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RESEARCH ARTICLE

Equilibrium, Kinetic and Thermodynamic Investigations on the Adsorption Capacity for Cr(VI) Removal from Water by Carbonised Garden Cress and Date Seeds.

Baydaa Awad Kadhim
College of Pharmacy, Jabir Ibn Hayyan University for Medical and Pharmaceutical Sciences, Najaf, Iraq

*Corresponding Author
Baydaa Awad Kadhim.

Email: Baydaa.a.kadhim@jmu.edu.iq

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Abstract: ***Background***: In this study, the use of inexpensive adsorbents, carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS), for hexavalent chromium [Cr(VI)] removal from aqueous solutions was explored. Adsorption experiments (batch) were conducted to investigate the effects of solution pH and the adsorbent dosage as well as contact time, initial chromium concentration and temperature. The results showed that removal efficiency was strongly pH dependent and the optimal pH for both adsorbents was pH 5. Decrease in removal efficiency was observed with increasing initial chromium concentration and temperature. In contrast, increased contact time and adsorbent dosage increased removal efficiency. Under the experimental conditions, maximum removal efficiencies by CDS and CGCS were 94% and 76.5%, respectively. Adsorption kinetics for both adsorbents was best described by the pseudo-second-order model. The adsorption equilibrium was better described by the Freundlich isotherm model, suggesting the presence of heterogeneity in the adsorbent microscopic structure. According to the results of this study, the adsorption process was exothermic with enthalpy changes of -66.25 and -52.81 kJ mol-1 for CDS and CGCS, respectively, indicating that the adsorption was exothermic. The results indicated that carbonised date seeds had a greater adsorption efficiency compared to carbonised garden cress seeds. Therefore, carbonised date seeds may be an effective, low-cost, and eco-friendly option to remove Cr (VI) from contaminated water.

Keywords: Cr (VI), Adsorption, Carbonised date seeds, Carbonised garden cress seeds, Kinetics, Isotherms, Thermodynamics, Wastewater treatment .

INTRODUCTION

Heavy metals are poisonous and persist in the environment and pollute ecosystems including aquatic habitats. Hexavalent chromium [Cr(VI)] is among the most dangerous of these heavy metals. Cr(VI) is soluble, persistent, and is a recognized carcinogen and mutagen. Thermal, mechanical, and chemical processes involved in electroplating, leather tanning, dyeing, pigment manufacture, and other metal finishing operations generate wastewater containing chromium. The uncontrolled discharge of this wastewater is a serious environmental and public health concern. Some of the proposed treatment technologies such as membrane separation, chemical precipitation, ion exchange and electrochemical treatment can remove chromium. Among these, adsorption is the most promising. There are a number of studies focused on the use of agricultural waste as an adsorbent to remove heavy metal ions from wastewater. The thermal treatment of agricultural waste transforms the raw material into an efficient adsorbent. Date seeds are a major agricultural waste material. Date seeds are a lignocellulosic material which transforms into a carbonaceous adsorbent. Carbonization of other agricultural waste, such as garden cress seeds, produces a carbonaceous, porous adsorbent.

Thus, converting agricultural waste into useful adsorbents decreases waste and improves environmental sustainability. The present study examines and compares the removal of Cr (VI) ions from aqueous solutions by carbonised date seeds and carbonised garden cress seeds. The effect of various parameters, including temperature, the concentration of chromium (VI) in the initial solution, contact time, adsorbent dose, and solution pH, were investigated. Additionally, adsorption kinetics and isotherm models were used to understand the adsorption process, and the scope and applicability of the carbonised adsorbents for the treatment of potential wastewater were evaluated.

MATERIALS AND METHODS

The adsorbent was synthesized by purchasing data and garden cress seeds from local markets. The preparation of hexavalent chromium employed potassium dichromate ($K2Cr2O4$), whereas the adjustment of pH was done with sodium hydroxide ($NaOH$) and hydrochloric acid (HCl). The solutions were prepared using distilled water. The collected data and garden cress seeds were cleaned with distilled water to remove dust and impurities. The materials underwent washing and drying using a hot air oven set at 105 °C for 24 h. Each of the samples was air dried, crushed into smaller particles and was placed in a covered ceramic crucible. Carbonization was done in a muffle furnace at a temperature of 500 °C for 2 h under low oxygen. The furnace was allowed to cool to room temperature to complete the carbonization process. The carbonized material was then crushed and screened to obtain a uniform particle size and was stored in sealed containers for use.

