Peganum Harmala L. plant as green non-toxic adsorbent for iron removal from water

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Abstract: The present work focuses on examining the batch removal of Fe (III) from water using powdered Peganum Harmala seeds, characterized as FT-IR. In this work, several parameters are measured, including contact time, pH, Fe (III) concentration, reaction temperature effect, and adsorbent dose effect. Fe (III) adsorption was assessed using a UV-vis spectrophotometer at a wavelength of 620 nm. The findings demonstrated a positive correlation between the dosage of adsorbent and Fe (III) ions removal, with an increase in the adsorbent dose corresponding to higher elimination of Fe (III) ions. Therefore, the Langmuir isotherm model yielded more accurate equilibrium data compared to the Frendulich model. The kinetic data were mostly analyzed using a pseudo-second-order model rather than a pseudo-first-order model. Thermodynamic parameters, including enthalpy ($\Delta H\circ$), entropy ($\Delta S\circ$), and free energy ($\Delta G\circ$), were calculated. The adsorption process was found to be exothermic. Overall, Peganum Harmala was a favorable adsorbent for removing Fe (III) from aqueous solutions.

Introduction

Toxic metals are classified as non-biodegradable toxic pollutants. They can accumulate in the tissues of living organisms and pass through the food chain. For this reason, many studies have investigated the elimination of heavy metals from the food chain to protect public health. In small amounts, such heavy metals as zinc, iron, chromium, manganese, and copper are vital for human bodily functions. However, if accumulated in sufficient quantities to cause poisoning, high levels of heavy metals can result in significant damage. Metal ions such as Fe (III) are often discharged into the environment during various industrial processes, including electroplating, leather tanning, vehicle manufacturing, power plant construction, nuclear facility development, the manufacturing of paint pigments and dyes, and metal finishing (Ayaz et al. 2020). The release of heavy metals into marine ecosystems has become a significant concern in recent years. Iron toxicity in living organisms arises from Fenton and Haber–Weiss reactions, generating reactive oxygen species that cause substantial damage to proteins, lipids, DNA, and other cytoplasmic molecules (Hejna et al. 2020). It is imperative to remove Fe (III) from wastewater prior to disposal into oceans and seas to mitigate its harmful effects. Several physicochemical techniques, including chemical oxidation or reduction, chemical precipitation, membrane filtration, ion exchange, flotation, adsorption, coagulation-flocculation, and electrochemical methods, can be used to address metal contamination (Kučić at al. 2017, Trus et al. 2021, Wu et al. 2019). However, these processes often require significant energy input, and the resulting residual sludge may lead to secondary environmental pollution (Mamba, Dlamini, and Mulaba-Bafubiandi 2009).

The elimination of industrial effluents using traditional methods is costly and sometimes ineffective. Therefore, there is a pressing need to identify new, effective, environmentally friendly, and cost-efficient techniques for treating integrated wastewater. To achieve this goal and ensure economical removal of Fe (III), readily available and inexpensive materials are essential. Surface adsorption is one effective method for purifying aqueous samples by removing heavy metals is. In such processes, various inexpensive and widely available natural resources, including mineral rocks, agricultural waste, and industrial byproducts, have been employed as adsorbents (Laghrib et al. 2021, Rasgele 2021).

Several bio-adsorbents have proven effective in eliminating heavy metal from aqueous solutions, including sugar beet pulp, waste tea, coconut shells, coconut husk, rice husk, spent grain, sago waste, wood waste, chitosan and poultry feathers (Abdel-

Ghani, Hefny, and El-Chaghaby 2007). Peganum Harmala, a commonly self-growing plant, stands out as an easily accessible and straightforward option for preparation and use.

Based on a literature scan conducted by the authors across peer-reviewed publications, the adsorption of Fe (III) using Peganum Harmala seed as an adsorbent has not been previously studied. Therefore, this research represents the first instigation of its kind conducted by the authors. The primary objective of this research is to use powdered seeds of Peganum Harmala for the removal of Fe (III) from water. Multiple parameters, including the pH level of the aqueous solution, the initial metal concentration, the effect of temperature, and the stirring effect will be assessed and analyzed for their impact on the adsorption process.

Materials and methods

Preparation of adsorbent

The Peganum Harmala seeds and sheath were gathered from the nearby region during the arid period and thereafter subjected to gradual pounding. They were then strained through a sieve to purify and isolate them. The purified seeds were exposed to sunlight for 5 days to ensure thorough desiccation. To create the Peganum Harmala seed powder (PPH), granular seeds were ground, pulverized, and calcinated at 300 °C, after which they were applied as an adsorbent. This investigation involved a series of batch adsorption studies, conducted 100 ml Erlenmeyer flasks placed inside an incubator. Magnetic stirrers were used to mix the contents of the Erlenmeyer flasks.

Preparation of Fe (III) as an Adsorbate

The stirrers were set at a predetermined setting to maintain a consistent pace. To prepare a stock solution with a concentration of 1000 mg/l of Fe (III), the required quantity of ammonium iron (III) sulfate dodecahydrate $NH_4Fe (SO_4)_2.12H_2O$ (Aldrich, purity 97%) was dissolved in 1000 ml of double-distilled water. Dilutions of the stock solution were made to achieve the desired concentrations of Fe (III) for the standard solution. In each study, a 100 ml sample containing the determined concentration was placed in the Erlenmeyer flask. Throughout the investigation, HCl (Aldrich, purity 99%) or NaOH (Aldrich, purity 99%) 1N solution was used to regulate the pH level. The pH levels were adjusted using a Metrohm digital pH meter (model 780) equipped with a combination glass electrode. Once the determined adsorbent dose was added to the flask, it was shaken at a regulated speed using a magnetic stirrer. After the designated duration had elapsed, the samples were passed through filter paper, and the resulting filtrates were examined to determine the remaining concentration of Fe (III).

