Peganum Harmala plant as an adsorbent for the removal of Copper(II) ions from water

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Batch removal of Cu(II) from water by powdered seeds of Peganum Harmala has been investigated in this research. The Peganum Harmala seeds were collected after which they have been beaten slowly, separated and then cleaned using a sieve. The prepared sorption is characterized by FT-IR. Batch adsorption studies have been undertaken in 100 ml Erlenmeyer flasks, inside an incubator container. The main process parameters that are considered are pH, contact time, Cu(II) concentration, the Adsorbent dose effect and reaction temperature effect. Cu(II) is measured at a wavelength of 620 nm, using a UV-vis spectrophotometer. The result evidence that the maximum removal of Cu(II) is observed at pH 6.2, with the pH over 6.2 result to participate the copper hydroxide. Clearly, the uptake process of the Cu(II) ion occurres very swiftly from the outset of the experiments during the first 15 min, after which there is a low decrease until 40 min, when maximum adsorption of Cu(II) ion onto Peganum Harmala is observed. An increased Cu(II) ions removal percentage occurres with increasing dose of adsorbents, increasing from 0.2 to 0.6 g followed by an increased percentage removal from 63.50% to 66.02%. Subsequently, the removal of Cu(II) ions decline, with an increased dose to 1g. Langmuir adsorption isotherm is more appropriate than the Freundlich adsorption isotherm, while the pseudo second-order reaction model is suitable for adsorption of the Copper ion onto the active centers of the Peganum Harmala surface compared with the pseudo first-order model.

Keywords: Adsorption, Adsorption isotherm, Cu(II), Heavy metal, Langmuir, Peganum harmala, Water purification

Although heavy metals are recognized as non-biodegradable toxic pollutants, some such as copper, chromium, iron manganese and zinc are fundamental to animal life. However, the doses of heavy metal required for normal body function are very small and excessive doses can accumulate in living tissues causing poisoning. This presents a particular problem when heavy metals from industrial and manufacturing processes accumulate in the environment and enter the food chain. Cu(II) and other heavy metals are used in diverse processes including making automobile, dyes and paint pigments, nuclear facilities and power plants, steel, electroplating, leather tanning and metal finishing[1]. To help protect public health and to minimize the risks of heavy metal poisoning, many researchers have dedicated their efforts to eliminating heavy metals from the food chain. Heavy metal pollution of aquatic ecosystems is of particular concern. Copper is a toxic metal; in the environment, it is mainly present in the divalent state (Cu(II))[2]. The toxicity of copper is attributed to its ability to produce reactive oxygen species (ROS); copper catalyzes these through the Fenton reaction and the Haber–Weiss cycle[2]. The resultant ROS leads to oxidative stress, which is severely damaging to DNA, lipids, proteins, and other molecules in the cytoplasm. Before waste water enters the aquatic system, it is vital that Cu(II) is removed first.

The physicochemical methods that can be used to remove heavy metal contaminants from the environment are diverse. They include adsorption, chemical precipitation, chemical oxidation or reduction, coagulation-flocculation, electrochemical, flotation, ion exchange and membrane filtration[3]. However, the energy required for many of these methods is often high. Also, the issue of secondary environmental pollution arises once the heavy metals have been isolated from the environment as sludge remains, which also needs disposing[4].

Traditional methods of cleaning industrial waste are typically costly, and their effectiveness is often suboptimal. Devising novel methods of treating wastewater that removes and recovers Cu(II) effectively, cheaply and in a manner that is environmentally friendly and integrated into the industrial process is essential[5]. Decontaminating aqueous samples can be effectively achieved using the surface adsorption

method of adsorbing heavy metals. There are many adsorbent materials available including agricultural waste, industrial by-products and mineral rocks. These are abundant, inexpensive materials and include biosorbents. Examples of this category are chitosan, coconut husk and shell, poultry feathers, rice husk, sugar beet pulp, spent grain, sago waste, waste tea and wood waste[6].

The perennial plant, Peganum Harmala, or wild rue, is considered a weed, which can be prepared and used easily. The authors reviewed peer-reviewed journals for literature relating to the use of Peganum Harmala seed as an adsorbent of Cu(II). Finding no published studies of using Peganum Harmala seeds to remove Cu(II) from water, the authors undertook such a study. It considers the various factors that could influence the effectiveness of the adsorbent. These parameters include the pH of the water, the amount of sorbent, the initial concentration of Cu(II) and duration of contact time. The adsorption isotherms and kinetics of the process investigated.