A stock solution concentration of 1000 mg L-1 of Cr (VI) was prepared by weighing potassium dichromate and dissolving it in distilled water. The desired concentrations of working solutions were prepared by serial dilution of the stock solution. Batch adsorption studies were performed by adding 100 mL of chromium solution into 250 mL Erlenmeyer flasks. A known amount of adsorbent was added and placed in an orbital shaker at the constant speed of 250 rpm. The effect of operational parameters was determined by changing one parameter at a time while the rest of the parameters were kept constant. The amount of absorbent was changed to 0.5, 1.0, 1.5, and 2.0 g. pH values of the solution were set to 2, 4, 6, 8 and 9. These values along with contact times of 10, 30, 60, 90, 120 min were adjusted as well. Different initial concentrations of Cr(VI) in the solutions (20, 40, 60, 80, 100 mg L-1) were also prepared to study the effect of initial concentration on chromium removal. For the thermodynamic study, the effect of temperature was studied in the range of 25 to 60 °C. Suspensions were filtered to separate the solid from the liquid phase after each adsorption time interval. Residual chromium was determined by Atomic Adsorption Spectroscopy (AAS). All tests were carried out in triplicate. Average results were reported. Standard formulas were used to determine the removal and the adsorption capacity. Adsorption equilibrium data were analyzed using the Langmuir and Freundlich adsorption isotherms. Kinetics of the adsorption process was studied using the pseudo-first-order and the pseudo-second-order models. For the thermodynamic study, results were analyzed to determine the feasibility and the nature of the adsorption process. Changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were reported.

Result and Discussion

Effect of Solution pH

As shown in Figure 1, the impact of solution pH on Cr (VI) removal using carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS) are explained. The solution pH greatly impacts the adsorption behaviour of both material constructs. Removing efficiency in the acidic range increased for both material constructs, achieving maximum removal efficiencies of 86% for CDS and 79% for CGCS at pH 5. Above pH 5, the rate of chromium removal declined significantly.

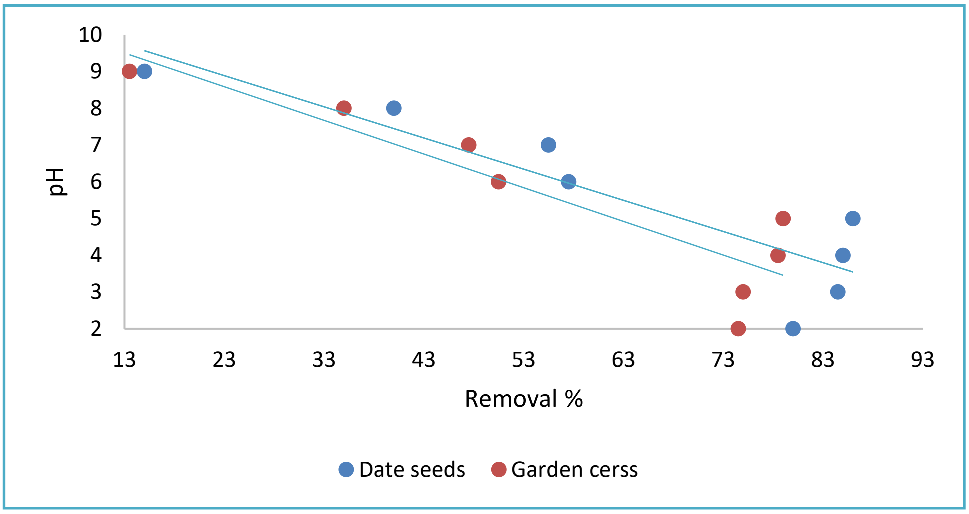

Figure 1. Effect of solution pH on the removal of Cr(VI) by carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS).

