



Removal of cobalt (II) ions from aqueous solution by *Peganum Harmala* seeds

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The batch extraction of cobalt [Co(II)] ions from an aqueous solution, utilizing the seeds of *Peganum harmala* has been evaluated in this study. After gathering *Peganum harmala*, the plants are beaten to separate the seeds, after which the seed undergo a fine filtration process to remove any debris. The prepared adsorption material is defined by Fourier transform infrared spectroscopy (FTIR). The adsorption process is conducted in an incubator in 50 mL flasks. The studied process variables included pH, contact time, Co(II) concentration, adsorbent dose and reaction temperature. Co(II) is assessed with the use of a UV-vis spectrophotometer at a wavelength of 512 nm. Optimal Co(II) removal is noted at a pH of 6; increased alkalinity resulted in the generation of cobalt hydroxide. When contact time is increased from 5 to 40 min, the removal of Co(II) ions increased from 8 to 88%. This represented the maximum adsorption of Co(II) into *Peganum harmala*. After this time, equilibrium was achieved, with no further Co(II) extraction occurring. The higher the dose of adsorbent, the higher the degree of Co(II) ion removal; increasing the adsorbent from 0.1 to 0.4 g/L result in an increase in extraction from 60 to 84%. A larger dose of adsorbent, up to 0.5 g/L, diminished further Co(II) ion subtraction. The Langmuir adsorption isotherm shows a superior model fit compared with the Freundlich isotherm.

Keywords: Adsorption, Co(II), Heavy metal, Langmuir adsorption isotherm, *Peganum harmala*, Water purification

Heavy metals are well-established as being non-biodegradable with the potential to form poisonous waste products. Some of these elements, e.g. cobalt, chromium, iron, manganese and zinc, are essential for the survival of organisms naturally. Physiological quantities are minute, and higher amounts amassing within biological tissues can lead to toxic effects. This is a notable issue when heavy metals from industrial sources or production plants build up in the environment to the point where they are present within the food chain. Cobalt and similar heavy metals are utilized in a spectrum of industrial sectors including car production, dyes and paint colourants, nuclear power plant, steel manufacturing, electroplating, leather tanning and metal coatings¹.

To safeguard public welfare and to reduce the risks associated with heavy metal toxicity, many researchers have studied how to eradicate heavy metals from the food chain. A specific issue is the contamination of water-based ecosystems by these elements. Cobalt is a poisonous metal, predominantly existing within the environment in its divalent form Co(II)². Its capacity to catalyze the creation of reactive oxygen species (ROS) via the Fenton reaction and the Haber-Weiss cycle accounts for its toxic

properties². ROS products cause oxidative stress, which is highly injurious to DNA, lipids, proteins and other cytoplasmic compounds. Prior to aqueous waste products entering water-based environments, it is essential that Co(II) be removed.

A spectrum of physical and chemical techniques exist that can be deployed to subtract heavy metal pollutants from the environment. These include adsorption, chemical precipitation, chemical oxidation or reduction, coagulation-flocculation, electrochemistry, flotation, ion exchange and membrane filtration³. The energy requirements for most of these processes are frequently exorbitantly expensive. Furthermore, the sludge remaining following heavy metal extraction must be discarded, and this generates a potential secondary environmental contamination problem⁴.

Conventional ways of decontaminating industrial by-products are usually expensive, and their efficacy is often less than ideal. Designing new processes to clean aqueous industrial waste that subtracts and salvages Co(II) efficiently and cost-effectively and use a technique that is safe for the environment and that can be assimilated into industrial mechanisms is crucial⁵. Aqueous products can be efficaciously cleansed utilizing heavy metal surface adsorption

methods. Numerous products for this process are available, including secondary waste products from agricultural and other industries and mineral stones. These are all plentiful, cheap resources that incorporate biosorbents, e.g., chitosan, coconut husks and shells, poultry feathers, rice husks, sugar beet pulp, spent grain, sago waste, waste tea and wood waste⁶.

Peganum harmala, also known as wild rue, is a perennial shrub generally thought of as a weed that can be easily grown and utilized. A literature search was performed in peer-reviewed publications pertinent to the deployment of *Peganum harmala* seeds as a Co(II) adsorbent. A previous study showed that powder *Peganum harmala*-L seed can be used as an effective and natural low-cost adsorbent for the removal of Ni(II) from aqueous solutions⁷. No articles were found relating to the use of this plant to subtract Co(II) from water, so the current study was performed. It takes into account the diverse factors that could impact the adsorbent's efficacy, such as the pH, quantity of sorbent, initial Co(II) concentration and contact time. Also the adsorption isotherms were explored.