Adsorption pr♦ocess

Various parameters were used to measure the adsorption of Fe (III) onto Peganum Harmala. The parameters used included different pH levels (1.3, 2.5, 3.5, 5, 6.2), varying Fe (III) concentration (50, 70, 100, 150 mg/l), reaction temperatures (30, 40, 50, 60 ∘C), stirring speeds (50, 100, 150, 200, 300 rpm), Peganum Harmala adsorbent doses (0.2, 0.4, 0.6, 0.8, 1g) and contact times (10, 20, 30, 40, 50, 60 min). To ensure accuracy, each sample underwent two examinations, and the average value was recorded. The concentration of iron ions was

determined by analyzing the UV-visible absorption spectrum using a Genesys, Thermo 10S UV-VIS Scientific spectrometer, identifying the ammonia complex. Fourier transform infrared spectroscopy (FTIR-KBr) was conducted using a Perkin Elmer Spectrum 100 FT-IR Spectrometer to identify the specific surface functional groups of Peganum Harmala. The analysis spanned wave numbers from 400 to 4000 cm^{-1}. Nitrogen adsorption-desorption measurements were carried out at 77.35 K on a Nova Touch LX4 Quantachrome, USA to determine the Brunauer–Emmett–Teller (BET) surface area.

Results and discussion

Adsorbent characteristics

FTIR spectra analysis was performed on the fresh Peganum Harmala sample, covering wavelengths ranging from 400 and 4000 cm^{-1} (see Figure 1). The analysis revealed the presence of many significant functional groups on the adsorbents' surface. The novel adsorbent exhibited a wide adsorption band spanning a wavelength range of 3000 to 3633 cm^{-1}, with a maximum at 3400 cm^{-1}. These findings align with prior studies (Gładysz-Płaska et al. 2012), indicating the formation of chemical bonds between both free and bound hydroxyl groups (OH) and the surface. Furthermore, the novel adsorbent materials exhibited a broad adsorption band spanning wavelengths from 2800 to 3000 cm^{-1}, with a peak at 2931 cm^{-1}, indicating the presence of C-H groups on the Peganum Harmala surfaces. Wide absorption bands at wavelengths 1300-1500 cm^{-1} could be attributed to the presence of phenolic groups. Peaks at wavelengths between 1550-1700cm^{-1} suggest the presence of carbonyl groups (C-O) on the surface of the new adsorbents (Moussavi and Khosravi 2012)
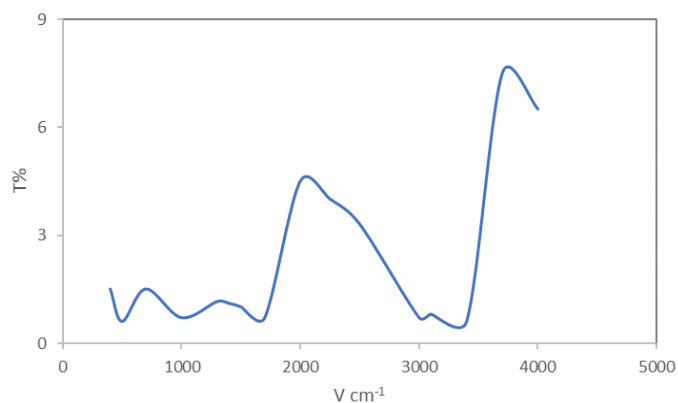

Fig. 1. FTIR spectrum of Peganum Harmala at wave numbers from 400 to 4000 cm -1.

The Brunauer-Emmett-Teller (BET) surface area was determined by conducting nitrogen adsorption-desorption experiments at a temperature of 77.35 K. Prior to measurement, the samples were stored in a desiccator until testing. The samples were subjected to cooling using liquid nitrogen and were then examined by quantifying the volume of gas (N_2) adsorbed at designated pressures. The pore volume was determined by extracting data from the adsorption branch of the isotherm at a pressure ratio (P/Po) of 0.995, assuming complete pore saturation. The results revealed that the BET surface area of Peganum Harmala powder was 132.957 m²/g, with a pore diameter of 1.5711 nm and a pore volume of 0.10445 cm³/g.

The effect of pH

The pH values significantly impact the charges on adsorbent surfaces, influencing the ionization process. Therefore, the solution's pH level plays a crucial role in the adsorption process (Sud, Mahajan, and Kaur 2008). This parameter also affects the heavy metal solution, which, in turn, influences the biosorbents' capacity (Chakravarty, Sarma, and Sarma 2010). Combing 1 g of Peganum Harmala adsorbent with 100 mL of 40 mg/L of Fe (III) ion solution and allowing it to stand for 1 hour enabled researchers to test the removal efficiency of Fe (III) cations at various pH levels. The pH range for the solutions ranged from 1.3 to 6.2. As illustrated in Figure 2 (a, b), the removal of Fe (III) ions was significantly low at acidic pH levels and increased as the pH of the Fe (III) ion solution increased. Similar findings were observed in lead removal using pomegranate peel (El-Ashtoukhy, Amin, and Abdelwahab 2008), where iron removal increased from 47% to 80% at equilibrium. However, at pH levels higher than 6, retardation was observed, possibly due to the involvement of iron hydroxide in the process (Oo et al. 2013). Consequently, pH 6.2 was determined to be optimal for removing Fe (III). The pH value in these circumstances is often referred to as the "adsorption edge" because the metal's removal

and adsorption efficiency increase from very low to very high (Skwarek et al. 2008).

Several factors contribute to the reduction in removal efficiency at low pH levels. Firstly, at low pH values, there is a competition between Fe (III) ions and H+ ions on the surface of Peganum Harmala (Kumar Meena, Rajagopal, and Mishra 2010). Secondly, high concentrations of H+ ions in the solution result in a positively charged Peganum Harmala surface, leading to electrostatic repulsion between the positively charged surface and Fe (III) ions in the solution, thereby causing poor adsorption (Veli and Alyüz 2007). Thirdly, an increase in Cl$^-$ ions in the solution leads to the development of chloro-complexes, reducing the number of available Fe (III) ions for adsorption. Additionally, the larger size of Fe (III) complex molecules compared to free Fe (III) ions minimizes Fe (III) adsorption, further reducing the effectiveness of the process (Zendelska et al. 2015). Higher pH values result in lower hydronium ion concentrations on the adsorbent's surface, thereby reducing proton presence and increasing Fe (III) adsorption (Pandey et al. 2009).