The behaviour seen can be explained by the protonation of the adsorbent surface due to the change in adsorbent surface charge and the speciation of the chromium ions in solution [5]. In acidic media, adsorbents surfaces are fully protonated which increases the adsorption of negatively charged chromium species. As the pH increases, the hydroxide ions increase and compete with chromium species for adsorption sites and reduce the adsorption capacity [6]. The adsorption studies of the three adsorbents showed that the carbonised date seed performed better in the entire pH range. The maximum uptake with carbonised date seeds indicates that the surface of the carbonised date seeds has better active sites and stronger attraction to the Cr(VI) ions compared to the carbonised garden cress seeds. It is therefore evident that pH 5 is the most optimum for further studies.3.2 Effect of Adsorbent Dosage The impact of the dosage of the adsorbents on the removal of Cr(VI) ions by carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS) was evaluated in the range of 0.5–2.0 g and is shown in Figure 2. The removal efficiencies for both the adsorbents CDS and CGCS, respectively, increased with the dosage of the adsorbent. The adsorbent dosage of 2.0 g achieved the maximum removal efficiencies of 89% and 84%, respectively.

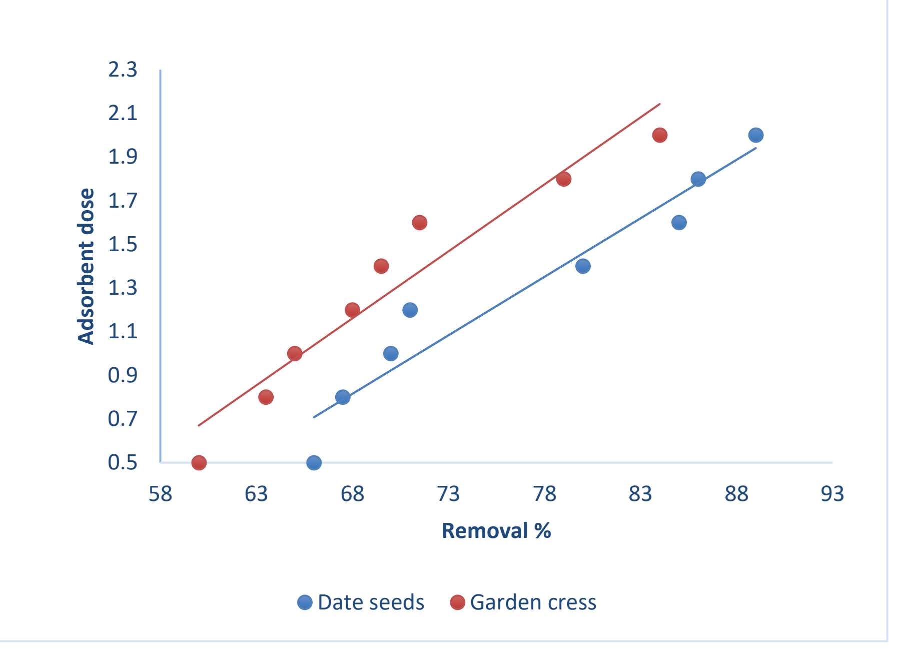

Figure 2. Effect of adsorbent dosage on the removal of Cr(VI) by carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS).

Adsorption capability is enhanced by increasing adsorbent dosage because more binding sites become available as surface area gets larger. More adsorbent means greater uptake of chromium and better removal efficiencies and lower residual chromium in the solutions [7]. Greater adsorbent dosage also means greater chromium concentration equilibrium (Ce), showing better performance. The best removal efficiency was due to an adsorbent dosage of 2.0 g. This dosage had the most adsorption sites of the dosages tested. Of the two adsorbents, carbonized date seeds (CDS) showed better adsorption than carbonized garden cress seeds (CGCS) in the dosages that were tested. At the best dosage (2.0 g), CDS removal efficiency was 89% and that of CGCS was 84%. These results indicate that the conditions of the experiments allowed better capability of date seeds to remove Cr(VI) ions compared to the garden cress seeds [8]. Therefore, 2.0 g of adsorbent was used for all other adsorption experiments.

Effect of Contact Time

The effect of contact time on the adsorption of Cr(VI) by carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS) was studied for the time period of 10 to 120 minutes. The results are shown in Figure 3. As the contact time increased, the removal efficiency of both adsorbents increased in a similar manner, indicating the timely consumption of available adsorption sites by chromium ions.