Experimental Section

Preparation of adsorbent

The covered seeds of *Peganum harmala* were gathered from ripening vegetation within the locality (Sharurah, south of Saudi Arabia) over the period of six months. The plants were beaten to strip the seeds, which were filtered finely to eliminate unwanted material and then placed in the sun for five days to achieve desiccation. The adsorbent was then manufactured by pulverizing the seeds into a powder using mortar and pestle, which was examined in detail to define its morphological architecture and its functional chemical groups.

Experimental procedure

In this work, the following process variables were considered: pH of 2.5, 4, 5, 6 and 7 as less than 2.5 and higher than 7 is not effective for the adsorption process; Co(II) concentration (100, 200, 300, 400 ppm); the adsorbent quantity of *Peganum harmala*, i.e. 0.1, 0.2, 0.3, 0.4 and 0.5 g/L and time of contact, (i.e. 5, 10, 15, 20, 30, 40, 50, and 60 min). A batch process of adsorption studies was conducted with 50 mL flasks within an incubator. To guarantee that the mixture within the flasks remained uniform, magnetic stirrers at a fixed rate were deployed. The stock

solution consisted of 1000 mg/L of Co(II), (i.e. 2 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solute [Aldrich, purity 96%] in a 500 mL of double-distilled water). The Co(II) stock solution was diluted to create the necessary Co(II) standard concentrations. The cobalt ion concentration was determined using the ultraviolet visible absorption spectrum (Genesys, Thermo 10S UV-VIS Scientific spectrometer).

In each experimental run, 50 mL of the determinate concentration solution was placed into a flask. Hydrochloric acid (1N) (Aldrich, purity 98%) or sodium hydroxide (1N) (Aldrich, purity 97%) were utilized to control the pH, which was measured utilizing a Metrohm (model 780) digital pH meter with a combined glass electrode. The definitive adsorbent quantity was then admixed into the flask contents and directly shaken at a constant rate. When the designated contact period was complete, the flask contents were drained onto filter paper to extract the solution. The Co(II) concentration of the isolated filtrates was then measured.

The amount of Fe(III) adsorbed on PPH, q_e (mg/g) was calculated as follow:

$$q_e = (C_o - C_e)V/M$$

where C_o is the initial concentration, C_e is the equilibrium concentration, M is the mass of *Peganum harmala* and V is the volume of the liquid phase.

In order to recognise the functional chemical groups on the *Peganum harmala* seed surface, Fourier transform infrared spectroscopy (FTIR-KBr) was employed. The analysis was carried out using an EVO40VP model Carl Zeiss scanning electron microscope (SEM).

Results and Discussion

Adsorbent characteristics

For the purposes of this study, FTIR (FTIR-KBr) analysis utilised wave numbers on a spectrum ranging from 400 to 4000 cm^{-1} in order to study *Peganum harmala* seed (Fig. 1). A number of functional groups was recognised on the surface of the adsorbent. A broad adsorption band was noted in the range 3000-3633 cm^{-1} with a peak at 3400 cm^{-1} , suggestive of the existence of free hydroxyl (-OH) groups attached to the surface. A further adsorption band was observed in the spectra data when the wave numbers were fixed between 2800-3000 cm^{-1} , with a peak at 2931 cm^{-1} , consistent with the presence of C-H groups on the adsorbent's surface. A third adsorption band, within

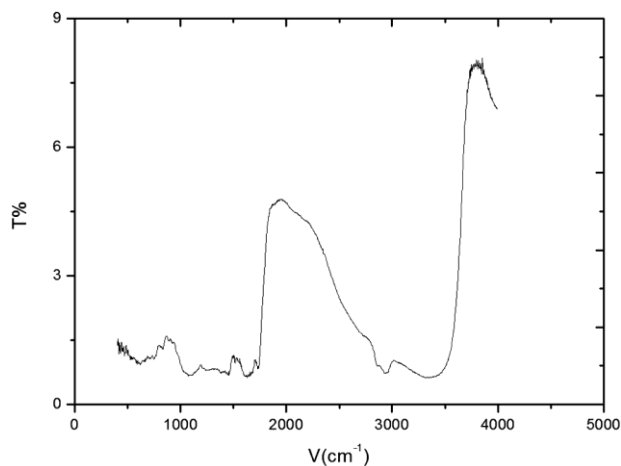


Fig. 1 — FTIR spectrum of *Peganum harmala* at wave numbers from 400 to 4000 cm^{-1}

the range 1500-1700 cm^{-1} identified the existence of carbonyl groups (C-O). Phenolic groups were also recognised from an adsorption band at wave numbers between 1100 and 1200 cm^{-1} (Ref.80).

