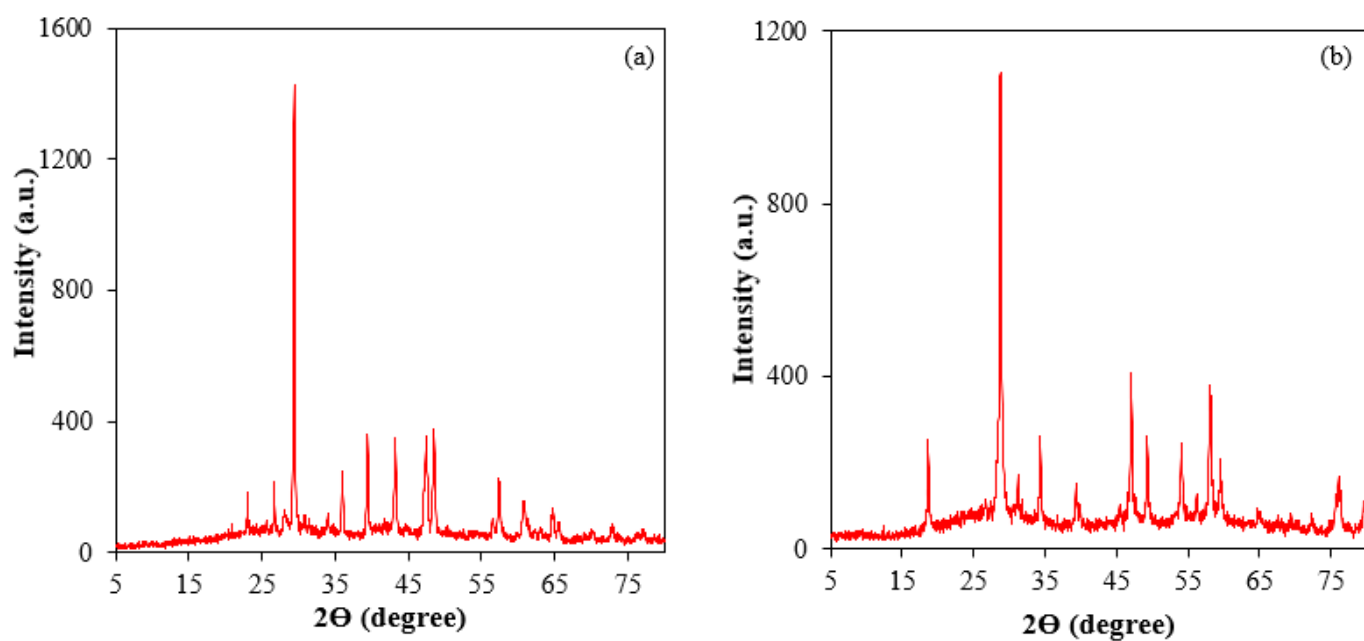


Figure 2

XRD patterns of a) activated carbon produced from *Mespilus Germanica* leaves and b) AC/ $\text{Fe}_2(\text{MoO}_4)_3$ composite

