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Removal of hexavalent chromium from aqueous solutions using *Argania spinosa* leaves

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ABSTRACT

The objective of this study is to evaluate the performance of novel powdered leaves of the Argan tree (*Argania spinosa* (L) Skeels) to remove Cr(VI) ions from artificially contaminated aqueous solutions. The evaluation was done by studying the effect of pH, adsorbent amount, time and initial metal concentration. The adsorbent was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FT-IR) analysis. The experimental results show that the optimum conditions for maximum removal Cr(VI) ions were accomplished by applying pH 2, a dose of 1 g and contact time of 20 min. The maximum removal capacity of *Argania spinosa* leaves was found to be 9.09 mg/g. Kinetic and equilibrium data showed that the adsorption process of chromium follows pseudo second-order kinetic model and the Freundlich isothermal model was found to better describe the adsorption process. The study implied that *Argania spinosa* leaves could be used as an effective adsorbent for the removal of Cr(VI) from aqueous solution.

Keywords: Chromium (IV) removal; Argan tree leaves; Adsorption isotherms; Kinetics

1. Introduction

Water pollution by heavy metals resulting from anthropogenic impact is causing serious ecological problems in many parts of the world. This situation is aggravated by the lack of natural elimination process of metals [1]. Among many other metal pollutants chromium is one of the toxic heavy metals due to its harmful effects on human beings and nature. It is widely used in various sectors such as metallurgical, electroplating, electronics, leather tanning and wood preservatives [2].

In aqueous phase, chromium mostly exists in two oxidation states, trivalent Cr(III) or hexavalent Cr(VI) [3]. Chromium(VI) is toxic and carcinogenic to humans. Chronic exposure to Cr(VI) may cause nausea, vomiting, kidney and liver damage [4,5].

The removal of chromium ion from solutions can be achieved by several processes such as chemical precipitation, solvent extraction, adsorption, ion exchange, reduction, evaporation, membrane separation, electrolysis, etc [6–9]. Among all these methods, adsorption is considered attractive because of being relatively simple (in the application viewpoint) economical and cost-effective method [10]. Various naturally materials such as *Undaria pinnatifida*, sugarcane bagasse, *Eucalyptus bark*, actived *Neem* leaves, *Halimeda gracilis* and olive leaves [11–16] have been widely used for adsorption of metal ions.

In this contribution we aim to propose new natural material: powdered *Argania spinosa* leaves from Morocco for evaluate its efficiency for the removal of Cr(VI) ions from artificially contaminated aqueous solutions. The adsorption

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on batch mode was evaluated by the variation of pH, adsorbent amount, time and initial metal concentration. Analytical techniques such as FTIR and SEM were employed for adsorbent characterization. Langmuir and Freundlich isotherm equations were employed to quantify the adsorption equilibrium. Two kinetic models are used to the fit experimental data and the associated parameters have been evaluated.

2. Materials and methods

2.1. Preparation of adsorbent

Argania spinosa leaves (ASL) were collected from Taroudant region. This plant is only endemic in southwestern Morocco. Argan leaves are used in livestock feed and in traditionally used for their antipyretic and anti-inflammatory properties [17]. The recent discovery of the crude flavonoid fraction of argan leaves has led to envisage their introduction in cosmetic preparations [18].

After collection, this leaves was washed thoroughly with tap water, followed by deionized water. The adsorbent was oven-dried at 80°C for 24 h [19]. The dried leaves was ground and sieved to obtain the fraction of diameter between 2 and 2.5 mm in order to be used in all the experiments.

2.2. Adsorbents characterization

The surface morphologies, of ASL before and after Cr(VI) adsorption were, visualized using scanning electron microscope (FEI Quanta 200 instrument). An infrared spectrum was used to identify of functional groups before and after adsorption by Fourier transform, infrared spectrophotometer (FTIR Vertex 70 spectrometer) in the range of 4,000–400 cm^{-1}. The zero point charge was determined by pH drift method [20].

2.3. Experimental

Adsorption of Cr(VI) from aqueous solutions was investigated in batch experiments. The experimental studies were carried out in a 250 mL conical flask with the total volume of 100 mL solution. Desired Cr(VI) concentrations were prepared from a 1,000 mg/L stock solution of chromium. The chromium stock was prepared from $K_2Cr_2O_7$. The pH of the chromium solutions was adjusted using NaOH and HCl (0.1 N) solutions. Then, certain adsorbent doses were introduced into the flasks and placed immediately on magnetic stirrer with a fixed setting to achieve a constant speed.