Experimental Section

Preparation of adsorbent

Peganum Harmala sheathed seeds were collected from ripening plants in the local area. Seeds were separated from the plants by beating slowly and then they were sieved to remove debris. The cleaned seeds were left in the sun for five days to allow them to dry out completely. Then to form the adsorbent, the seeds were ground into a powder. The adsorbent powder was examined closely to determine its morphological structure and its specific surface area and functional groups.

Experimental

The factors considered in this study were pH (1.3, 2.1, 3.1, 3.9, 4.4, 5.1, 6.2), initial concentration of Cu(II), dose of Peganum Harmala adsorbent (0.2, 0.4, 0.6, 0.8, 1), contact time (10, 20, 30, 40, 50, 60 min), effect of temperature (30, 40, 50, 60, 70). The adsorptions studies were performed in a batch system, using 100 mL Erlenmeyer flasks inside an incubator. Magnetic stirrers with a fixed setting to achieve a constant speed were used to ensure the contents of all the Erlenmeyer flasks were homogenous. A stock solution was prepared by dissolving 1000 mg/L Cu(II), 3.93 g of $CuSO_4.5H_2O$ in 1000 mL of double distilled water. Appropriate dilutions of the Cu(II) stock solution were made to achieve the desired concentrations of Cu(II) standards. Concentration was

measured copper ions using the UV-visible (Genesys, Thermo 10S UV-VIS Scientific spectrometer) absorption spectrum for their complex with ammonia. For each test, the first 100 mL of the determinate concentration sample was added into the Erlenmeyer flask. HCl (1N) or NaOH (1N) was used to regulate the pH, which was monitored using a Metrohm digital pH meter (model 780) fitted with a combined glass electrode. The determinate dose of adsorbent was then added to the Erlenmeyer flask and the contents were immediately shaken at a constant speed. After desired contact time, samples were poured into a filter paper to remove the solution. The concentration of Cu(II) in the resulting filtrates was determined. Sample accuracy was assured by evaluating each one twice and reporting the average result. Fourier transform infrared spectroscopy (FTIR-KBr) was used at wave numbers ranging from 400 to 4000 cm^{-1} to identify the surface functional groups of Peganum Harmala.

Results and Discussion

Adsorbent characteristics

In this experiment, FTIR spectra analyses were performed using wave numbers varying between 400 and 4000 cm^{-1} of the Peganum Harmala as shown in Fig. 1. The findings revealed that several functional groups are present on the adsorbent's surface. A wide adsorption band was identified at wavenumbers between 3000 and 3633 cm^{-1} (maximum 3400 cm^{-1}). This indicates the presence of free hydroxyl groups (-OH) bonded to the adsorbents' surface. This is in line with the results of prior research[7]. A second adsorption band was revealed in the Peganum Harmala spectra when the wave numbers were set
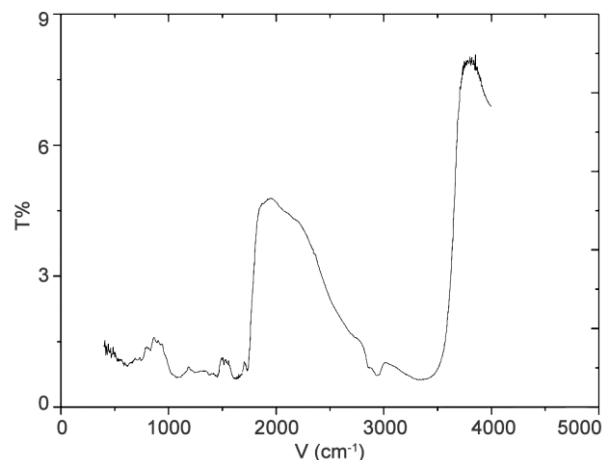

Fig. 1 — FTIR spectrum of Peganum Harmala at wave numbers from 400 to 4000 cm^{-1}

between 2800 and 3000 cm^{-1} (maximum 2931 cm^{-1}), which indicates the existence of C-H groups on the Peganum Harmala's surface[8]. Another adsorption band between 1500-1700 cm^{-1} indicate the presence of carbonyl groups (C-O). Additionally, the investigation revealed an adsorption band at between 1100-1200 cm^{-1}, which could indicate the presence of phenolic groups[9].