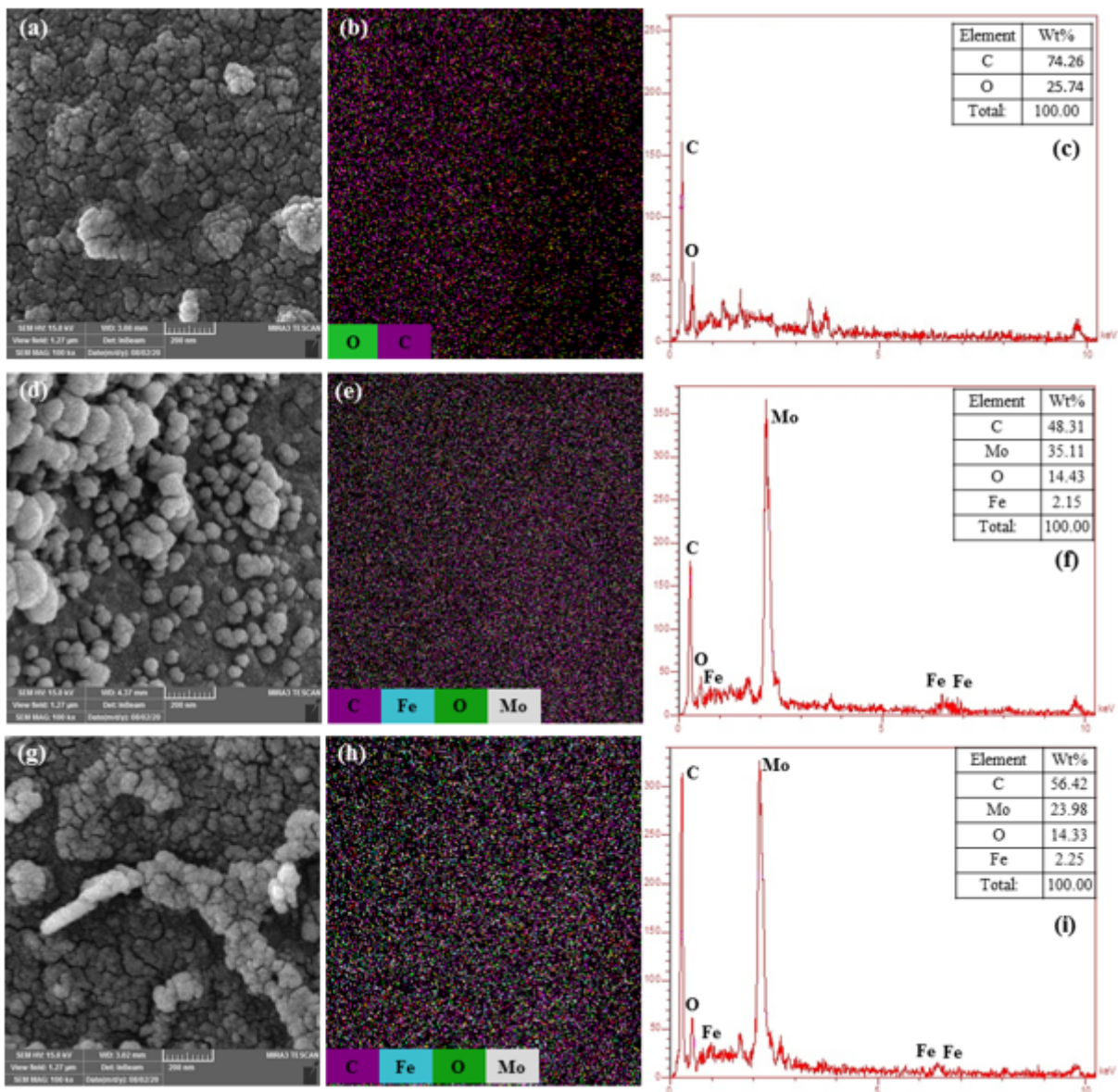


Figure 3

The results of a) SEM, b) Map, and c) EDX of the activated carbon produced from *Mespilus Germanica* leaves; d) SEM, e) Map, and f) EDX of AC/Fe₂(MoO₄)₃ composite before the adsorption; g) SEM, h) Map, and i) EDX of AC/Fe₂(MoO₄)₃ composite after the adsorption