Scanning electron microscopy (SEM) widely used to study the morphological features of the adsorbent of *Peganum harmala* is shown in Fig. 2. It can be seen that the morphology and surface of *Peganum harmala* was relatively smooth and contained deep pores.

Effect of initial solution pH

The pH of the solution is an important contributor to the adsorption mechanism; changing pH parameters impact the charges on the surface of the adsorbent, and thus the ionisation process. Both the chemical properties of dissolved heavy metals and the capacity of the biosorbent are likely to be influenced by the pH.

The removal efficacy of Co(II) ions in the presence of varying pH values was established by weighing 0.5 g of *Peganum harmala* adsorbent with 50 mL of 40 mg/L Co (II) ion solution for 60 min. The solutions' pH differed, ranging from 2.5 to 7. The subtraction of Co(II) ions was notably diminished in lower pH as shown in Fig. 3(a), which then increased in accordance with increased pH of Co(II) ion solution. There is an increase in the sorption capacity from 5.5 to 9.5 when pH increase from 2.5 to 6. The pH range for the solutions was therefore selected to be between 2.5 and 6; a more alkaline pH than 6 causes obstruction to the process and leads to the engagement of cobalt hydroxide. Thus, the superior pH for Co(II) removal was 6.

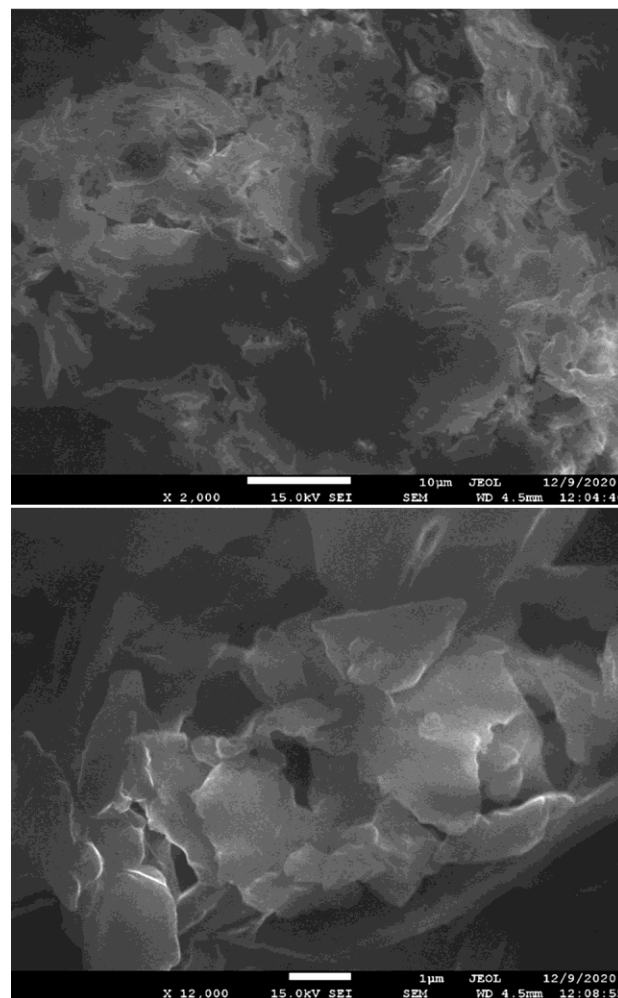


Fig. 2 — Scanning electron micrograph (SEM) of *Peganum harmala*.