*p*H effect

Solution *p*H play an essential role in the adsorption process because verifying of *p*H values has an influence on the charges of adsorbents surfaces also the ionization process[10]. Chemistry of heavy metals solution may be affected by this parameter, which also markedly affects the ability of bio-sorbents[11]. The determination of the removal efficiency of Cu(II) cations by different values of *p*H was performed through weighing 1 gm of Peganum Harmala adsorbent with 100 mL of 40 mg/L concentration of Cu(II) ion solution for 1hr. The *p*H of solutions was varied between 1.3 to 6.2. Figure 2 indicates that Cu(II) ions removal was very low at acidic *p*H, which increased in accordance with increased *p*H of Cu(II) ion solution. A similar trend was found for lead removal by pomegranate peel[12,13], while increased removal of copper at equilibrium being observed from 14.54% to 57.09%. The *p*H values for solutions will be altered from 1.3 to 6.2, because above a magnitude of *p*H 6 this results in hindrance and result to participation of the copper hydroxide[14,15]. Therefore, the optimum removal was *p*H 6 for Cu(II). The metal's removal and adsorption efficiency increase from a small level to a high value, meaning that the *p*H value in such cases is called "adsorption edge[16,17].
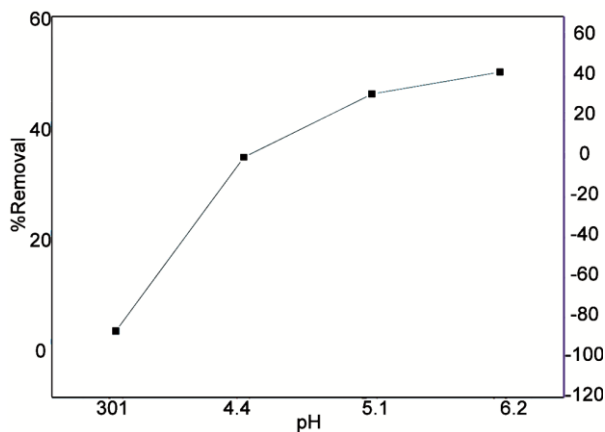

Fig. 2 — *p*H effect on the Cu(II) ions removal by Peganum Harmala. Reaction conditions: Peganum Harmala (1 g), Cu (II) (40 mg/L), reaction temperature (323 K), time (1 hour), rate stirring (300 rpm).

Low *p*H decreases removal performance due to the following reasons:

a) The competition on the adsorption surface between Cu(II) ions and H$^+$ ions on the surface of the Peganum Harmala with a low *p*H value[18].

b) At low *p*H, the positive charge of the Peganum Harmala surface was a result of the presence of H$^+$ ions in a high concentration in the solution. The occurrence of electrostatic repulsion between the Peganum Harmala surface which is positively charged and the copper (II) ions in the solution led to unfavourable adsorption arising[19,20].

c) Adjusting *p*H and increasing Cl$^-$ ions in the solution results in the formation of a chloro complex, decreasing Cu(II) ions. Additionally, the larger size of the complex molecules compared with the free Cu(II) caused less copper(II) uptake to a limited effect[21]. The effect of high *p*H values decreases the hydronium ion concentration on the surface of the adsorbent, thus it becomes free of protons and the increase uptake of Cu(II) is observed[22].

Contact time effect and initial dye concentration on the adsorption equilibrium

Time is the crucial variables describing the adsorption and removal process of Cu(II) ions, according to the various contact time of the aqueous solution with the adsorbent. Adsorption's dependence on contact time was investigated using a constant amount (1 g) of the Peganum Harmala in a constant volume (100 ml) Cu(II) solution, with the initial concentration of copper being 40 mg/L at *p*H 5, reaction temperature 323 K and the speed of shaking was of 300 rpm with contact time of 10, 20, 30, 40, 50 and 60 min. A plot was plotted to see the results of increasing adsorption related to increased contact time. During the first ten minutes, a high fast step was observed, followed by a slow step until maximum adsorption was reached in the following 15 min. Evidently, the uptake process of Cu(II) ions occurred very quickly from the outset of the experiments during the first 15 min, followed by a slow decrease until 40 min, where Cu(II) ion's maximum adsorption onto Peganum Harmala was observed. Beyond this, the results evidenced no increased uptake or adsorption, resulting in a period of equilibrium.

The reason of increasing steps in the percentage uptake of the adsorbate metal ions during the first minutes is that during the fast stage, the occupation of the adsorbent surface on active centers by high amounts of metal ions in the solutions was seen.

During the slow stage, there was a low rate of adsorption until saturation appears, reaching a steady stage where no more Cu(II) ions are adsorbed on the Peganum Harmala surface. This step may be explained further based on the following point. Small amounts of metal ions are linked on the adsorbent activecenters, attributed to declining solute diffusion of the solute into the adsorbent [23]. This is due to limitation of binding sites, alongside the resistance to occupation of metal ions on the remaining surface centers, as well as due to the emergence of repulsive force between the remaining metal ions in the liquid phase and the metal ions on the solid surface[24]. The removal process of the copper ions onto Peganum Harmala surface was 99.01% after 10 min of contact time.