The effect of contact time and initial concentration on the adsorption equilibrium

Time is the only variable that impacts the processes of Fe (III) ion adsorption and removal process when left in contact with the adsorbent for varying periods. Figure 3 illustrates the investigation of the correlation between adsorption and contact time. This study involved using a consistent quantity (1 g) of Peganum Harmala placed in a set volume (100 ml) of Fe (III) solution. Initially, the iron concentration was established at 40 mg/L under a pH of 5. The reaction temperature was set at 323 K, and agitation occurring at 300 rpm. To visualize the impact of increasing contact time on adsorption, a plot was created. A rapid increase in adsorption was observed during the first ten minutes, followed by a slower phase that continued for 20 minutes until maximum adsorption was reached. It is evident that the Fe (III) uptake process occurred rapidly during the initial 15 minutes, followed by a gradual slowdown until the 60-minute mark, where maximum adsorption of Fe (III) ions onto Peganum Harmala q_e at 40 min occurred. Furthermore, the findings indicate that there was no further increase in adsorption beyond this point, indicating equilibrium. The primary aim of increasing the duration throughout the process is to enhance the percentage uptake of the adsorbate metal ions. During the initial minutes of the rapid stage, there was a build-up of metal ions on the active centers of the adsorbent's surface.

A low adsorption rate persisted throughout the slow stage until saturation was reached, marking the stable stage where no further Fe (III) ions could be adsorbed on the Peganum Harmala surface. This phenomenon is elucidated in light of the following point: the reduction of the solution into the adsorbent in solute diffusion leads to the bonding of small quantities of metal ions on the active centers of the adsorbent (El-Araby et al. 2017). This occurs because the binding sites become fixed, resulting in significant resistance to the presence of metal ions at the center of the remaining surface. Furthermore, this process is influenced by the increasing repulsive force between metal ions on the solid surface and the remaining metal ions in the liquid phase (Belay and Hayelom 2014). After 40 minutes, 88 % of the iron ions were removed and remained on the Peganum Harmala surface.
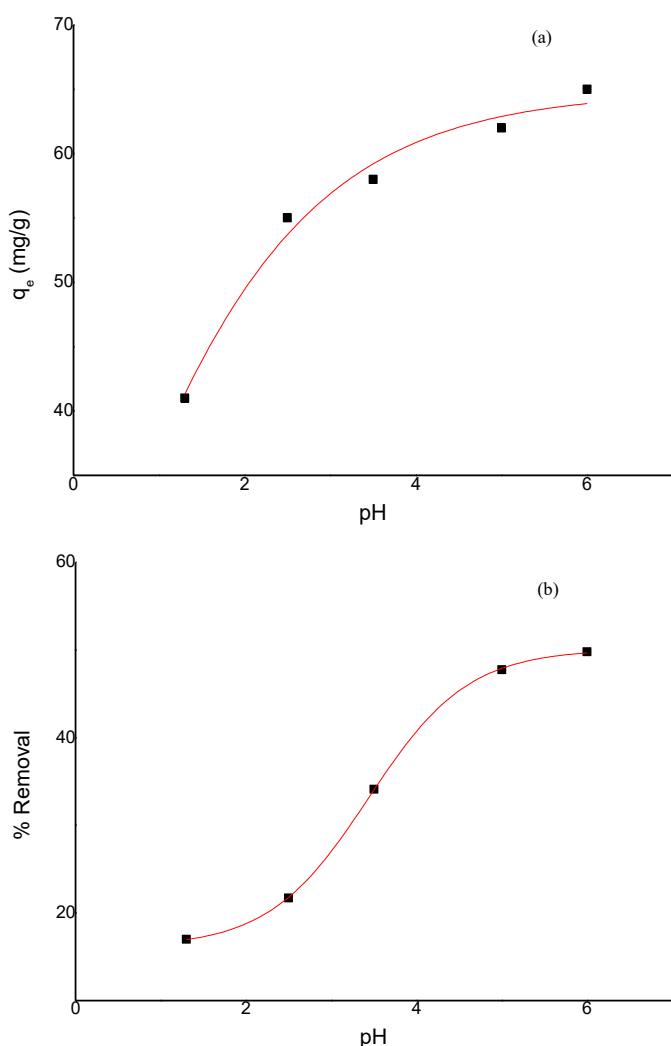