An acidic pH diminishes the efficiency of Co(II) sorption capacity and that may due to that the adsorption surface competitive binding between Co(II) and hydrogen ions on *Peganum harmala* in the presence of an acidic solution⁹. Furthermore, the positive charge on the adsorbent's surface as a consequence of the increased concentration of hydrogen ions within the solution; electrostatic repulsion between the positively charged *Peganum harmala* surface and the Co(II) ions diminishes the efficiency of the adsorption process¹⁰. In addition, the chloro complex, arising from the increasing acidity and number of chloride ions reduces the Co(II) ion number. Furthermore, these higher molecular weight complexes, as opposed to the free Co(II) ions, also decrease Co(II) intake to some extent. Therefore, Increasing the alkalinity of the pH reduces the concentration of hydrogen ions on the

adsorbent's surface, thus giving rise to greater Co(II) adsorption¹¹.

Effect of contact time

One of the critical variables described within the adsorption and Co(II) ion extraction process is the time that the aqueous solution spends in contact with the adsorbent. In order to explore the reliance of the adsorption process on contact time, a 0.5 g, of *Peganum harmala* was utilised in a constant volume, 50 mL, of the Co(II) solution. The starting Co(II) concentration was 40 mg/L; additional parameters encompassed a pH of 6, reaction temperature of 298 K and a shaking speed of 200 rpm. The differing contact times appraised were 5, 10, 15, 20, 30, 40, 50 and 60 minutes.

The data presented in Figure 3(b) demonstrate the positive association between the degree of adsorption and contact time. When contact time increase from 5 to 40 min, the removal of Co(II) ions were rapidly increase from 8 to 88%. This represented the maximum adsorption of Co(II) onto *Peganum harmala*. After this time, equilibrium was achieved, with no further Co(II) extraction occurring.

The rapid nature of the metal ion adsorbance during the first few minutes arises owing to the utilisation of the active centres on the adsorbent surface by large numbers of metal ions. In the slow phase, which approached equilibrium, a lower number of metal ions bind to the active adsorbent centres, which is thought to reflect a gradual lessening of solute diffusion into the adsorbent.

Effect of the adsorbent dose

The removal percentage of Co(II) and adsorption in relation to the differing amount of *Peganum harmala* is displayed in Fig. 3(c). The starting Co(II) concentration was 40 mg/L; additional parameters encompassed a pH of 6, reaction temperature of 298 K, shaking speed of 200 rpm and a contact time of 60 min. The varying adsorbent doses evaluated were 0.1, 0.2, 0.3, 0.4 and 0.5 g/L. A rise in the percentage of Co(II) ions subtracted from the solution was seen with a higher quantity of adsorbent, i.e. with an increase from 0.1 to 0.4g/L, the corresponding Co(II) ion removal was 60% and 84%, respectively. These results were unsurprising; the increase in