Effect of the adsorbent dose

Figure 3 presents the percentage removal and adsorption of Cu(II) ions according to the various doses of Peganum Harmala. The different doses used in this research were: 0.2, 0.4, 0.6, 0.8 and 1.0 in 100 mL of 40 mg/L Cu(II), with the pH adjusted at 5, temperature being 323 K and at rpm 300, a contact time of 60 min. The results indicate that there is an increase of Cu(II) ions removal in the percentage when the dose of adsorbents increased, increasing from 0.2 to 0.6 g, result to an increase in the percentage removal from 63.50% to 66.02%. Subsequently, the removal of Cu(II) ions increases from 83.33% to 83.97%, with an increase in the dose to 1g. The increase in Cu(II) ion removal is reasonable, the reason being that the adsorbent's surface area leads to a more capable exchange on the linkage places of the adsorbent pores, also for copper ion uptake[25,26]. The reasons for decrease in adsorption with increased dosage exceeding 0.6 g is because of the saturation of adsorbent pores by copper (II) ions[27].

The active sites interact with the adsorbent and with the adsorbate, as a consequence of the adsorption surface being completely minimized[28]. The adsorption of Cu(II) ions and the uptake capacity progressivelydecreases as the adsorbent dose increases, as evidenced in Figs 3 a,b. The low adsorption capacity values from 311 mg/g at 0.2 g to 1 mg/g is due to the adsorbent surface pores not completely accumulating the adsorbate ions, meaning that certain adsorbent sites remain empty during the adsorption process. An increased adsorbent dose results in a greater number of unsaturated active sites, because of insufficiency of metal ions in the solution compared to the available binding sites[29,30]. Moreover, the large mass of sorbent and increased adsorbent dosage are the reason to decrease q_e, while the large mass of sorbent and increasing adsorbent dosage are the reasons for decreased q_e. Lowering of the adsorbate surface area therefore results in the binding sites being shielded from the copper ions, as well as increasing the diffusion path of adsorbent particles[31,32].

Effect of adsorbate concentration

Adsorption was carried out with various initial concentrations of the Cu(II) ion (50, 100, 120, 300, 400 and 500 mg/L) as shown in Fig. 4. With increasing the initial metal ions concentration, a decrease in the removal rate of copper ions was observed. The reason may that the active sites are available for the sorbent and they are prepared for accumulation and occupation by metal ions, which achieve adsorption with low initial concentrations. Therefore, a substantial amount of Cu(II) ions may be adsorbed at the sites at low initial concentrations. However, at higher concentrations, the active sites are unavailable for occupation and the adsorption active sites become fewer, resulting in Cu (II) ions being
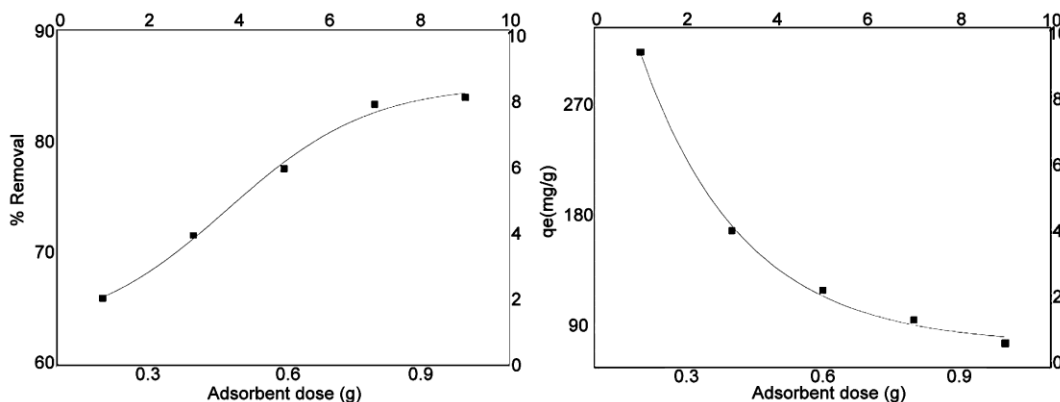