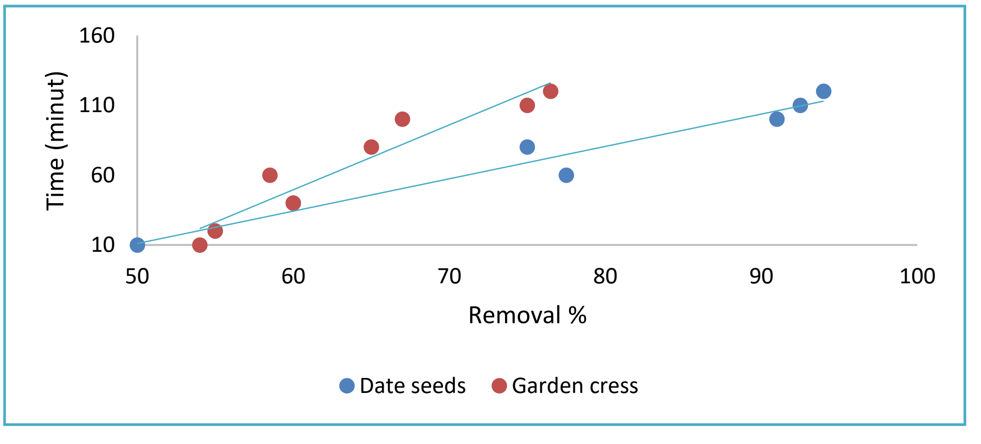

Figure 3. Effect of contact time on the removal of Cr(VI) by carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS).

For CDS, the removal efficiencies improved from 50% at 10 minutes to 94% at 120 minutes. Similarly, CGCS removal efficiencies improved from 54% at 10 minutes to 76.5% at 120 minutes. The improvement in the adsorption process in the beginning stages can be attributed to the large number of open adsorption sites on the adsorbent. Longer contact time resulted in the diffusion of larger amounts of chromium ions from the solution to the surface of the adsorbent and occupied the sites. During the first stage of the adsorption process, the rate of adsorption was high and slowed down as the adsorption sites were filled. The equilibrium was achieved between the adsorbed and the remaining chromium ions in the solution and the rate of adsorption slowed down. From the study of the two adsorbents, carbonised date seeds performed better for all the contact time ranges. The maximum removal efficiencies for carbonised date seeds and for carbonised garden cress seeds were 94% and 76.5%, respectively. From this, it can be concluded that for the removal of Cr(VI) ions, the carbonised date seeds were superior to the carbonised garden cress seeds. The optimum contact time for the adsorption studies was therefore determined to be 120 minutes [10].

Effect of Initial Chromium Concentration

We studied how initial Cr(VI) concentrations between 20 and 100 mg L^{-1} affected the adsorption by carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS). Removal efficiency using both adsorbents decreased as the initial concentration of chromium increased. Additional details are reported in Figure 4.

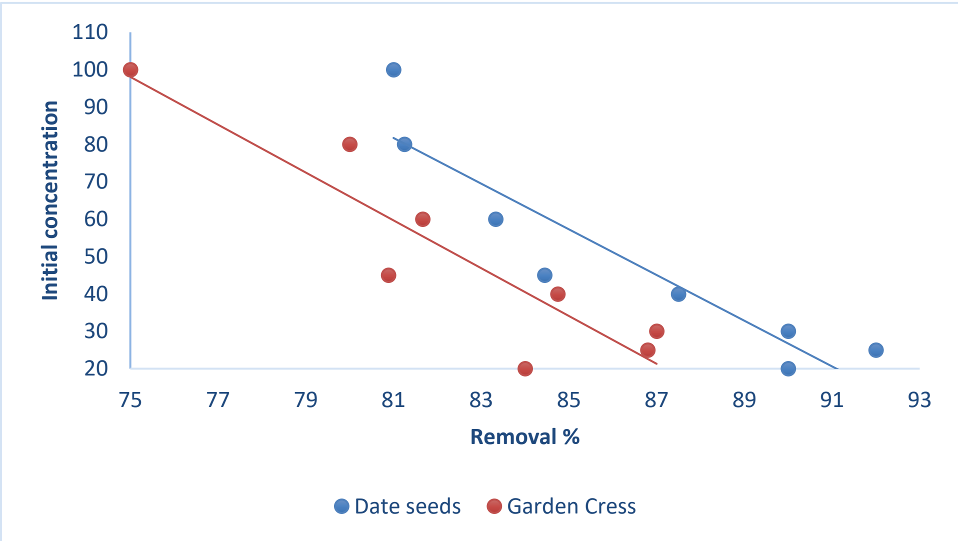

Figure 4. Effect of initial Cr(VI) concentration on the removal of chromium ions by carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS).