After the contact time elapsed, the sample was filtered using filter paper (Whatman No. 42). Then, the filtered sample was analyzed for the determination of chromium level. The main process parameters considered were pH (2, 3, 4, 5, 6, 7), initial Cr(VI) concentration (5, 10, 15, 20, and 25 mg/L), adsorbent dose (1, 2, 3, 4, 5, 10, and 20, g/L), and contact time (1, 4, 5, 10, 15, 20, 25, 30, 45, 60, and 120 min).

The final residual metal concentration after adsorption was determined by Atomic Absorption Spectrophotometry (AAS). The quantity adsorbed at equilibrium Q_e (mg/g) was calculated by using the following equation:

$$Q_e = \left(\frac{C_0 - C_e}{m}\right) \times V \tag{1}$$

where C_0 and C_e are the initial and equilibrium ion concentrations (mg/L), V (L) is the total volume of the solution and m (g) is the mass of adsorbent.

To estimate the percentage removal of chromium(VI) from aqueous solution, the following relation was used:

$$\text{Removal }\% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of the adsorbents

The infrared spectra of ASL, display a number of absorption peaks, indicating the complex nature of the material (Fig. 1). The major changes in peak positions in the FT-IR spectrum of the adsorbent, before and after contact with chromium solutions, are presented in Table 1. The FTIR results indicate that the ASL contains a variety of functional groups such as hydroxyl, alkene, carboxyl, etc. Significant shift of adsorption peak frequencies from 3,268.75 is to 3,336.65 cm^{-1} indicates that stretching of –OH group might be responsible for the binding of Cr(VI) ions onto the adsorbent.

The morphology of adsorbent surface was analyzed by SEM before and after Cr(VI) loading (Fig. 2). As shown in Fig. 2(a), the ASL posses irregular and porous surface. In Fig. 2(b) it can be observed that after exposure of ASL, to the chromium ions solution, the pores have been occupied and lead to form a white layer. The formation of white layer on the surface of the adsorbent indicates that the sorbent is loaded with Cr(VI) ions [21].

3.2. Effect of pH

The effect of pH on the evolution of the adsorption capacity was analyzed over a pH range from 2 to 7. The results presented in Fig. 3 show that the maximum amount of Cr(VI) adsorbed reached at pH equal 2 with 3.241 mg/g, for an initial concentration of 10 mg/L. This adsorption efficiency decreases proportionally by increasing the pH which

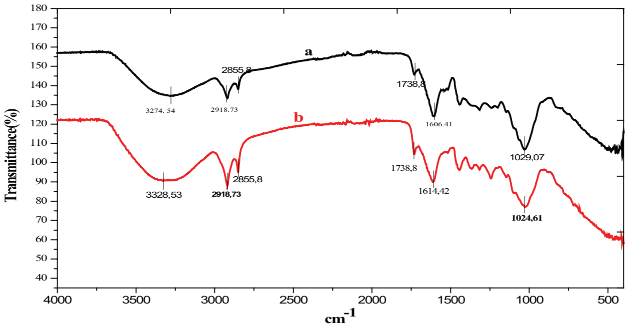

Fig. 1. FT-IR spectra of ASL (a) before adsorption and (b) after adsorption.

Table 1
FT-IR spectral bands in the ASL before and after contact with Cr(VI) solutions

Wavelength range (cm^{-1})	After adsorption	Before adsorption	Functional groups
3,400–3,200	3,274.54	3,328.53	OH groups (Alcohol/phenol)
3,000–2,850	2,918.73	2,918.73	C–H methyl and methylene groups
3,000–2,850	2,855.8	2,855.46	C–H stretching
1,750–1,680	1,738.8	1,738.8	C=O carbonyls
1,640–1,500	1,606.41	1,614.42	Carboxylic groups
1,300–1,000	1,029.8	1,024.98	C–O stretching

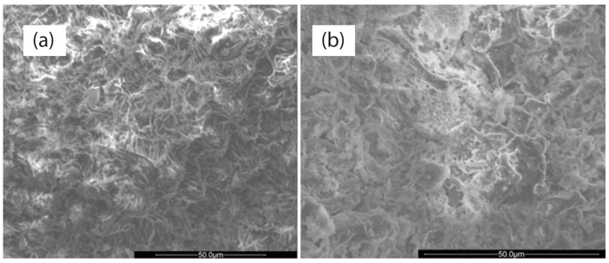

Fig. 2. SEM micrograph of ASL (a) before adsorption and (b) after adsorption.