Fig. 3 — (a) Effect of Peganum Harmala dose on the % removal b) adsorption capacity at equilibrium of Cu(II) ions.Reaction conditions: Cu (II) (40 mg/L), PH (5), time (1 hour), reaction temperature (323 K), rate stirring (300 rpm).
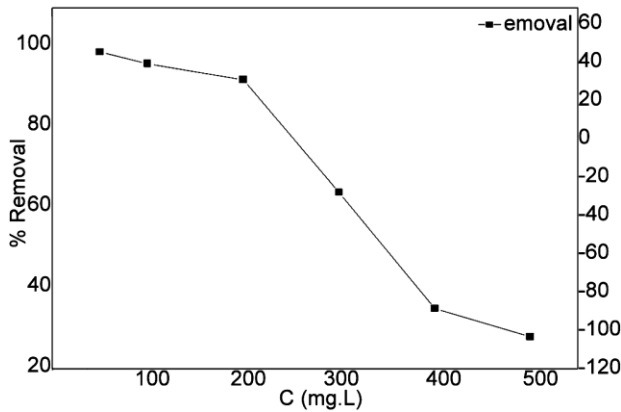
Fig. 4 ─ The Effect of Cu(II) initial concentration. Reaction conditions: Peganum Harmala (1g), PH (5), time (1 hour), reaction temperature (303 K), rate stirring (300 rpm).
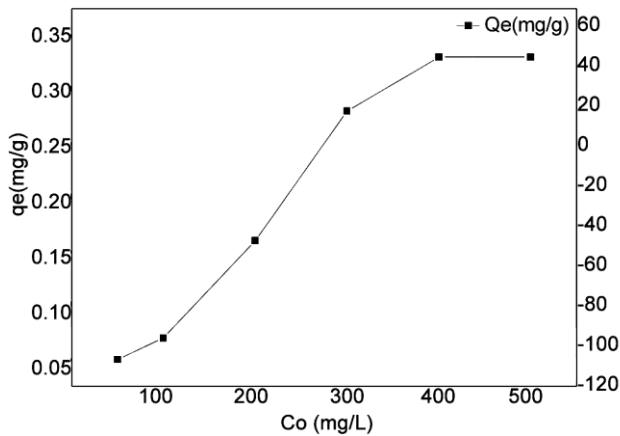

Fig.5 ─ The effect of initial concentrations of Cu (II) on the adsorption capacity at equilibrium. Reaction conditions: Peganum Harmala (1g), PH (5), time (1 hour), reaction temperature (323 K), rate stirring (300 rpm).

non-adsorbed in the liquid phase and the reduction of metal ions removal being dependent on the initial concentration. These observations in agreement with previous studies by Bahatti *et al*.[33], Azouaou *et al*.[34] and Yao *et al*.[35].

Isotherms of Adsorption

The significant stage in the adsorption process is the selection of appropriate adsorption isotherms to fit the results analysis[36]. The results presented in Figure 6 explain that the equilibrium adsorption isotherms of Cu(II) ions onto the Peganum Harmala seeds. A vertical raise with small amounts of concentrations suggests that at a high concentration, it would have a strong relevance to the solute, the adsorbed amounts marginally increase, while a horizontal curve appears. Figure 5 shows also that the adsorption capacity at equilibrium (q_e) increased from 6 mg/g to 34 mg/g, with a rise in the initial dye

concentrations from 50 to 500 mg/L, the amount of Cu(II) ions concentration of 40 mg/L to the highest value of 34 mg/g at 400 mg/L of Cu(II) ions, followed by a decline to 33 mg/g at 500 mg/L. The mass transfer driving force would expand when the initial concentration increases, thus explaining the higher adsorption of Cu(II)ions[37,38]. Similar results were found by Ang *et al*[39], who specified the adsorption of copper(II) by using neem leaf powder. The analysis of results established that the adsorption capacity increased as the initial concentration of metal ions increased, until in this case the maximum adsorption reached the saturation of active molecules, causing the observed decline in adsorption.

Two models of adsorption isotherms have been chosen for this research, namely the Langmuir and Freundlich isotherm models.

Langmuir Isotherm

One of the most effective models used to represent the adsorption isotherm process is the Langmuir model. When C_e/q_e is plotted against C_e, a straight line may be obtained, with the value of the correlation coefficient, R^2 and Langmiur constants b and q_e also possible to calculate. The equation of Langmuir [40] can be written as follows:

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

where q_{max} (mg/g) is the adsorbent's maximum capacity, while q_e (mg/g) is the equilibrium adsorption capacity of ions on the adsorbent. The equilibrium ion concentration in solution can be written as C_e, representing the monolayer coverage of adsorbent with adsorbate. The Langmuir constants are q_{max} and b, related to adsorption efficiency and adsorption energy respective[41].