For CDS, removal efficiency decreased from 90% at 20 mg L^{-1}, to 81% at 100 mg L^{-1}. With CGCS, removal efficiency also decreased (84 mg L^{-1} to 75% mg L^{-1}) as concentration increased from 20 to 100 mg L^{-1}. Removal efficiencies are better for lower concentrations of chromium. The reduction of removal efficiency at higher concentrations of initial chromium is attributed to the filling of the adsorption sites. Removal efficiencies are better for lower concentrations of chromium since the available sites are considerably more than the available chromium ions. At higher concentrations of chromium, the sites on the adsorbent are filled, and the percentage removal of chromium ions also decreases. Removal efficiencies decreased, and adsorption capacities (q_e) improved for both adsorbents at higher concentrations of chromium. For CDS, adsorption capacity improved from 0.90 to 4.05 mg g^{-1} with the increase of concentration from 20 to 100 mg L^{-1}. For the same concentration range, CGCS also improved from 0.84 to 3.75 mg g^{-1}. Removal efficiencies and adsorption capacities of carbonised date seeds relative to carbonised garden cress seeds within the concentration range of the study were superior. The results indicate that CDS is superior to CGCS in terms of affinity and adsorption of Cr (VI) ions. Further analysis of the adsorption data was done using adsorption isotherm models to describe the equilibrium behaviour of the adsorption of chromium on the prepared adsorbents based on the results obtained [12].

Adsorption Kinetics

The adsorption kinetics of Cr(VI) on the carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS) was studied by pseudo-first-order and pseudo-second-order kinetic models. The obtained kinetic parameters are summarised in Table 1 and the corresponding linear plots are shown in Figures 5 and 6.

Table 1. Kinetic parameters for Cr(VI) adsorption onto CDS and CGCS.

Adsorbent	Pseudo-first-order equation	R^2	Pseudo-second-order equation	R^2
CDS	$y = -0.0315x - 0.1138$	0.8388	$y = 0.9358x + 19.783$	0.9664
CGCS	$y = -0.0195x - 1.0118$	0.6374	$y = 1.2727x + 14.09$	0.9754

Pseudo-First-Order Model

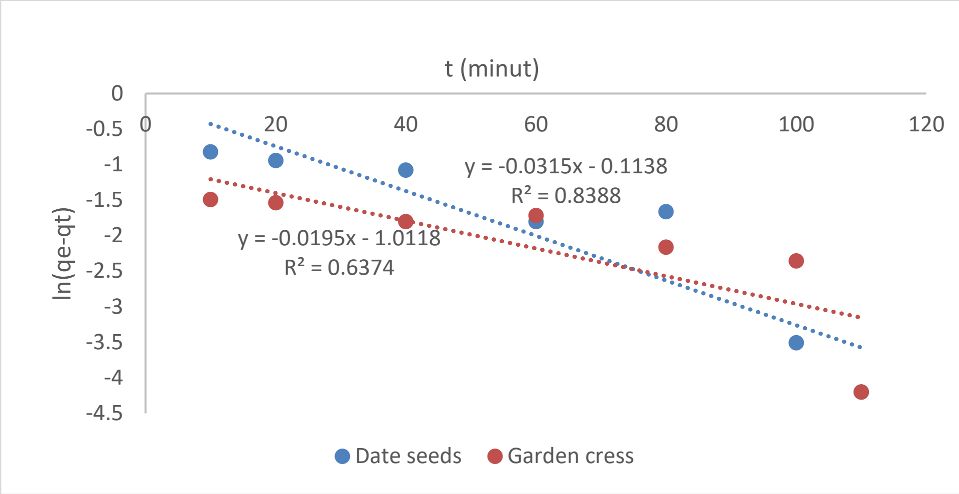

Figure 5. Pseudo-first-order kinetic plots for Cr(VI) adsorption onto CDS and CGCS.