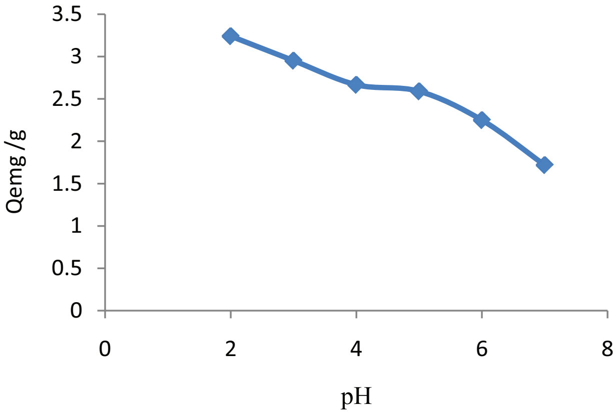

Fig. 3. Effect of pH on Cr(VI) on the adsorption of Cr(VI) on ASL.

registered his attains lowest value at pH 7 with 1.77 mg/g. The calculated of pH zero point charge (pH_{ZPC}) was found to be 6.5 as indicated in Fig. 4. The pH_{ZPC} of ASL indicates that the surface of the adsorbent positively charged at pH less than 6.5 and negatively charged at pH values above 6.5. The increase in Cr(VI) removal efficiency at pH 2 is due, at least in part, to the electrostatic force existing between the adsorbent surface and Cr(VI) ions. A strong attraction will exist between these oxyanions of Cr(VI) i.e., $HCrO_4^-$ and the positively charged surface of the adsorbent at low pH.

The Cr(VI) exists in various ionic forms in solution Fig. 5 Chromate ion (CrO_4^-), dichromate ion ($Cr_2O_7^{2-}$), hydrogen chromate ion ($HCrO_4^-$) or chromic acid (H_2CrO_4). The $HCrO_4^-$ ions are most numerous in the solution compared with $Cr_2O_7^{2-}$ at pH = 2–6 and it are moreover small size [22]. At pH < 2, the molecular form H_2CrO_4 prevails in the solution as a species polycyclic anhydride is difficulty adsorbable by the pores of material [7,23].

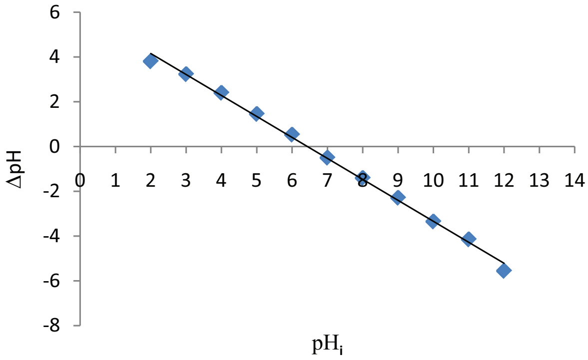

Fig. 4. Determination of pH_{ZPC} of the ASL.

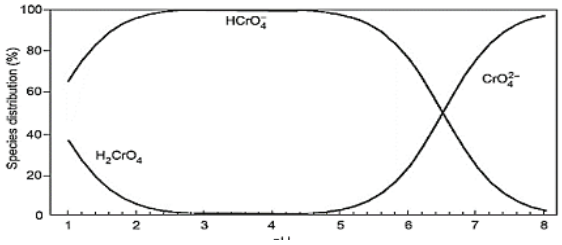

Fig. 5. Distribution of the inorganic species Cr(VI) according to the pH.

As a result, the mechanism of Cr(VI) adsorption by natural biomaterial ASL under acidic conditions can be suggested as electrostatic attraction reaction between positively charged surface groups and the $HCrO_4^-$ ions according to the chemical reaction:

$$\equiv S\text{–}OH + H_3O^+ + Cr_2O_7^{2-} \rightleftarrows \equiv S\text{–}OH_2^+ + HCrO_4^- + H_2O \qquad (R1)$$

Such observations are common for many natural adsorbents [24]. In this accordance, for all other experiments the pH was fixed at 2.0.

3.3. Effect of contact time

At this stage, all of the parameters except contact time, including initial Cr(VI) concentration 10 mg/L, pH 2 and adsorbent dose 2 g/L were kept constant. The effect of contact time on chromium adsorption efficiency is shown in Fig. 6.