As presented in Fig. 6, a straight line obtained from the linear plot of C_e/q_e versus C_e, in addition to the Langmuir constants q_{max} and b, were

calculated. The correlation coefficient R^2 value was 0.93, with the constants of Langmuir b and q_e recorded in Table 1. The results analysis suggests that adsorption has a good fit with the Langmuir model, as well as being of monolayer adsorption. A dimensionless equilibrium parameter (R_L)[42] has been adopted to describe the Langmuir isotherm, which can be stated as follows:

$$R_L = \frac{1}{bC_i}$$

$$... (2)$$

where R_L shows the favourable and unfavourable adsorption when:

((Unfavorable: ($R_L > 1$); (Linear: $R_L = 1$); (Favorable: $0 < R_L < 1$) ;(Irreversible: $R_L = 0$); C_i is the different concentrations of Cu (II) ions. Additionally, the analysis results of Langmuir isotherms were listed in Table 1, with the following values of R_L established as 0.02, 0.00058 and 0.00038, 0.0029 and 0.0023. Accordingly, the R_L values ranged between 0 and 1, suggesting the adsorption of Cu (II) ions onto the active centers of Peganum Harmala is appropriate[43].

Freundlich Isotherm

The logarithmic form of Freundlich is written in the equation 3[44], where K_F and n are Freundlich constants; when plotting log q_e versus log C_e, a straight line is identified.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

...(3)

Favourable adsorption may be determined by the empirical parameter n, associated with the adsorbent's adsorption intensity in the form of solid variety
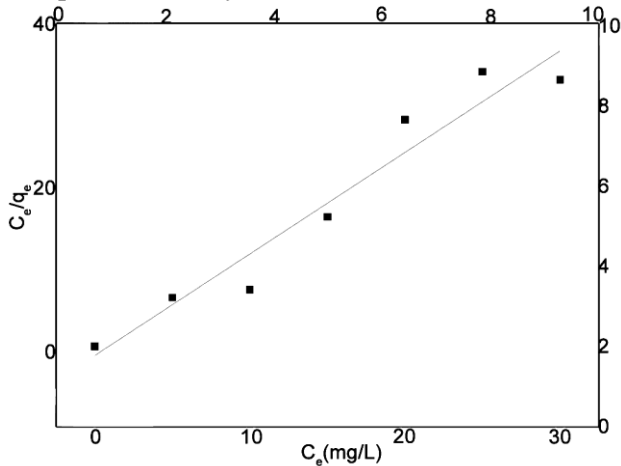

Fig. 6 — Adsorption isotherm for Cu(II) ions onto Peganum Harmala by Langmuir model' Reaction conditions: Peganum Harmala (1g), PH (5), time (1h), reaction temperature (323 K), rate stirring (300 rpm).

according to the material's heterogeneity. Therefore, the measure of appropriate adsorption is n parameter. If the n value lies between 1 and 10 (1/n is below 1), this suggests adsorption was straightforward on the heterogeneous surface of the adsorbent[45], as well as showing that adsorption is of multilayer sorption[46].

Adsorption kinetics

Adsorption's kinetic mechanism is expressed by kinetic models as pseudo first-order and pseudo second-order models[47] also describing the rate-limiting step during the adsorption process[48].

Pseudo First-Order

Regarding the first-order model adsorption rate constant described in previous study[49], the first-order kinetic reaction can be presented with the following Equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

... (4)

The linear form of above equation is written as follow:

$$\text{Ln}(q_e - q_t) = \ln q_e - k_1 t \qquad \dots (5)$$

At equilibrium and at time t, q_e and q_t (mg/g) are the described amounts of the adsorbate Cu (II) ions onto the surface of Peganum Harmala respectively, with the rate constant of the pseudo first-order kinetic model defined by K_1 (min^{-1}). When ln $(q_e - q_t)$ is plotted against t, a straight line is obtained, with the constant K_1, correlation coefficient R_2, as well as theoretical q_e being calculated. Figure 7 shows that the values calculated (q_e, calc.) and the experimental value (q_e, exp.) not being the same. The low value of the correlation coefficient R_2 for the pseudo first-order compared with the pseudo second-order kinetic model means that the adsorption of the poor pseudo first-order kinetic model was not fit for adsorption kinetics.

Table 1 — Parameters of Langmuir, Freundlich isotherms for the adsorption of Cu (II) ions.