The adsorption behaviour of Cr (VI) on the prepared adsorbents was evaluated using the pseudo-first-order kinetic model. The time ln (qe − qt) plotted model is shown in Fig. 5. The obtained R 2 values were 0.8388 for CDS and 0.6374 for CGCS. The low correlation coefficients indicate that the process of adsorption is not well represented by the pseudo-first-order model. Also, the described adsorption mechanism by the pseudo-first-order equation is insufficient, considering the experimental data and the model predictions [13].

Pseudo-Second-Order Model

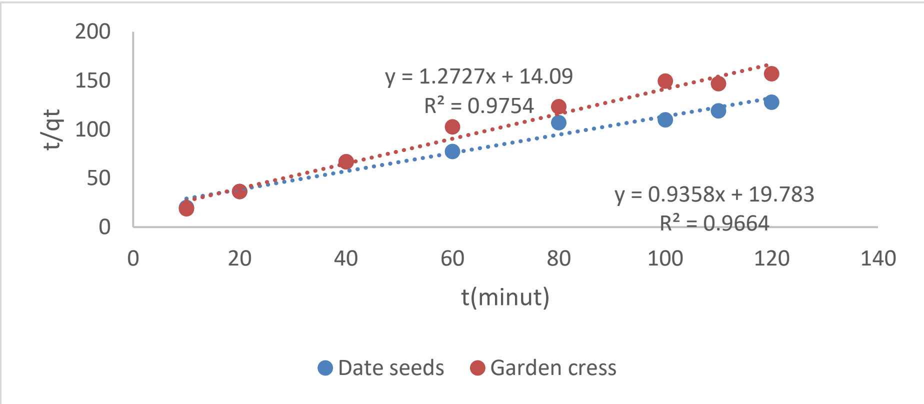

Figure 6. Pseudo-second-order kinetic plots for Cr(VI) adsorption onto CDS and CGCS.

The pseudo-second order kinetic model was used next to fit the experimental data. The associated plots (shown in Figure 6) of t/qt versus time were linear. While the best correlation coefficients obtained for the pseudo-first order model were 0.9664 and 0.9754 for CDS and CGCS, respectively, the pseudo second order model was in much better agreement with the data. The second order model also indicates that the rate of the adsorption process is most probably due to the chemical bonding of the Cr(VI) ions with the functional groups of the carbonised adsorbents. The fact that the pseudo-second-order model was applicable to both adsorbents illustrates the considerable extent of the adsorbent-adsorbate interaction during the adsorption of chromium. This phenomenon and these results corroborate similar findings of other researchers on the adsorption of various heavy metal ions using carbonised agricultural waste. From the results obtained in this study, the adsorption of Cr(VI) ions onto carbonised date seeds and carbonised garden cress seeds was better described by the pseudo second order model [14].

Adsorption Isotherms

Langmuir and the Freundlich isotherm models were applied to the equilibrium adsorption data to study the adsorption behaviour of Cr (VI) on carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS). The isotherm parameters are listed in Table 2, and the related linear plots are represented in Figures 7 and 8.

Table 2. Isotherm parameters for Cr(VI) adsorption onto CDS and CGCS

Model	Parameter	CDS	CGCS
Langmuir	qmax (mg g^{-1})	5.85	6.58
Langmuir	KL (L mg^{-1})	0.0896	0.0538
Langmuir	R^2	0.8887	0.9075
Freundlich	KF	0.68	0.47
Freundlich	n	1.72	1.49
Freundlich	R^2	0.9734	0.9595