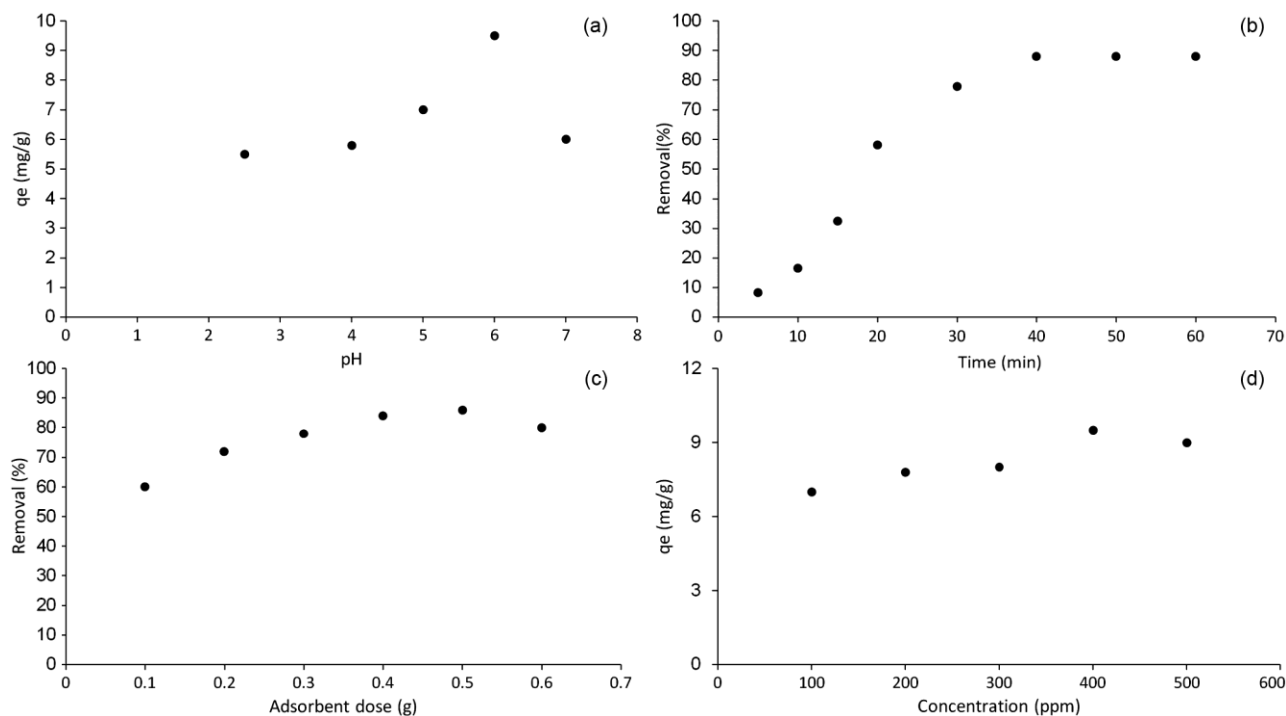


Fig. 3 — (a) pH effect on the Co(II) ions sorption capacity by *Peganum harmala*. [Reaction conditions: *Peganum harmala* (0.5 g), Co (II) (40 mg/L), reaction temperature (298 K), time (1 h), rate stirring (200 rpm)]; (b) Removal of Co(II) ions with various contact time. [Reaction conditions: *Peganum harmala* (0.5 g), Co (II) (40 mg/L), pH (6), reaction temperature (298 K), rate stirring (200 rpm)]; (c) Effect of *Peganum harmala* dose on the % removal of Co(II) ions. [Reaction conditions: Co (II) (40 mg/L), pH (6), time (1 h), reaction temperature (298 K), rate stirring (200 rpm)] and (d) The effect of initial concentrations of Co (II) on the adsorption capacity at equilibrium. [Reaction conditions: *Peganum harmala* (0.5 g), Co (II) (40 mg/L), pH (6), reaction temperature (298 K), rate stirring (200 rpm)].

surface area of the adsorbent gives rise to a higher rate of exchange within the linkage points on the adsorbent pores, thus enhancing Co(II) ion bonding. The rise in adsorption diminishes at doses over 0.5 g, largely owing to the Co(II) ions saturating the adsorbent pores. The active sites engage with both the adsorbent and the substance being adsorbed as a result of the total minimisation of the adsorption surface¹². Thus, Co(II) ion adsorption and the removal ability of the adsorbent both gradually diminish as the adsorbent quantity rises, as shown in Fig. 3(c).

Isotherms of adsorption

A notable phase in the process of adsorption is the choosing of apposite adsorption isotherms that fit the data analysis¹³. Figure 3(d) illustrates data that describe the Co(II) ion equilibrium adsorption isotherms in relation to the *Peganum harmala* seed adsorbent. A vertical increase with low concentrations implies that with a high concentration, the solute would be extremely relevant and the adsorbed quantities would only be modestly elevated giving rise to a more horizontal curve. It can be seen that the adsorption capacity at equilibrium rose from 7 mg/g to 9.5 mg/g with an increase in the starting dye concentrations from 10 to 40 mg/L of a Co(II) ion solution, with a little subsequent decrease to 9 mg/g at 50 mg/L.

When the starting concentration rises, the mass transfer driving force would increase, providing the rationale for the increased Co(II) ion removal. The data analysis determined that there was a rise in adsorption capacity as the Co(II) ion starting concentration became higher until the active molecules saturated, indicating maximum adsorption, and resulting in the subsequent noted adsorption decrease. Two adsorption isotherm models have been selected for use in this study, i.e. the Langmuir and Freundlich models.

Langmuir isotherm model

The Langmuir isotherm model is an efficacious model which can be utilised to describe the adsorption isotherm process. When the equilibrium ion concentration in solution, C_e , divided by the equilibrium adsorption capacity of ions on the adsorbent, q_e , is plotted versus C_e , this may yield a straight line; Langmuir constants, b and q_e , can also be calculated. Langmuir's equation¹⁴ can be represented as:

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

where q_{\max} (mg/g) is the maximum capacity of the adsorbent. C_e reflects the adsorbent's monolayer coverage by adsorbate whereas b is the Langmuir isotherm constant which related to the energy of adsorption (L/mg).