Isotherms	Concentrations mg/L	R_L	Parameters		
	100	0.02	q_{max} (mg/g)	b (l/mg)	R^2
Langmuir	120	0.00058	0.79	0.86	0.93
	300	0.00038			
	400	, 0.0029			
	500	0.0023			
Freundlich			Parameters		
			K_F (L/g)	n	R^2
			1.161	10.72	0.92

The appropriate kinetic model of the adsorption mechanism is the pseudo second-order model, which is explained by the chemical reactions wherein electrons share or exchange in the adsorbate and adsorbent as a consequence of valance forces, with the equilibrium adsorption calculated according to the following relationship:

$$\frac{t}{q_t} = \frac{1}{k_2\, q^2_e} + \frac{1}{q_e} \cdot t$$

...(6)

where the plot of t/q_t against t is a straight line obtained. Therefore, it is adopted to evaluate the rate constant k_2 (g /(mg.min)) of the pseudo second-order kinetic model g /(mg. min), as well as q_e, calc. These results are seen in Table 2, showing that the R^2 value was almost 1. The equilibrium adsorption capacity values q_e, calc. were equivalent or had the relative value to the experimental q_e, exp. This value indicates that the adsorption kinetic mechanism conforms to pseudo second-order model kinetics at all initial Cu (II) concentrations.

Effect of temperature

Figures 8 (a) and 8 (b) present the adsorption of Cu (II) ions on the surface of Peganum Harmala at varying temperatures, ranging from 313, 323, 333 and 343 K. These figures explain the percentage removal
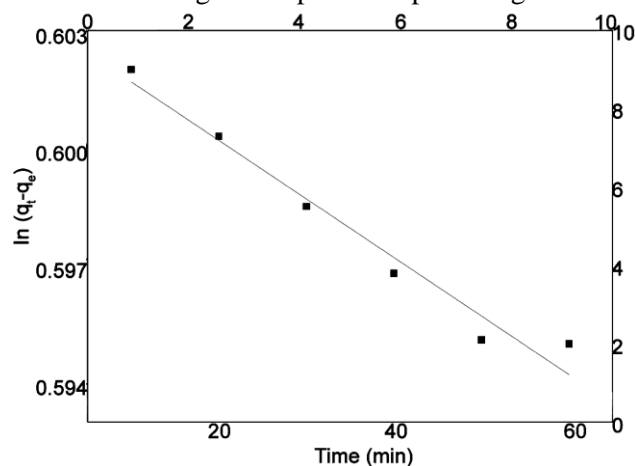

Fig. 7—The Pseudo first-order for the adsorption. Reaction conditions: Peganum Harmala (1g), PH (5), time (1 hour), reaction temperature (323 K), rate stirring (300 rpm).

of copper (II) ions declines from 29.4% to 8.03% respectively with increasing the reaction temperature from 313 to 323 K, followed by a decline from 8.03 mg/g to 2.21 mg/g at 333 K. The adsorbent's degradation occurs, resulting in a change to the sorbent's surface chemistry, with a decrease of heavy metal adsorption observed at higher temperatures; the bonds become ruptured and desorption is favored. High temperature causes a decline in the thickness border, thus facilitating the escape of cu (II) ions from the surface to the liquid phase, therefore limiting the adsorption capacity50.

The thermodynamic parameters such as free energy (G◦), standard enthalpy (H◦) and standard entropy (S◦) are calculated (Figure 9). The process can be explained through the movement of the solute in the mole unit onto the solid-liquid interface. The thermodynamic parameters may be calculated according to the following equation:

$$lnKc = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

...(7)

$$\Delta G = \Delta H° - T.\Delta S°$$

... (12)

$$\Delta G = -RT\, lnK_d$$ ... (13)

$$\Delta G = \Delta H - T\Delta S$$ ... (14)

The parameters in the above equations may be expressed in accordance with the following information:

R is the expression of (8.314 J/(mol·K)), the universal gas constant, while the distribution coefficient is written as Kc = Co/Ce, where the initial adsorbate concentrations and adsorbate concentrations found during the liquid phase being written as C_o and C_e (mg/L) respectively.

The above three thermodynamics parameters of H◦, $\Delta G°$ and $\Delta S°$ are calculated through plotting ln Kc versus 1/T and the results were recorded in Table 3. The magnitude of the thermodynamic parameters was negative in value, meaning that the adsorption process was exothermic. As presented in the Table 3, the reason for the negative value of $\Delta S°$ may by that $\Delta S°$

Table 2 — Results data of Pseudo-first-order and pseudo-second-order kinetic model parameters Cu (II) ions concentrations at 323 K