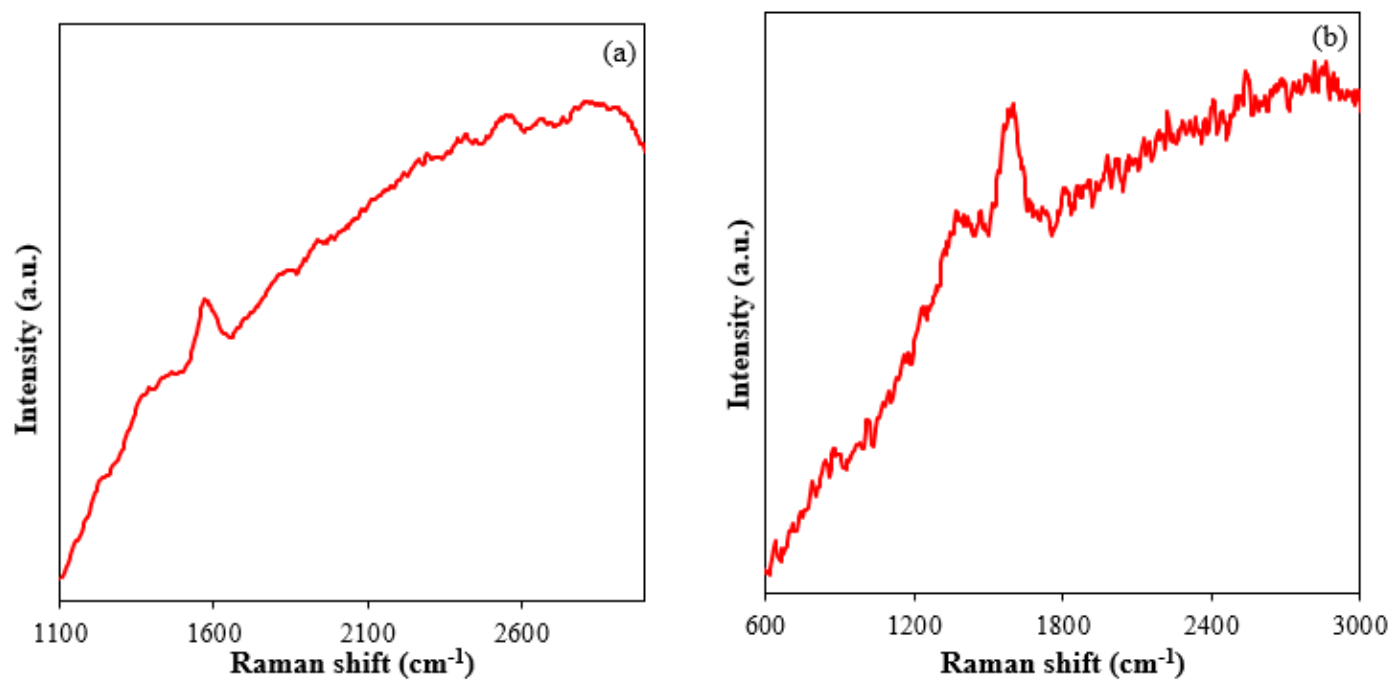


Figure 4

Raman spectra of a) the *Mespilus Germanica* derived activated carbon and b) AC/ $\text{Fe}_2(\text{MoO}_4)_3$ composite

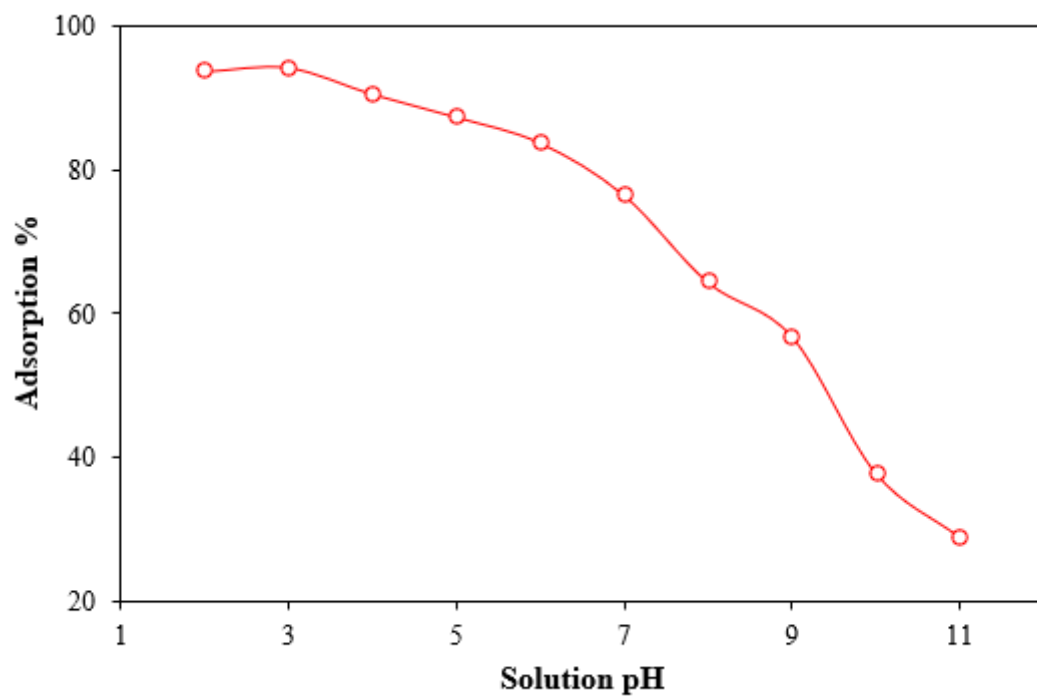


Figure 5

Solution pH effect of on the adsorption efficiency (stirring rate: 700 rpm, T: 30°C, dosage of adsorbent: 1 g/L, conc. 10 mg/L, t: 60 min)