Langmuir Isotherm

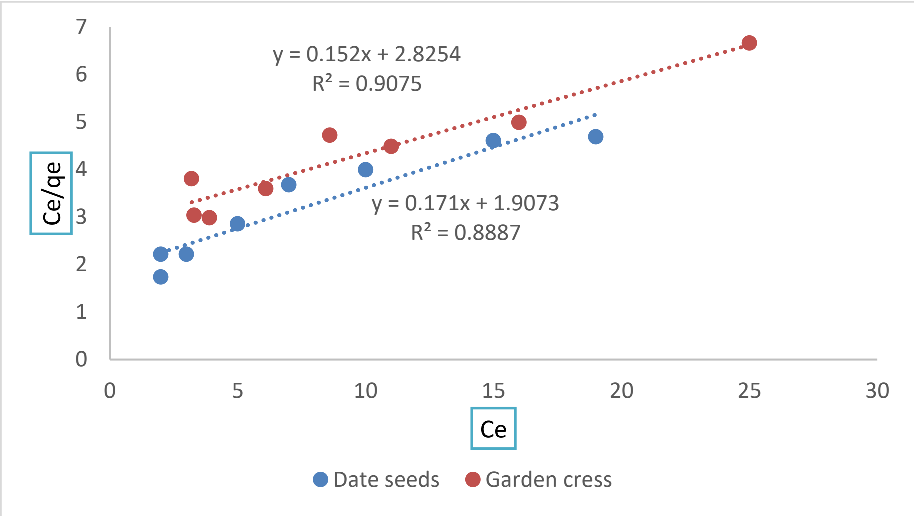

Figure 7. Langmuir isotherm plots for Cr(VI) adsorption onto CDS and CGCS.

The Langmuir isotherm model describes the adsorption of chromium ions on sites of a homogeneous adsorbent. The values of the correlation coefficient (R^2) that resulted from the linear plots of Ce/qe versus Ce were 0.8887 and 0.9075 for CDS and CGCS, respectively. The qmax values of the Langmuir model, for CDS and CGCS, were 5.85 mg g^{-1} and 6.58 mg g^{-1}, respectively. These values exhibit a high ability of CDS and CGCS to adsorb chromium ions. Nevertheless, the low correlation coefficient values signify that the Langmuir model is not suitable for the adsorption of Cr(VI) ions on the synthesized adsorbents [15].

Freundlich Isotherm

The Freundlich isotherm model was also applied to non-uniform surfaces. For CDS and CGCS, R^2 values of 0.9734 and 0.9595, respectively, indicated that the Freundlich model plots had better fits than the Langmuir model.

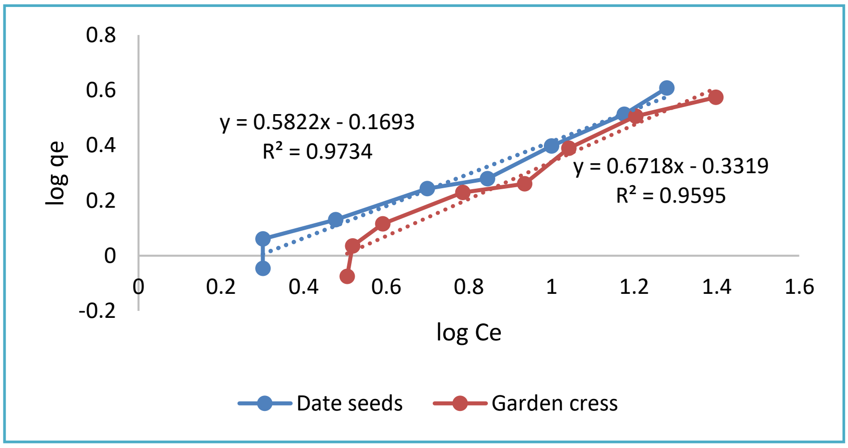

Figure 8. Freundlich isotherm plots for Cr(VI) adsorption onto CDS and CGCS.

The Freundlich adsorption coefficient KF for CDS and CGCS was 0.68 and 0.47, respectively. The values for the adsorption intensity parameters n were 1.72 for CDS and 1.49 for CGCS. Because the values of n are greater than 1, the adsorption process is said to be favourable for both adsorbents. The greater correlation coefficients of the Freundlich model in all cases indicate that the adsorption of Cr (VI) on both carbonised date seeds and carbonised garden cress seeds was on a surface of heterogeneous nature and of varying adsorption energies. As a result, the Freundlich isotherm is a better representation of the adsorption equilibrium than the Langmuir isotherm for the experimental conditions studied [16].

Thermodynamic Studies

According to Van't Hoff equation, the adsorption behavior of Cr(VI) ions on carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS) was studied from the perspective of thermodynamics. The calculations of balance of the thermodynamic parameters from the Van't Hoff plots are illustrated in Table 3, and the associated plots are illustrated in Figure 9.