Fig. 2. (a) Effect pH on the Fe (III) ions adsorption capacity at equilibrium on the surface of Peganum Harmala
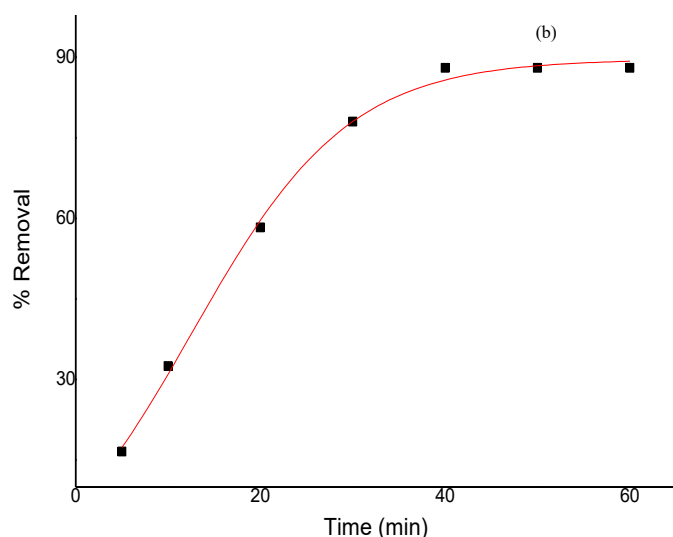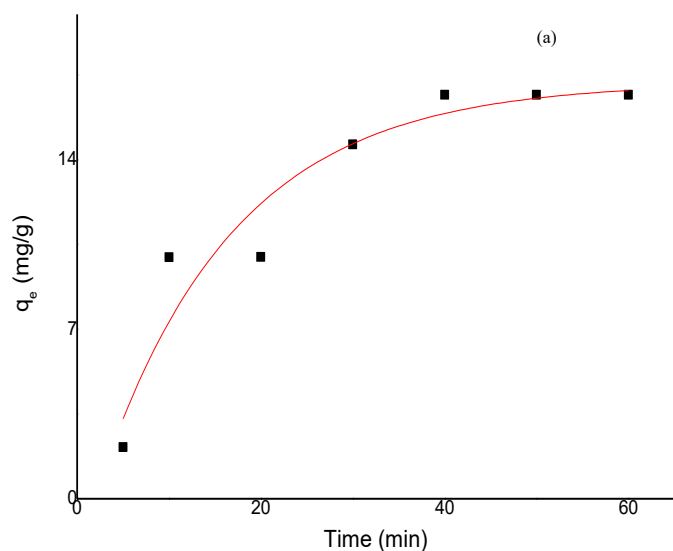(b) Effect pH on the Fe (III) ions removal by Peganum Harmala

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Fig. 3. (a) Effect of time of Fe (III) adsorption by Peganum Harmala.,
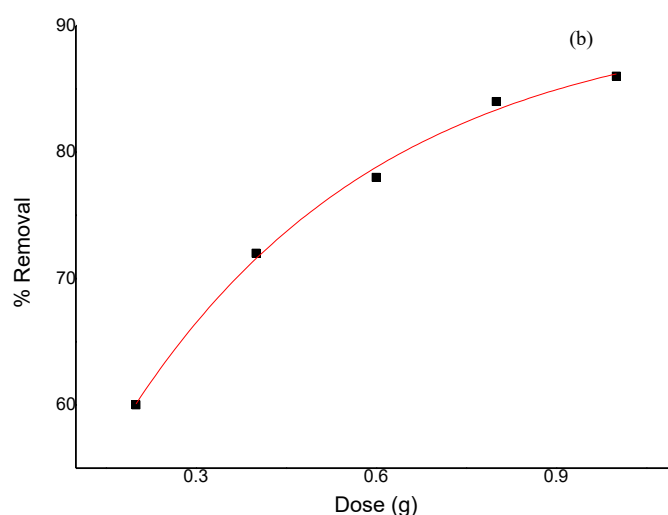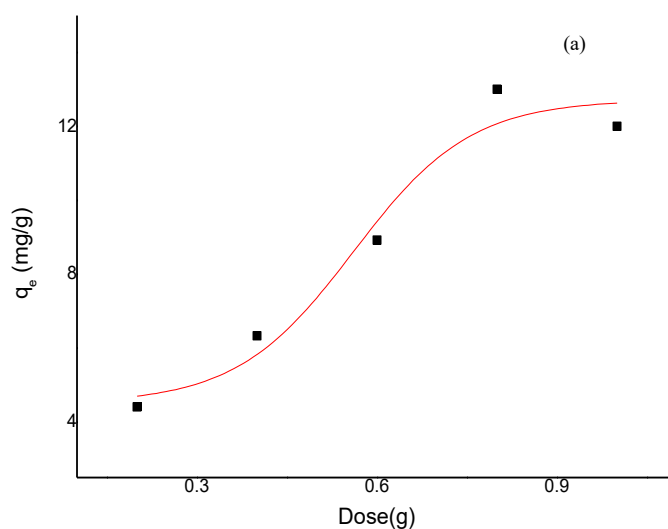(b) Effect of time for removal Fe (III) by Peganum Harmala.

Fig. 4. (a) Effect of Peganum Harmala dose on adsorption capacity at equilibrium
(b) Effect of Peganum Harmala dose on % removal of Fe (III)

Effect of the Adsorbent Dose

The impact of various concentrations of Peganum Harmala as an adsorbent for the elimination and adsorption of Fe (III) ions is illustrated in Figure 4. This study investigated various concentrations of Fe (III) in 100 mL: 0.2, 0.4, 0.6, 0.8, and 1.0 g/100 mL. The pH level was adjusted to 5, the temperature maintained at 323 K, and the revolutions per minute were set to 300. The experiment lasted for a total of sixty minutes. The results emphasized that the elimination of Fe (III) ions increased with the dosage of the adsorbent rising from 0.2 to 1g. As a result, the percentage of removal increased as follows: 60%, 72%, 78%, 84%, and finally 86% for 1 g. The increase in Fe (III) ion removal is sensible as the adsorbent's surface area facilitates more exchanges on the connecting areas of adsorbent pores, leading to an increase in the number of Fe (III) ions removed. This phenomenon is also observed in iron ions uptake (Hossain et al. 2012). However, there is a decrease in adsorption after the dose exceeds 0.6 g. This decrease is primarily because

the adsorbent pores become saturated by the Fe (III) ions (Vijayaraghavan et al. 2009).