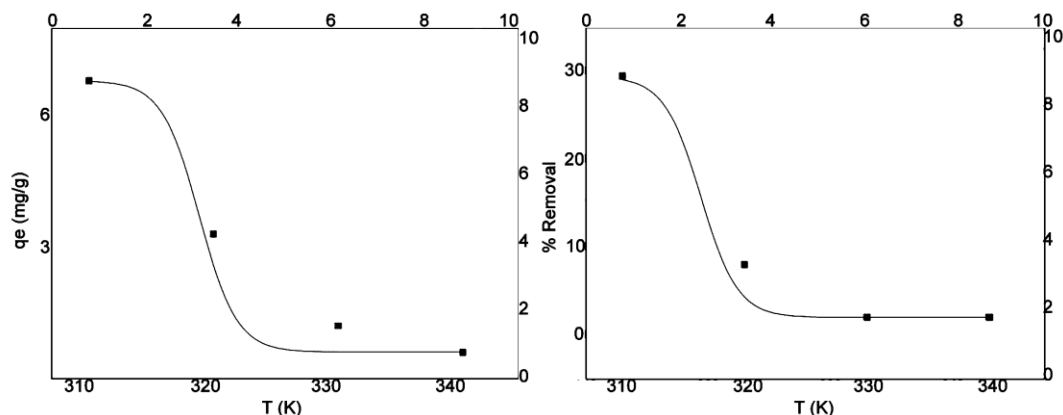| Initial concentration (mg/L) Harmala	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min)	R^2	$q_{e,cal}$ (mg/g)	k_2(g/gmin)	R^2
40	3.31	1.66	1.49	0.95	3.59	0.97	0.95

Fig. 8 — (a) The effect of temperature on the removal of Cu (II) ions. Figure 8(b): The effect of temperature on the adsorption capacity at equilibrium of Cu (II) ions. Reaction conditions: Peganum Harmala (1g), PH (5), Cu (II) 40 (mg/L), time (1 hour), rate stirring (300 rpm).
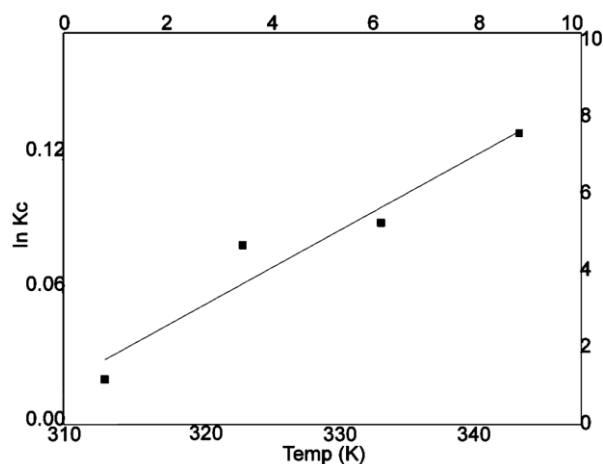

Fig. 9—Thermodynamic behavior during the adsorption of Cu (II) ions. Reaction conditions: Peganum Harmala (1 g), PH (5), Cu (II) 40 (mg/L), time (1 hour), rate stirring (300 rpm).

Table 3—Thermodynamic parameters during the adsorption of Cu(II) ions.

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	37.11.7		
343	37.75		

is an associative mechanism involved in the adsorption process. The adsorption of Cu (II) ions on the active centres of Peganum Harmala seeds was more orderly during the formation of the activated complex between the adsorbate and adsorbent[49]. Moreover, the ΔS may describe the order state and the less random adsorbate at the interface of the solid/solution during the adsorption process in such cases $(\Delta S° < 0)$[50].

The $\Delta G°$ denotes whether the adsorption process is spontaneous or not, at high temperature $\Delta G°$ value is positive, indicating that the adsorption process is no-spontaneous, thus the spontaneous nature and temperature have an inversely proportional relationship.

Conclusion

The results of the present work have clarified how the Langmuir adsorption isotherm is more appropriate than the Frendulich adsorption isotherm, while the second pseudo order reaction model is more appropriate for the adsorption of Cu(II) ions on the active centres of the surface of Peganum Harmala compared with the pseudo first order model. The negative values of the thermodynamic parameters indicate that the adsorption process is exothermic, with the negative value of entropy exposure showing that the situation of adsorbate is orderly and less random at the liquid-solid interface. Furthermore, associative adsorption occurred, with the positive magnitude providing an explanation that the adsorption of copper ions onto 1 g of Harmala was non-spontaneous, as well as the inverse proportion between the spontaneous and the non-spontaneous, meaning that Harmala is considered as the most effective natural adsorbent compared with synthetic adsorbents. Peganum Harmala is simple to use and readily available and inexpensive technique for cleaning impurities and heavy metals from water.

Acknowledgement

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