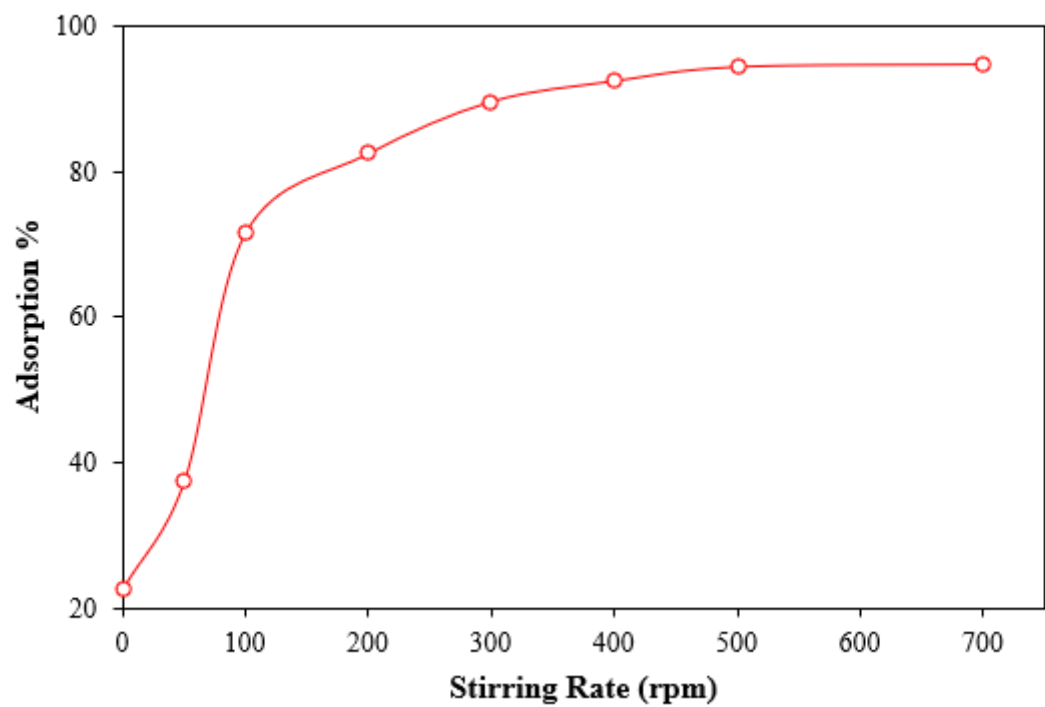


Figure 6

Effect of stirring rate on the adsorption efficiency (pH: 3, T: 30°C, dosage of adsorbent: 1 g/L, conc. 10 mg/L, t: 60 min)

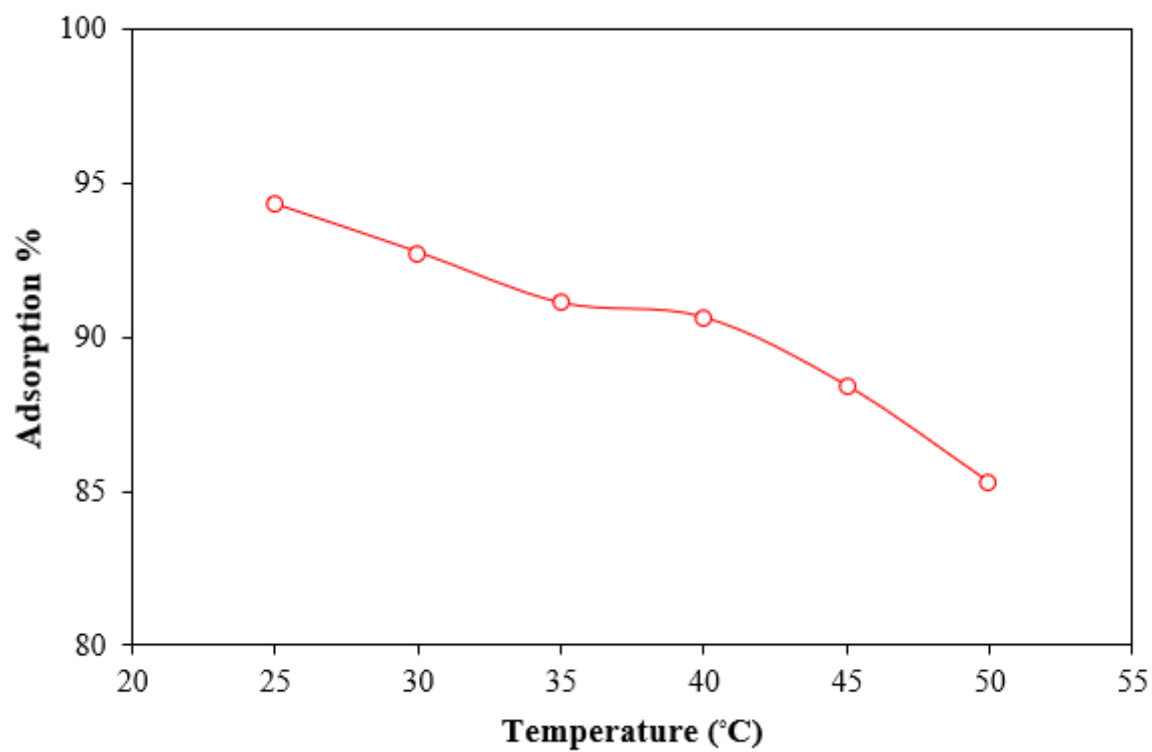


Figure 7

Effect of temperature on the adsorption efficiency (pH: 3, stirring rate: 500 rpm, dosage of adsorbent: 1 g/L, conc. 10 mg/L, t: 60 min,)