The adsorbent accumulates at the active centers alongside the adsorbate, leading to a significant reduction in available surface adsorption sites (Joseph et al. 2019). Interestingly, it appears that as the adsorbent dose increases, the adsorption of Fe (III) ions and the uptake ability decline. The poor adsorption capacity values, ranging between 4 mg/g to 12 mg/g, result from some adsorbent sites remaining vacant throughout the adsorption process due to incomplete absorption of adsorbate ions by the adsorbent surface pores. An increase in the adsorbent dose results in a greater number of unsaturated active sites because the solution contains fewer metal ions compared to the number of available binding sites (Annadurai, Juang, and Lee 2003). Moreover, elevated adsorbent concentrations nord sorbent concentrations decrease the qe, whereas increases in adsorbent concentration and qe can elevate the qe. By reducing the adsorbate surface area, the binding sites become isolated from the iron ions, thereby prolonging the diffusion path of the adsorbent particles (Tumin et al. 2008).
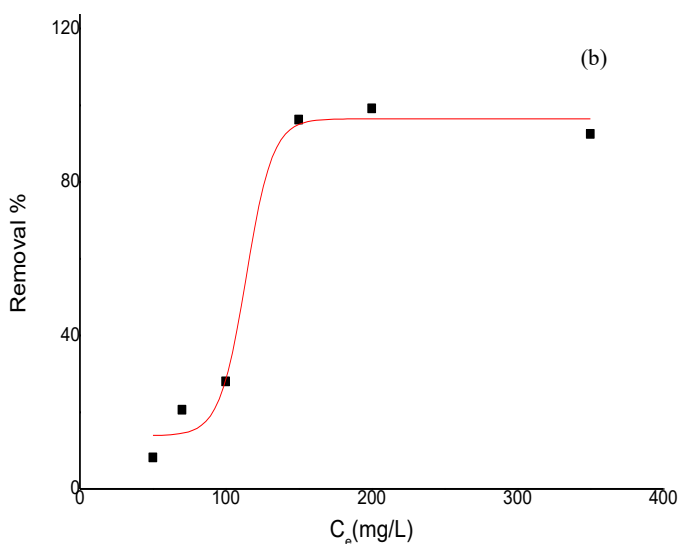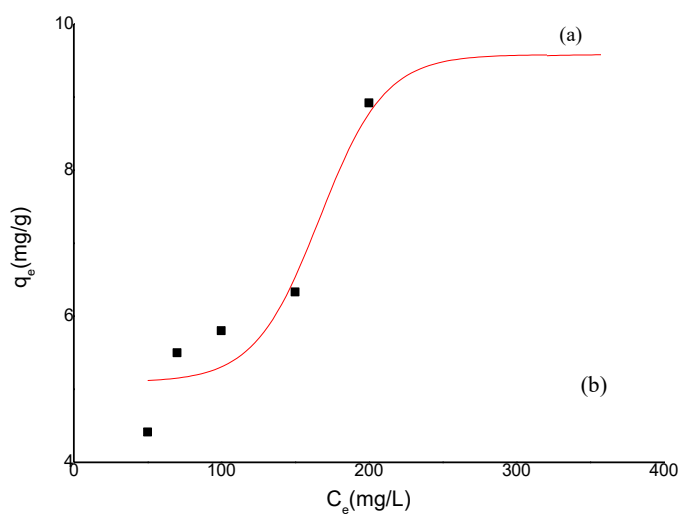
Fig. 6. Effect of temperature of Fe (III) adsorption by Peganum Harmala.

Fig. 5. (a) Effect of initial concentrations on the adsorption capacity at equilibrium
(b) The Effect of initial concentration on removal Fe (III).

The effects of adsorbate concentration

Figure 5 (a, b), shows that as the concentration of the initial Fe (III) ions increases from 50 to 150 mg/L, the uptake of Fe (III) ions also increases. This phenomenon occurs because the adsorbent provides a better surface area ready for adsorption. With a higher concentration of Fe (III) ions, the ratio of the initial number of moles of Fe (III) ions to available adsorption sites increases. As a result, the adsorption percentage will be reduced. Initially, the rate of removal was slow. However, as the concentration of the adsorbate increased, the percentage of removal also increased. The presence of non-adsorbed ions in the liquid phase and the efficiency of removing metal ions by reduction are influenced by the initial concentration. These observations are in agreement with previous studies conducted by (Bhatti et al. 2008).

Effect of temperature

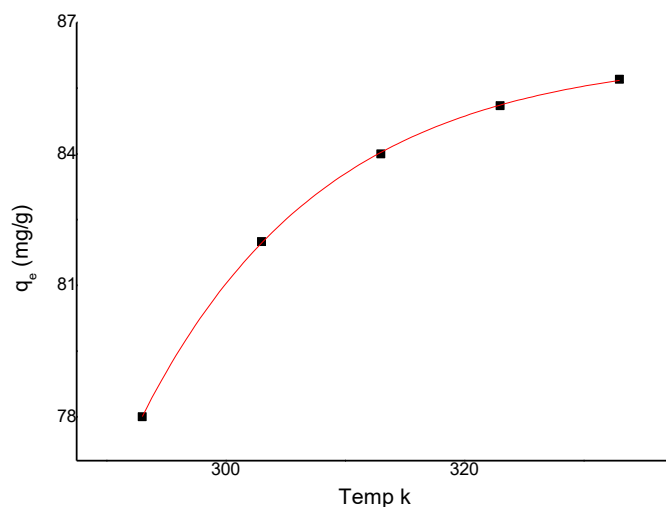The removal of Fe (III) ions by Peganum Harmala was investigated at temperatures of 303 K, 313 K, 333 K, and 343 K, with an initial concentration of 40 mg/L. The results indicate that as the temperature increased from 303 to 333 K, the removal of Fe (III) metal ions by Peganum Harmala increased from 78.0 % at 333 K to 84.1% but it decreased to 83.1% at 343 K. (see Figure 6).

The increase in temperature leads to enhanced effective adsorbate diffusion in the adsorbent's porous microstructure, as the adsorption process is notably influenced by temperature-dependent dispersion forces and electrostatic interactions. Consequently, significant changes occur to the surface chemistry of the adsorbent, potentially promoting desorption. At higher temperatures, the adsorption of heavy metals is reduced, and bonds between the adsorbent and adsorbate may break, facilitating desorption. Moreover, high temperatures result in a decrease in the thickness boundary, allowing Fe (III) ions to leave the surface and enter the liquid phase, thereby reducing the amount of available adsorbent surface area.