Figure 4(a) illustrates the straight line acquired from a linear plot of C_e/q_e against C_e at 298K. The correlation coefficient value R^2 , Langmuir's constants b and q_{\max} are documented in Table 1. The data show that the actual adsorption results have a good fit with the Langmuir model and reflect monolayer adsorption. A dimensionless constant parameter (R_L) has been conscripted to notate the Langmuir isotherm, i.e.:

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

where R_L indicates favourable and unfavourable adsorption: unfavourable: $R_L > 1$; linear: $R_L = 1$; favourable: $0 < R_L < 1$; irreversible: $R_L = 0$; and C_i is the different concentrations of Co (II) ions.

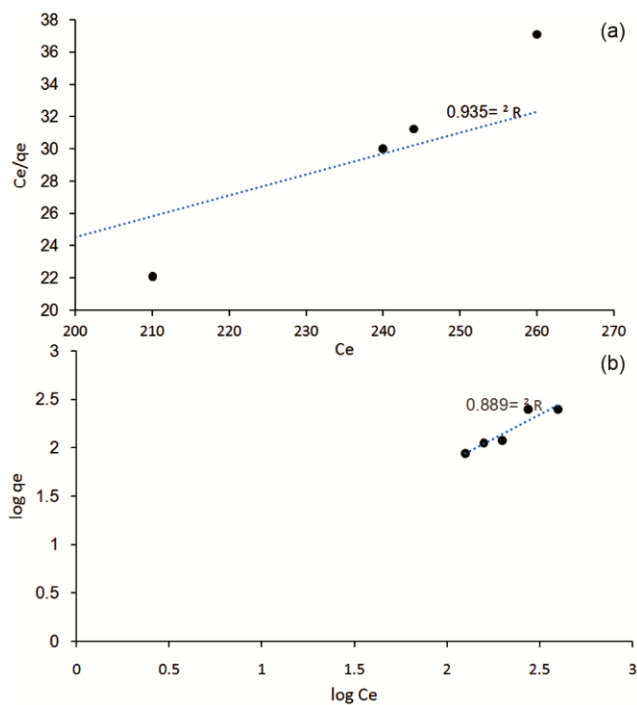


Fig. 4 — (a) Adsorption isotherm for Co(II) ions onto *Peganum harmala* by Langmuir model. [Reaction conditions: *Peganum harmala* (0.5 g), pH (6), time (1 h), reaction temperature (298 K), rate stirring (200 rpm)] and (b) Adsorption isotherm for Co (II) ions. [Reaction conditions: *Peganum harmala* (0.5 g), pH (6), time (1 h), reaction temperature (298 K), rate stirring (200 rpm)].

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

Isotherms	Concentrations mg/L	R_L	Parameters		
			q_{max} (mg/g)	b (l/mg)	R^2
Langmuir	10	0.74	7.7	0.035	0.935
	20	0.59			
	30	0.48			
	40	0.42			
	50	0.36			
Freundlich	Parameters				
		K_F (L/g)	n	R^2	
		0.69	0.72	0.889	

Table 1 also shows the analysis data of the Langmuir isotherms with R_L values. The R_L parameters remained between 0.36-0.74, implying that a favourable isotherm shape for adsorption of Co(II) ion adsorption onto the active sites of *Peganum harmala* in the concentration range of study.

Freundlich isotherm model

The Freundlich isotherm is used to explain the adsorption of organic and inorganic material. Its logarithmic form is presented in equation 3 (Ref.15), where K_F and n represent Freundlich constants, K_F is indicate the adsorption capacity and n is the adsorption intensity. A straight line is observed when $\log q_e$ is plotted against $\log C_e$ as shown in Fig. 4(b).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots (2)$$

Favourable adsorption may be extrapolated by the basic value n, linked with the intensity of the adsorbent's properties in the form of solid variation reflecting the sorbent's uniformity. Thus, n is a parameter of appropriate adsorption. where $n < 1$, $1 < n < 2$ and $2 < n < 10$ which represent poor, moderately difficult and favourable adsorption conditions, respectively¹⁶. The values of K_f and n can be determined by plotting $\log q_e$ versus $\log C_e$ Fig. 4(b), where values of the slope and intercept of the plot indicated the k_f and n respectively. Therefore, the n value may indicate that the process fit with monolayer adsorption ($n < 1$) as shown in Table 1.