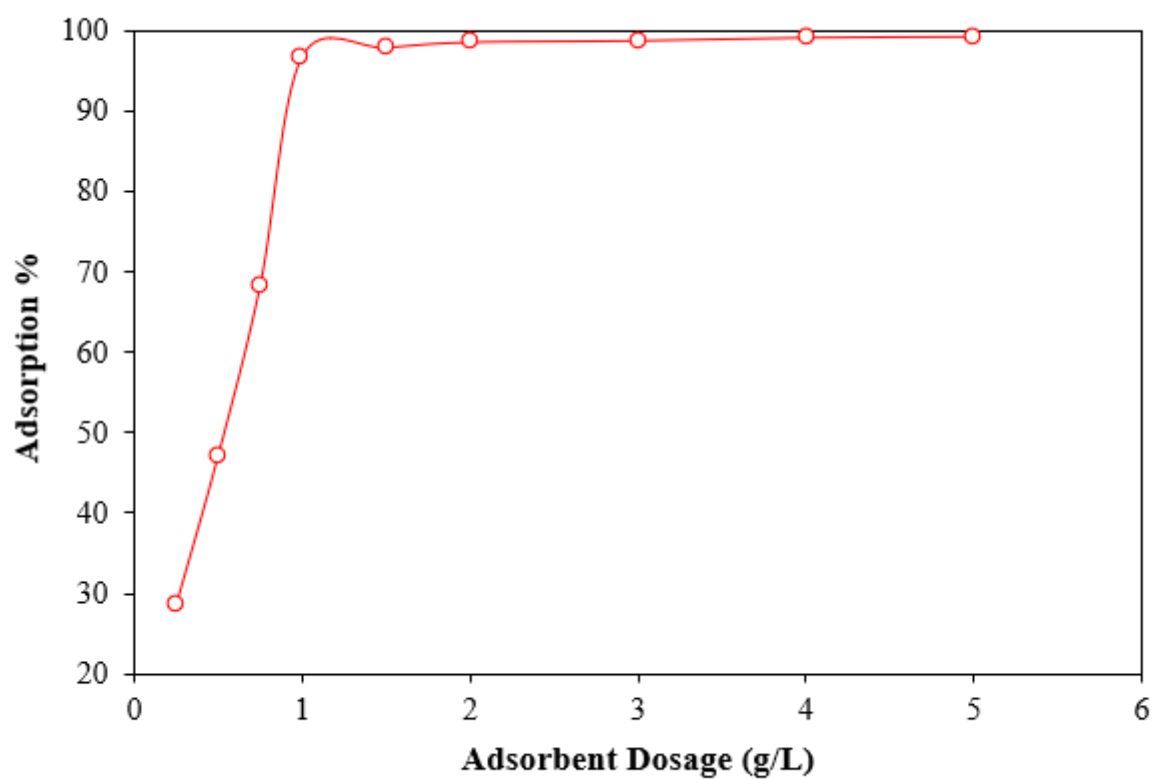


Figure 8

Effect of adsorbent dosage on the adsorption efficiency (pH: 3, stirring rate: 500 rpm, T; 25°C, conc. 10 mg/L, t: 60 min,)