Table 3. Thermodynamic parameters for Cr(VI) adsorption onto CDS and CGCS

Adsorbent	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
CDS (Date seeds)	-66.25	-226.93	0.8366
CGCS (Garden cress seeds)	-52.81	-187.42	0.7986

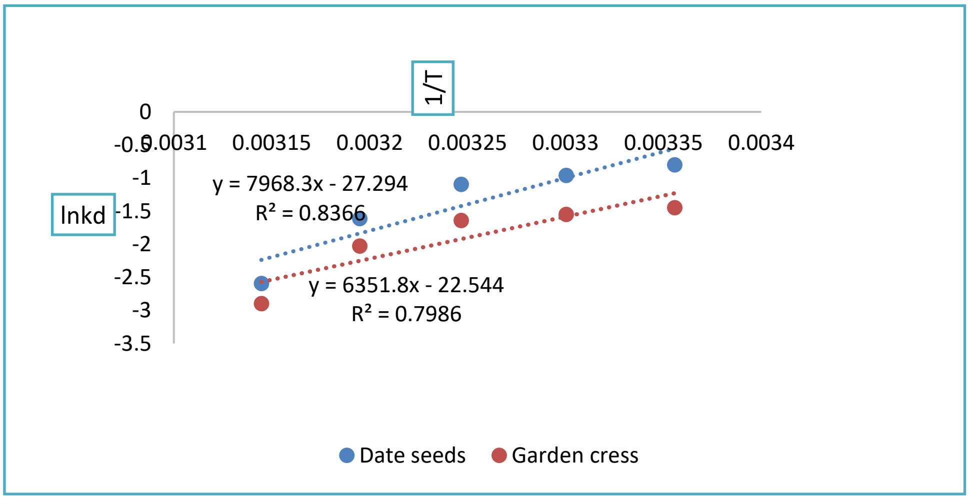

Figure 9. Van't Hoff plots for Cr(VI) adsorption onto carbonized date seeds (CDS) and carbonized garden cress seeds (CGCS).

The uptakes of temperatures on chromium for both adsorbents were proven to be negative as the adsorption efficiency decreased as temperature increased. The removal efficiencies of CDS and CGCS were 90% and 82.5% at 25 °C and were observed to decline to 60% and 52.5%, respectively, at 45 °C and 60 °C. The ΔH° values were calculated as −66.25 and −52.81kJmol−1 for CDS and CGCS, respectively. The adsorption of Cr(VI) ions was proven to be exothermic for the two adsorbents, since negative ΔH° values, along with the decreased chromium removal efficiencies for the raised temperature, were consistent with the results. The entropy changes, ΔS°, for CDS and CGCS, were calculated as −226.93 and −187.42 J mol-1 K-1, respectively. The ordering of within the solid adsorbent during the adsorption of Cr(VI) ions indicates negative ΔS°. This may be due to the ordering of the chromium ions on the surface of the adsorbent during the adsorption process. The results of the adsorption thermodynamics studies indicated that the adsorption of Cr(VI) ions onto both carbonised date seeds and carbonised garden cress seeds was preferable at lower temperatures and the process was exothermic adsorption.

CONCLUSION

Carbonised date seeds (CDS) and carbonised garden cress seeds (CGCS) have potential to be low cost, ecofriendly adsorbents for Cr (VI) ions removal from water. Findings indicated that Cr (VI) ions removal was dependent on solution pH, adsorbent dosage, contact time, initial chromium concentration and temperature. The maximum removal was observed at pH 5. Removal of chromium ions increased with an increase in adsorbent dosage and contact time. Maximum removal efficiency of 94% was achieved with carbonised date seeds as compared to carbonised garden cress seeds. It was also observed that the process was of kinetic order pseudo second and was in good agreement with the experimental data. The isothermal studies revealed better fit for the Freundlich model as compared to the Langmuir model, which indicated that the surfaces of the adsorbents were heterogeneous in nature and that the energies of adsorption varied. The results of the adsorption capacity decreasing with the increase in temperature indicated that the nature of the process was exothermic. From the above studies it can be concluded that carbonised date seeds and, to a lesser extent, carbonised garden cress seeds, can be utilized as effective and economic adsorbents for the removal of Cr(VI) from contaminated water.

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