Effects of mixing speed

Table 1 outlines the effects of mixing speed on Fe (III) sorption. The findings reveal that as the mixing speed increases, there is a corresponding increase in the amount of F (III) adsorbed. For instance, at a mixing speed of 300 rpm, 9 mg/g of Fe (III) is absorbed into the PPH. This suggests that the removal of Fe (III) is more effective at higher mixing speeds. The efficiency of Fe (III) removal is enhanced with higher mixing speed because iron ions are distributed more efficiently onto the

Table 1. Effect of mixing speed of Fe (III) adsorption by Peganum Harmala

MIXING SPEED (RPM)	QE (MG/G)
50	7.3
10	7.9
150	8.4
200	9
300	9

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surface of adsorbents. The increased agitation facilitates better contact between the Fe (III) ions and the adsorbent surface, leading to greater adsorption.

Isotherms of Adsorption

The result showed that as the initial concentration Fe (III) ions increases, there is an extension in the driving force for mass transfer, facilitating adsorption within the range of 50 to 150 mg/L. The highest adsorption of Fe (III) ions was observed at an initial concentration of 100 mg/L, reaching 65 mg/g, followed by a decrease to 59 mg/g at 150 mg/L. This trend suggests that the increased adsorption of Fe (III) ions can be attributed to the expansion of the mass transfer driving force with rising initial concentrations (Hema and Arivoli 2010). These findings are similar to those reported by Ang (Ang et al. 2013), who investigated the adsorption of Fe (III) using powdered neem leaf. In their study, they observed that the maximum adsorption capacity was reached when the active sites of the adsorbent became saturated, resulting in a subsequent decline in adsorption efficiency. This observation was further verified by the examination of the results, which indicated a proportional increase in adsorption capacity with rising initial concentrations of metal ions. Thus, the data suggest a direct correlation between the adsorption capacity and the initial concentration of Fe (III) ions.

The Langmuir and Freundlich isotherm models were both used in this study to analyze the adsorption of Fe (III) ions. The observed increase in Fe (III) ion adsorption can be attributed to the growing mass transfer driving force as the initial concentration of metal ions increases (Hema and Arivoli 2010). These findings are similar to those revealed by Ang (Ang et al. 2013), who investigated the adsorption of Fe (III) using powdered neem leaf. In their study, they observed that the maximum adsorption occurred when the active sites of the adsorbent became saturated, resulting in the observed decrease in adsorption. This trend was confirmed by the analysis of the findings, which also showed that the adsorption capacity rose as the initial concentration of metal ions increased. Therefore, both the Langmuir and Freundlich isotherm models were employed in this work.

Langmuir Isotherm

The Langmuir Model is a widely utilized and essential tool used to examine the adsorption isotherm process. It involves plotting C_e/q_e against C_e to obtain a linear relationship. This makes it possible to compute the correlation coefficient, R^2 value, and Langmuir constants b and q_e. In this study, the correlation coefficient R^2 value was found to be 0.93. This is presented in Table 2 alongside the values for the Langmuir b and q_e constants. The following equation represents the Langmuir (Langmuir 1916) model:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{1}{q_{max}} \cdot C_e \qquad (1)$$

The adsorbent's maximum capacity is represented as q_{max} (mg/g), while q_e (mg/g) denotes the equilibrium adsorption capacity for the ions present on the adsorbent. C_e denotes the equilibrium ion concentration in the solution, and this refers to the coverage monolayer of the adsorbate on the adsorbent.

Both the adsorption efficiency and adsorption energy are affected by the Langmuir constants q_{max} and b (Imran Ali and V. K. Gupta 2006). Figure 7 presents a straight line obtained from the linear plot of C_e/q_e versus C_e. Analysis of the results suggests that adsorption appears to be adequate when using the Langmuir model. Furthermore, there is a dimensionless equilibrium parameter known as the existence of monolayer adsorption. (R_L) (Weber and Chakravorti 1974) which can be applied to describe the Langmuir isotherm. This can be written in the following way:

$$R_L = \frac{1}{bC_i} \qquad (2)$$

R_L represents favorable and unfavorable adsorption: Unfavorable: $R_L > 1$; Linear: $R_L = 1$; Favorable: $0 < R_L < 1$; Irreversible: $R_L = 0$. C_i denotes different Fe (III) ion concentrations. Moreover, Table 2 also presents the analysis results for the Langmuir isotherms, and the following R_L values can be seen: 0.28, 0.14, 0.095, 0.071, and 0.0057. In this respect, the R_L values, which ranged from 0 to 1, indicate that there was adequate adsorption of Fe (III) ions onto the active Peganum Harmala centers (Yao, Qi, and Wang 2010).
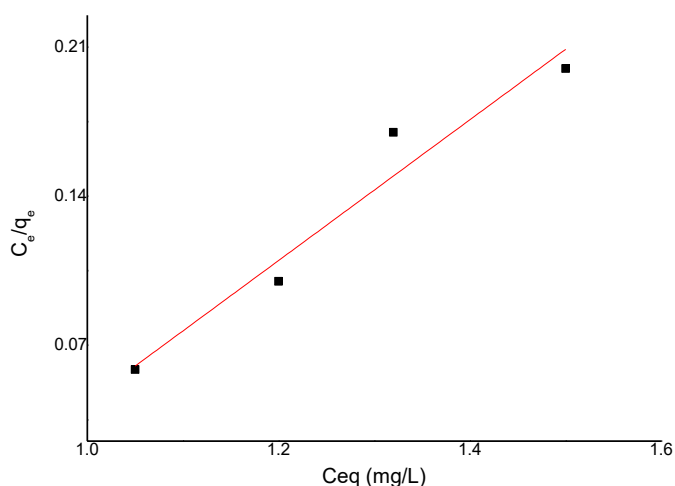
Fig. 7. Linear Adsorption isotherm for Fe (III) ions onto Peganum Harmala by Langmuir.