As can be seen in Fig. 6, the removal efficiency of Cr(VI) onto ASL by adsorption is rapid initially and then slows down gradually until it attains equilibrium. The increase in the adsorption capacity in the first 15 min was very rapid. This might be due to the diffusion of metal molecules into the surface pores of the ASL granules, but with the progresses of time, the active sites get occupied due to competitive adsorption of adsorbate molecules. Equilibrium is deduced to have been attained within 20 min.

3.4. Effect of initial concentration

The adsorption of Cr(VI) onto ASL is studied by varying Cr(VI) concentration in the range 5–25 mg/L. The experiments were conducted by keeping the contact time at 60 min, pH of 2 and adsorbent dose 2 g/L, at ambient temperature. The results are showing in Fig. 7. The Fig. 7 show that the adsorption capacity increases with an increase initial Cr(VI) concentration. This indicates that the adsorption is more favorable at higher concentration, since at high initial concentrations, there will be more ions capable of diffusing toward the surface of the particle sites of the adsorbent, and consequently the retention becomes more important.

3.5. Effect of mass

The adsorbent dose is an important parameter as it determines the capacity of an adsorbent for a given initial concentration [25]. The effect of adsorbent dose on percentage removal of Cr(VI) was analyzed in the range of 0.1–2 g at pH 2.0. The experimental results in Fig. 8 show that the chromium removal percentage has increased from 62% to 84% and the maximum removal was attained at the adsorbent dosage of 1.0 g. This result can be related to the availability of the number of active sites of the adsorbent [26].

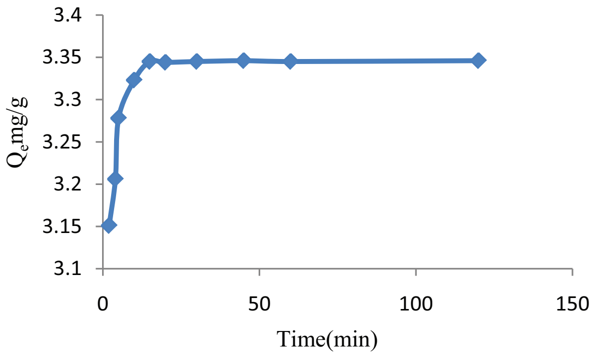

Fig. 6. Effect of contact time of Cr(VI) onto ASL.

3.6. Kinetic study

To explain the adsorption kinetics, pseudo-first-order and pseudo-second-order models [27] were tested to fit the experimental data obtained from the adsorption of Cr(VI) ion experiments.

The pseudo-first order equation in linear form can be expressed in Eq. (3):

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - K_1 t \tag{3}$$

where Q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, Q_t is the amount of Cr(VI) adsorbed at time t, and K_1 (min^{-1}) the pseudo first order rate constant. Second order equation can be expressed in Eq. (4):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^{\,2}} + \left(\frac{1}{Q_e}\right) \times t \tag{4}$$

where K_2 (mg/g min) is the rate constant of second order adsorption.

The pseudo first- order and pseudo second order kinetic plots for the adsorption are presented in Figs. 9 and 10. The calculated value of rate constants K_1, K_2 and their corresponding correlation coefficient values (R^2) are shown in Table 2. From the results of Figs. 8 and 9, it can be observed that pseudo-second-order kinetic model demonstrates high correlation coefficient (R^2 = 0.99) compared with the Pseudo first- order model (R^2 = 0.797); and also there is better agreement between the calculated $Q_{e,\text{cal}}$ and the experimental $Q_{e,\text{exp}}$ values. The biosorption of Cr(VI) onto ASL is explained well by the pseudo-second-order model kinetics. Therefore, the chemisorption is the rate-determining step in the adsorption of Cr(VI) ions on the ASL.

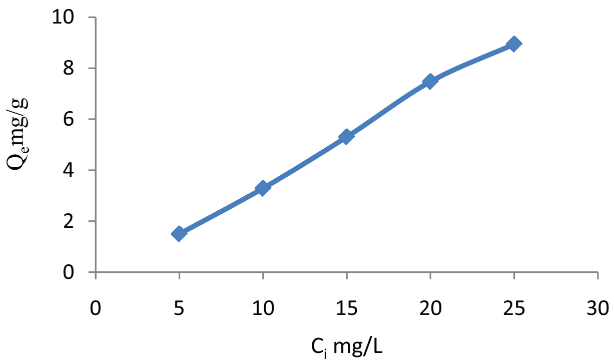

Fig. 7. Effect of initial Cr(VI) concentration on adsorption.