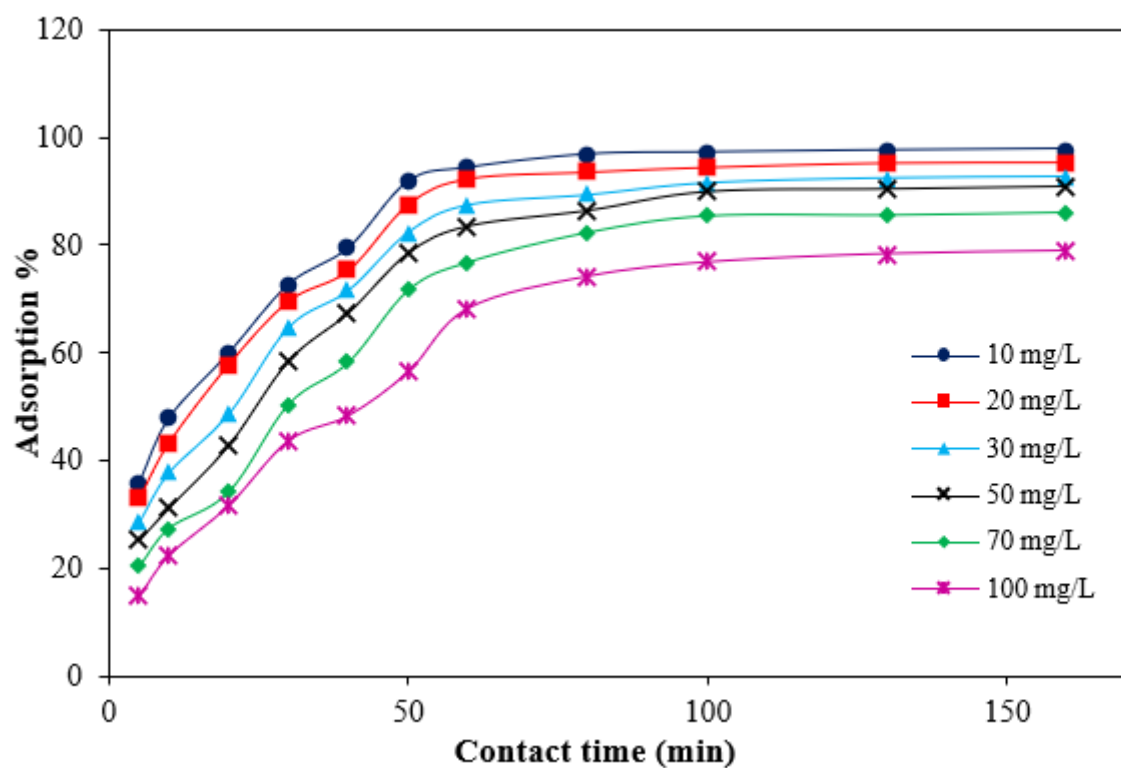


Figure 9

Effect of dye initial concentration and contact time on adsorption percentage (pH: 3, stirring rate: 500 rpm, T: 25°C, dosage of adsorbent: 1 g/L)

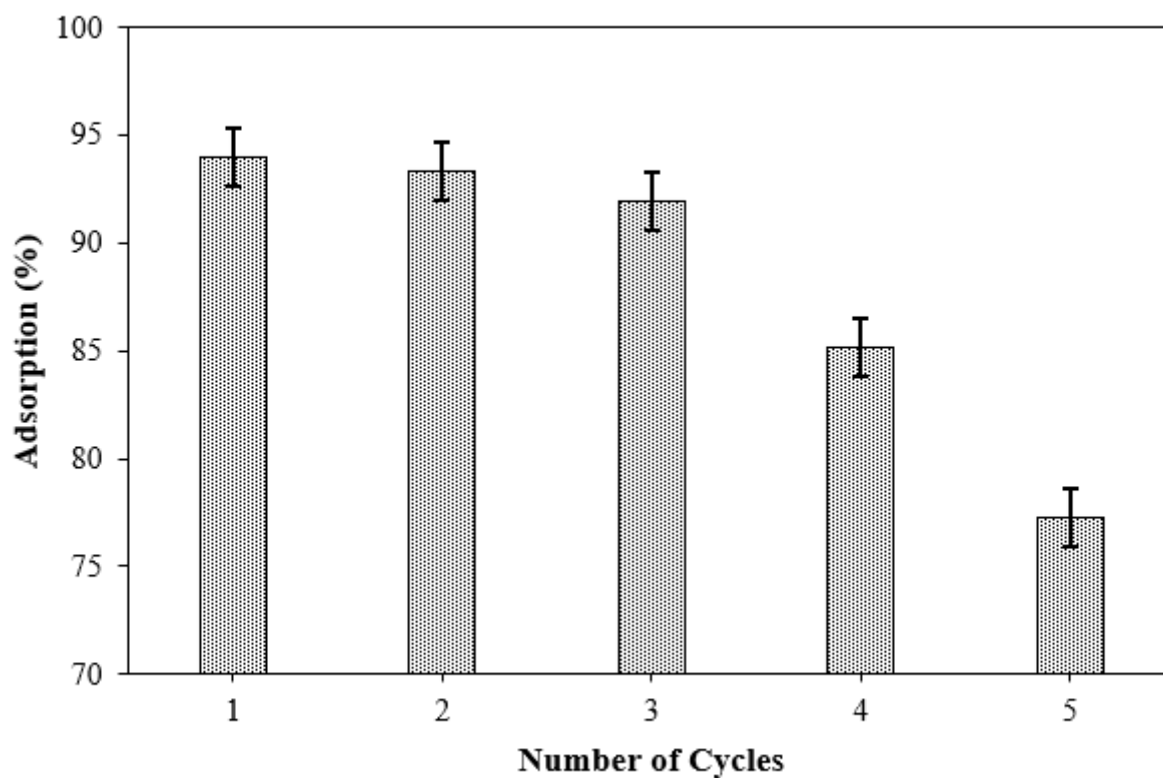


Figure 10

Adsorption/desorption studies of phenol red dyes using $\text{AC/Fe}_2(\text{MoO}_4)_3$ composite adsorbent