Freundlich isotherms

Equation 3 is derived from Freundlich's work (Freundlich 1906), and expresses the logarithmic form, with K_F and n being Freundlich constants. When plotting log q_e versus log C_e, a straight line is identified in Figure 8 and Table 2.

$$log\ q_e = log K_F + \frac{1}{n} log\ C_e \qquad (3)$$

The experimental parameter n, which is associated with the adsorption concentration of the adsorbent, serves as an indicator of the extent of favorable adsorption. This parameter is influenced by the solid variety and heterogeneity of the material, thereby quantifying the adsorption convenience represented by parameter n. When the value of n falls within

Table 2. Parameters of Langmuir and Freundlich isotherms for adsorption of Fe (III) onto Peganum Harmala surface

Isotherms	Parameters			
	q_{max} (mg/g)	b (l/mg)	R^2	R_L
Langmuir	300	0.86	0.93	0.28, 0.14, 0.095, 0.071 and 0.0057
Freundlich	K_F (L/g)	n	R^2	
	1.161	10.72	0.92	

Table 3. Maximum adsorption capacities q_{max} of Fe (III) by different adsorbents

Adsorbent	Maximum monolayer adsorption capacity (mg/g)	References
Coconut husk-based activated carbon	434.78	Dyes Pigments 51 (2001) 25–40
Oil palm fibre-based activated carbon	277.78	Chem. Eng. J. 127 (2007) 111–119
Wheat straw	4.96	Proc.1999 Conference on Hazardous Waste Research,
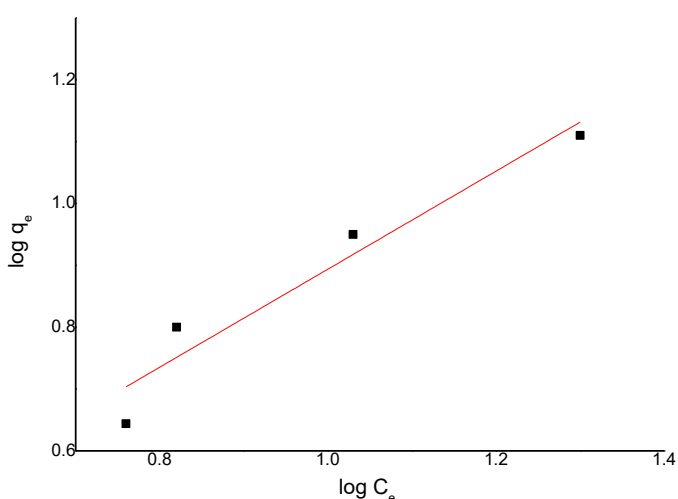
Fig. 8. Linear Freundlich adsorption isotherm for Fe (III) ions adsorption by Peganum Harmala.
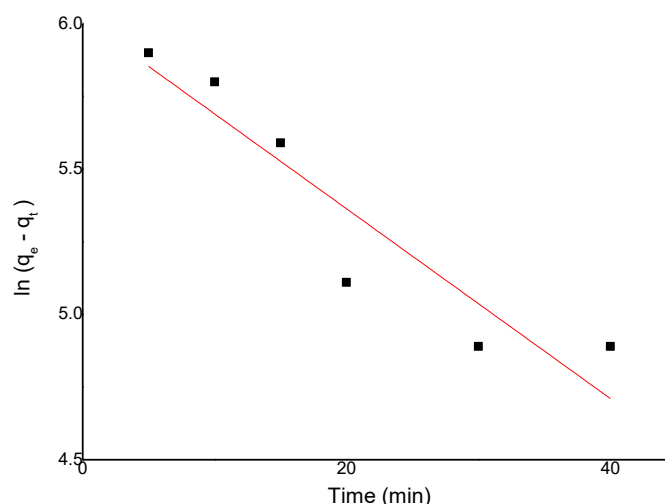
Fig. 9. Pseudo first-order plot for the adsorption of Fe (III) onto Peganum Harmala.

the range of 1 to 10 (with 1/n being less than 1), it indicates that adsorption occurred on the heterogeneous surface of the adsorbent (Ho and McKay 1998), indicating multilayer sorption as well (Aksu and Kutsal 1991).

As determined by both the linear and nonlinear Langmuir models, Table 3 displays the maximum adsorption capacities (mg/g) of Fe (III) using different adsorbents mentioned in the literature.

Adsorption kinetics

Pseudo-first- and pseudo-second-order kinetic models describe the kinetic mechanism of adsorption (Aksu and Işoğlu 2005). Moreover, the first-order model adsorption rate constant from prior work (Tran, You, and Chao 2016) and the rate-limiting phase in the adsorption process (Aregawi and Mengistie 2013) are detailed. The following equation may be used to represent the first-order kinetic reaction:

$$\frac{dq_t}{dt} \ K_1 (q_e - q_t) \quad (4)$$

The linear form of the above equation is written as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

At equilibrium and time t, the quantities of Fe (III) ions adsorbed onto the surface of Peganum Harmala are represented by q_e and q_t, respectively, in mg/g. The rate constant of the pseudo-first-order kinetic model is denoted as K_1 (min−1). By plotting ln (q_e-q_t) against t, a straight line can be created. This line also enables the derivation of the constant K_1, correlation coefficient R^2 and theoretical q_e. Figure 9 indicates discrepancies between the calculated (q_e, calc.) and experimental values. The poor correlation coefficient R_2 of the pseudo-first-order kinetic model, compared to the pseudo-second-order kinetic model, suggests that its adsorption kinetics were not suitable.