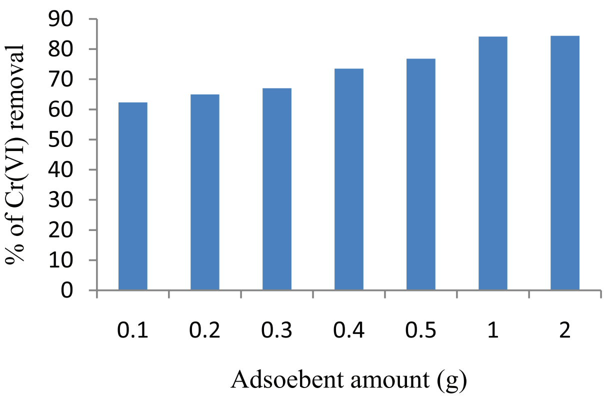

Fig. 8. Effect of adsorbent dose on the adsorption by ASL.

3.7. Adsorption isotherms

Adsorption isotherms are used to describe the equilibrium relationship between the amount of solute that is present in the solution and adsorbent [28]. The adsorption equilibrium data were analyzed using Langmuir and Freundlich isotherms expressions. Linear regression is commonly used to determine the best fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficient R^2.

The Langmuir isotherm equation is based on monolayer adsorption on a uniform surface with a finite number of identical sites, which are homogeneously distributed over the adsorbent surface [29]. Langmuir adsorption isotherm is, represented by Eq. (5):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{5}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of solute adsorbed per amount of adsorbent (mg/g), Q_m represents the maximum metal adsorption (mg/g), and K_L is the Langmuir isotherm constant (L/mg). The values of Q_m and K_L can be determined from the linear plot of C_e/Q_e vs. C_e (Fig. 11). The values of Langmuir parameters, Q_m, K_L and R^2 are presented in Table 3.

The Freundlich adsorption isotherms can be employed to describe heterogeneous surface [30]. The linear form of the Freundlich isotherm model is given by the following Eq. (6):

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where Q_e is the amount of solute adsorbed per amount of adsorbent (mg/g), C_e is the solute concentration in the solution (mg/L); K_F and n are the Freundlich constants related to adsorption capacity and intensity. The K_F and n values were determined from the slope of linear plot of log(Q_e) vs. log(C_e) (Fig. 12). The values of Freundlich parameters, K_F, n and R^2 are presented in Table 3.

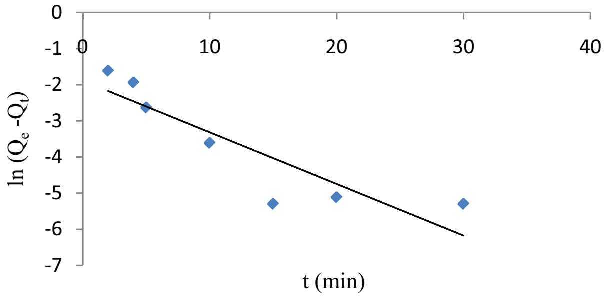

Fig. 9. Pseudo-first-order kinetic model for removal of Cr(VI) by ASL.

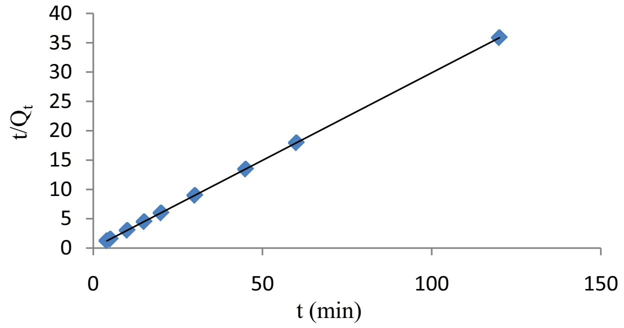

Fig. 10. Pseudo-second-order kinetic model for removal of Cr(VI) by ASL.