By comparing the activity of *Peganum harmala* as good adsorbent to others previous studies, it was found that Very recent study has showed that an efficient adsorptive removal of Cobalt(II) ions from water by dicalcium phosphate dihydrate. However,

it is not cheap and complicated to prepared as well as more generation of post-adsorption solid residue which adds burden on secondary waste management¹⁷. Another recent study using a flocculent-assisted settling (Superfloc C591-0.04%), the precipitation of metallic ions with chemicals (0.1 N Na_2CO_3 and 0.1 N Na_2S). However, it is consistent of an eight-stages treatment encompassing the removal of cobalt ions from water¹⁸. Another adsorbent for removal of cobalt ions from water is functionalized porous carbon (PC-KF) which prepared from less useful petroleum matrix. However, it still costly method comparing to harmala plant as an adsorbent¹⁹.

Kinetic study

The process of adsorption usually linked to the kinetic study. The kinetic adsorption of cobalt ion on the harmala plant was studied. The most common kinetic models used for studying the adsorption are pseudo-first order and pseudo-second order models.

The pseudo-first order model is described using the following equation:

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

The linear form of above equation is written as follow:

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

At equilibrium and at time t, q_e and q_t (mg/g) are the described amounts of the adsorbate Co (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 [Fig. 5(a)].

Pseudo-second order kinetic is expressed as follows:

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

K_2 is the rate constant, where the plot of t/q_t against t is a straight line obtained and presented in Fig 5(b). The high value of the correlation coefficient R^2 for the pseudo first-order compared with the pseudo second-order kinetic model means that the

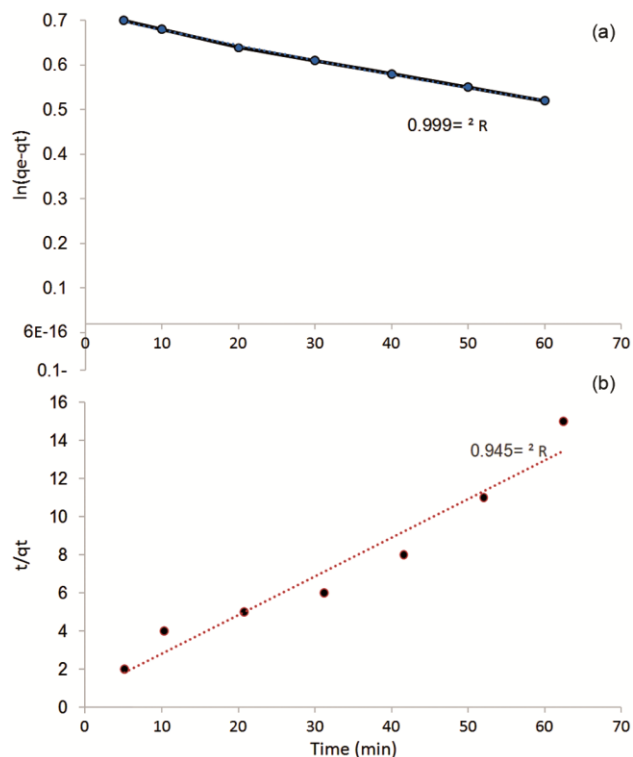


Fig. 5 — (a) Pseudo first-order for the adsorption. [Reaction conditions: *Peganum harmala* (0.5 g), pH (6), time (1 h), reaction temperature (298 K), rate stirring (200 rpm)] and (b) Plot of Pseudo second order adsorption of Co(II) ions. [Reaction conditions: *Peganum harmala* (0.5 g), pH (6), time (1 h), reaction temperature (298 K), rate stirring (200 rpm)].

adsorption of the poor pseudo second-order kinetic model was not fit for adsorption kinetics.

Conclusion

The data from the current study have delineated the way in which the Langmuir adsorption isotherm is a superior model fit to the Freundlich isotherm. The results found in this study show that seeds of *Peganum harmala* is able to remove toxic metal such as cobalt from water. However, we will conduct further study in near future to evaluate this study in different source of water in different cities in Saudi Arabia.

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