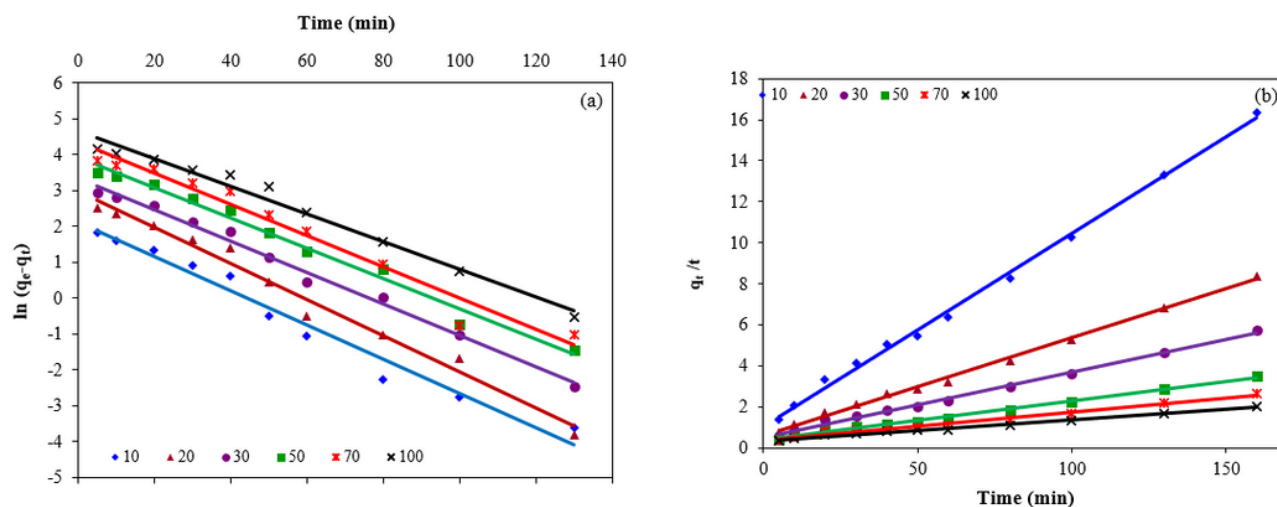


Figure 11

a) Pseudo-first-order and b) pseudo second order model diagrams for the adsorption of phenol red dyes using $\text{AC/Fe}_2(\text{MoO}_4)_3$ composite adsorbent