Table 2
Kinetic constants for the adsorption of Cr(VI) on ASL

Kinetics models	Parameters	
Pseudo first-order	$Q_e = 0.15$ mg/g $R^2 = 0.797$	$K_1 = 1.42$/min
Pseudo-second order	$Q_e = 3.35$ mg/g $R^2 = 0.999$	$K_2 = 3.70$ g/mg.min

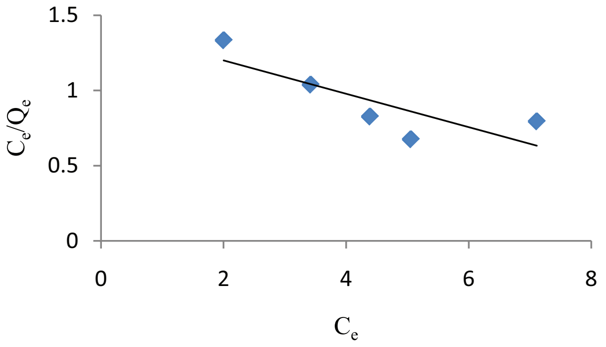

Fig. 11. Langmuir isotherm model for the Cr(VI) adsorption onto ASL.

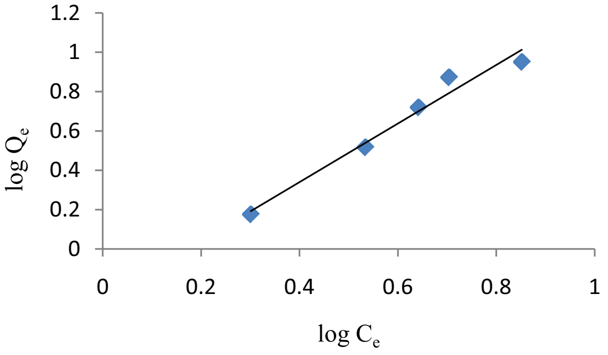

Fig. 12. Freundlich isotherm model for the Cr(VI) adsorption onto ASL

Table 3
Isotherms constants related to the adsorption of Cr(VI) adsorbed on ASL

Isotherm model	Parameters		
Langmuir	Q_m (mg/g) = 9.09 $R^2 = 0.664$	K_L (L/mg) = 0.077	
Freundlich	$K_F = 0.036$	$n = 0.675$	$R^2 = 0.970$

Table 4
Comparison of adsorption capacity of different adsorbents for the Cr(VI) removal

Adsorbent	Q_{max} (mg/g)	pH	C_0 (mg/L)	Reference
Cactus	7.08	2.0	2.5–25	[31]
Pineapple leaves	8.77	2.0	5–50	[32]
Helianthus annuus	3.6	2.0	10–70	[33]
Ficus auriculata leaves powder	13.33	2.0	20–100	[34]
Euclea schimperi	3.9463	2.0	5–20	[35]
Acacia albida	2.983	2.0	5–20	[35]
Enteromorpha sp	5.3475	2.0	20–100	[36]
Colocasia esculenta leaves powder	47.62	2.0	20–100	[37]
Strychnos nux-vomica shell	90.9	2.0	50–250	[38]
Mango kernel activated carbon	7.8	2.0	20–80	[39]
Argania spinosa leaves	9.09	2.0	5–25	This study

The application of the Langmuir model to the present experimental parameters gave a poor fit ($R^2 = 0{,}664$), and thus, it is clearly not appropriate for the Cr(VI) on ASLP adsorbent. From the Table 3 it's clear that Freundlich model had the greatest values of $R^2 = 0.970$ compared with the Langmuir model. The value of $n = 0.675$, which is significantly lower than unity, indicated that the Cr(VI) is favorably adsorbed by ASL. The Freundlich isotherm theory indicates multilayer adsorption with interaction between adsorbed molecules and also the heterogeneous distribution of active sites on the material, since the model presupposes that the surface is heterogeneous [31].

3.8. Comparison with other adsorbents

Table 4 shows comparison of adsorption capacity with other adsorbents reported in literature. The results of our investigation revealed that the performance of the adsorbent in the present study is better than many adsorbent used for chromium removal regardless to the different experimental conditions under which they were applied.

4. Conclusion

The present investigation was focused to the adsorption of Cr(VI) ions onto *Argania spinosa* leaves from artificially contaminated aqueous solutions. Experiments were performed as a function of pH, time, initial metal ion concentration and adsorbent dose. The obtained results showed that the adsorption capacity of Cr(VI) ions was highly pH-dependent, and the best adsorption capacity could be obtained at solution pH 2.0. The FT-IR and SEM methods were efficient techniques for investigating the physico-chemical characters; it demonstrates that the adsorbent has a surface irregular and revealed the existence of functional OH and carboxylic groups. Freundlich isotherm was found to be the best and the adsorption mechanism observed Pseudo second order kinetics. Consequently, it was concluded that *Argania spinosa* leaves appears as an interesting material for Cr(VI) ion. However, more study is therefore required to investigate the affinity of ASL with other pollutants.

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