The appropriate kinetic model for the adsorption mechanism is the pseudo-second-order model. This model is characterized by chemical reactions where electrons are shared
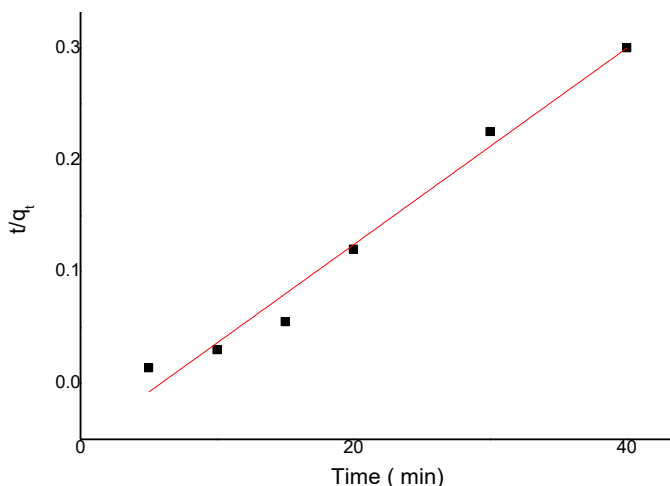
Fig. 10. Pseudo second-order plot for the adsorption of Fe (III) onto Peganum Harmala.

Fig. 11. Effect of temperature on thermodynamic behavior of adsorption of Fe (III) onto Haramla plant.

or exchanged between the adsorbate and adsorbent due to valence forces. The equilibrium adsorption can be determined using the following relationship:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \qquad (6)$$

A linear relationship between the plot of t/q_t versus t is observed (Figure 10). This relationship is used to determine the rate constant k_2 (g / (mg. min)) of the pseudo-second-order kinetic model, as well as the calculated value of q_e. The findings are summarized in Table 4, where the R^2 value approached 1. The calculated equilibrium adsorption capacity values, q_e, calc., were either identical to or had a relative value to the experimental q_e exp. The adsorption kinetics in this case conform to the pseudo-second-order model kinetics, regardless of the initial Fe (III) concentrations.

Thermodynamic Parameters

Figure 11 shows the calculation of thermodynamic parameters, including free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$). The process may be described by the transport of the solute in the mole unit to the solid-liquid interface. The thermodynamic parameters may be computed using the following equation:

$$ln\, K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (7)$$

$$\Delta G = \Delta H° - T\Delta S° \qquad (8)$$

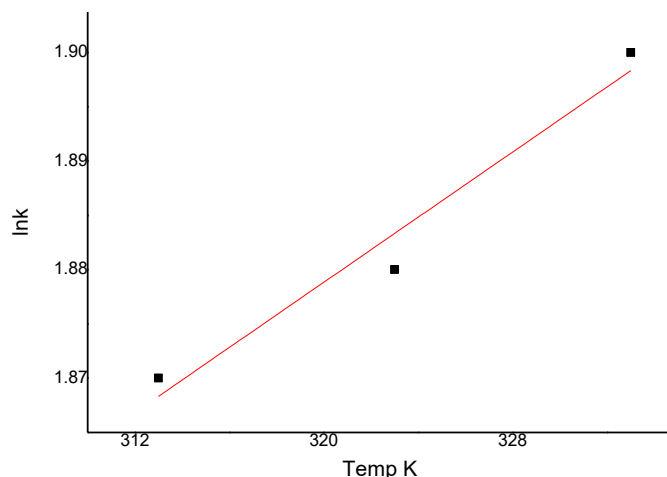**Table 5.** Thermodynamic parameters for the adsorption of Fe (III) onto Peganum Harmala

T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol•K)
313	-36.01	-3.828	-11.0197
323	-34.45		
333	-37.17		
343	-37.75		

$$\Delta G = -RT\, ln\, K_d \qquad (9)$$

The thermodynamic parameters mentioned earlier, namely, $\Delta H°$, $\Delta G°$, and $\Delta S°$ were determined through the calculation of ln Kc versus 1/T. The corresponding outcomes are presented in Table 5. The negative values of the thermodynamic parameters indicated that the adsorption process was characterized by exothermic. According to Table 5, the negative value of $\Delta S°$ may be attributed to the association between $\Delta S°$ and the adsorption process. The binding of Fe (III) ions to the active sites of Peganum Harmala seeds did not follow a specific pattern during the formation of the activated complex between the substance being adsorbed and the substance doing the adsorbing (Tran et al. 2016). Furthermore, in these circumstances ($\Delta S° < 0$), the negative value of ΔS indicated Peganum Harmala's affinity for Fe (III) ions as well as the growing unpredictability at the solid–solution interface throughout the adsorption process (Bulut and Tez 2007).

The process and spontaneous nature of the adsorption of Fe (III) ions onto the prepared Peganum Harmala were indicated by the negative value of $\Delta G°$. It was observed that

Table 4. Kinetic parameters and correlation coefficients of two kinetic equations for initial Fe (III) ion concentrations onto Peganum Harmala surface

Initial concentration Peganum Harmala (mg/l)	Pseudo-second-order kinetic model				Pseudo-first-order kinetic model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/g.min)	R^2
40 mg/L	331	1.66	1.49	0.95	359	0.97	0.95

as the temperature increased, the magnitude of ΫG° decreased, indicating a reduction in driving force and consequently a decline in adsorption capacity.

Conclusion

● The findings of the current study clearly indicate that the pseudo-first-order model is more suitable for describing the adsorption of Fe (III) ions on the active centers of the surface of Peganum Harmala compared to the pseudo-second-order reaction model. Additionally, the Langmuir adsorption isotherm proves to be more appropriate than the Freundlich adsorption isotherm. The negative values of thermodynamic parameters suggest the exothermic nature of the adsorption process, while the negative values of entropy exposure indicate the absence of randomness and organized structure at the liquid-solid interface.

● In addition, it is noteworthy that associative adsorption took place; the adsorption of Fe (III) ions onto 1 g of Peganum Harmala was spontaneous, as indicated by the negative magnitude of free energy ΔG. This suggests that Peganum Harmala is a more effective natural adsorbent in comparison to synthetic adsorbents.

● Peganum Harmala is a convenient, easily accessible, and cost-effective plant for reducing the amount of pollutants and some heavy metals in water.

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