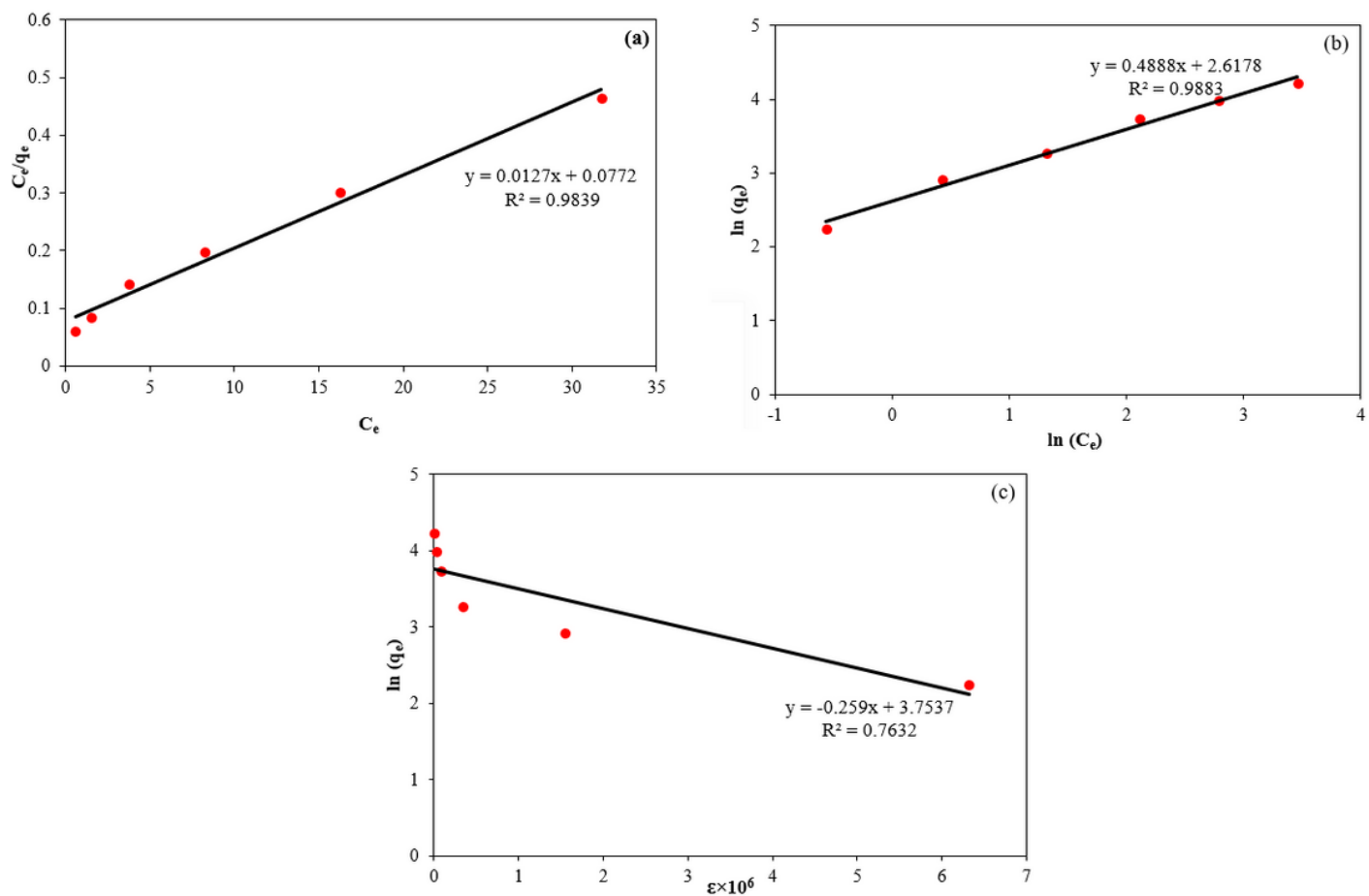


Figure 12

The diagrams of (a) Langmuir, (b) Freundlich, (c) Dubinin–Radushkevich isotherms for the adsorption of phenol red dyes using AC/Fe₂(MoO₄)₃ composite adsorbent

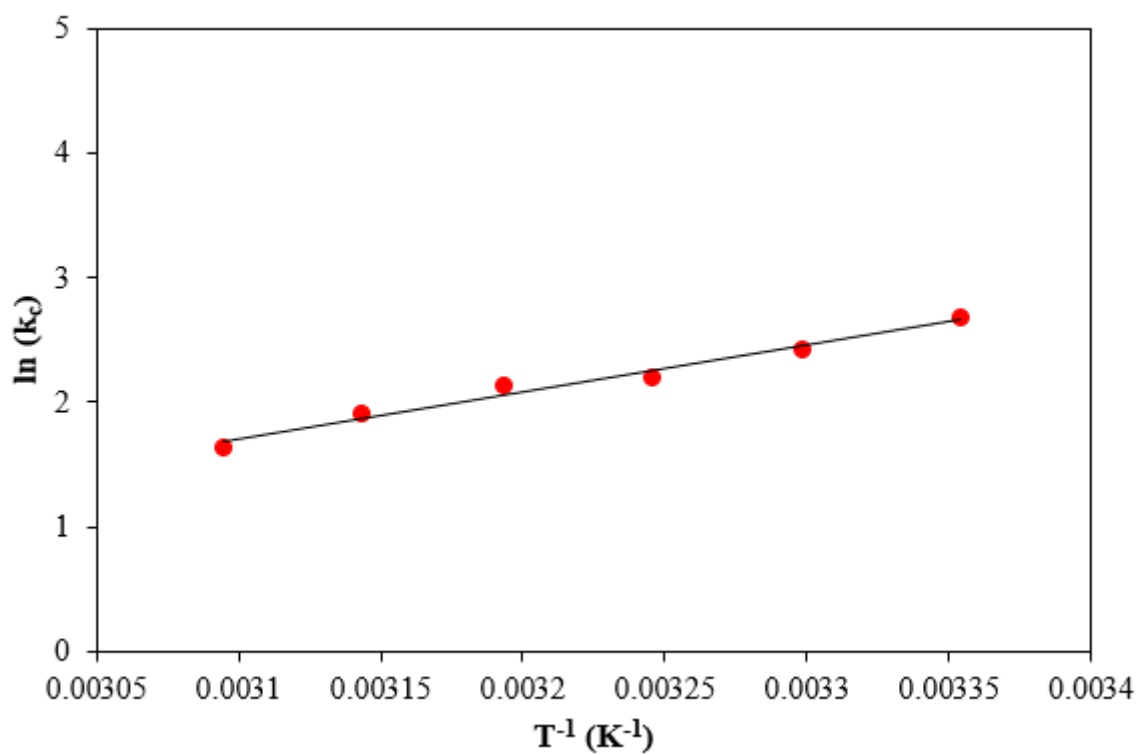


Figure 13

Thermodynamic diagram for the adsorption of phenol red dyes using AC/ $Fe_2(MoO_4)_3$ composite adsorbent