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Hexavalent chromium removal using agricultural waste "rye husk"

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ABSTRACT

The adsorption of Cr(VI) on rye husk (RH) was studied at varying Cr(VI) concentrations, adsorbent dose, contact time, and pH. Maximum Cr(VI) was sequestered from the solution within 140 min and the maximum removal of 5.0 mM Cr(VI) was about 68% at pH of 3.0 for 0.5 g RH. The removal of Cr(VI) was maximum (80.0%) when the initial pH of the solution was kept at 3.0. The Cr(VI) adsorption capacity of RH samples was calculated as 0.435 mmol/g at pH 3.0 from Langmuir isotherm. The adsorption kinetics data were evaluated with first-order reversible and pseudo-second-order kinetics models.

Keywords: Rye husk; Adsorption; Kinetics; Chromium(VI); Equilibrium

1. Introduction

Huge amounts of chromium waste come out from industrial process; hence, large quantities of this metal are discharged into aquatic medium. Many industries such as electroplating, mining, tanning of leather, photography industries, textile dyeing, metal processing, and wood preservation produces wastewater containing large quantities of chromium. Chromium(VI), Cr(VI) is toxic and carcinogenic to both animals and humans even in small concentrations in the medium, but trivalent chromium species is an essential nutrient for them [1,2].

The maximum contaminant levels of Cr(VI) determined by USEPA were 0.05 and 0.1 mg/L for the drinking water and inland surface waters, respectively. Accordingly, chromium containing wastewaters must be treated to lower the Cr(VI) to allowable limits before discharging into the sewers or drains. The amount of chromium discharged to the aquatic environment should be reduced, or recycled if possible. Several traditional purification methods are usually applied for the removal of Cr(VI) present in the drinking water. Cold and hot lime precipitation, microfiltration, ultrafiltration, membrane, and osmosis are basic treatment methods for the metal removal [3–5]. The precipitation method causes huge amount of sludge to be collected in the systems. Although some of these methods are considered to be a suitable technique for chromium removal, they can be expensive and do not have good selectivity for specified metal ions. Adsorption is one of traditional techniques and it is favorable because of its efficiency and carry outs removal of chromium even at low-concentration values in the treatment plant [6].

Large increase in the quantities and varieties chromium makes the conventional purification techniques inefficient and more expensive in the buildup of the plant. Hence, to develop a new and an effective adsorbent for the treatment units has become important, cost-effective or inexpensive for the water pollution

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control [7]. Agricultural byproducts or a certain waste as a result of harvesting can be alternatives as low-cost adsorbents, since they represent unused resources, are widely available and eco-friendly product. It has been reported that wastes such as sawdust, barks [8], pine leaves [9], *Ocimum Americanum* L. seed pods [10], wool, olive cake, pine needles, almond shells, cactus leaves [11], leaf mold [12], coconut husk and palm pressed fibers [13], coconut coir [14], polyaniline composite [15], coffee husk [16], sugar cane bagasse, maize corncobs and Jatropha oil cake [17], corncob [18], sawdust [19], sunflower husk [20], quaternized wood [21], Japanese Cedar Bark [22], grape waste [23], wheat bran [24], oil-free *Moringa oleifera* cake and sweet potatoes peels [25], walnut, hazelnut and almond shell [26], and cork waste [27] have been applied effectively in different ways to remove chromium species from certain types of systems.

The agro byproducts matrix contained a variety of functional groups in the matrix, such as carboxylic, hydroxyl, amine, sulfonic, etc. which have high affinity for Cr(VI) ions [13]. Agro-wastes or byproducts contain polysaccharides, some proteins, cellulose, hemicellulose, and lignin which contain some functional groups in their structure which can enter certain mechanism with chromium ion. The presence of large amount of surface functional groups in them makes various agricultural byproducts better alternatives for expensive adsorbents [28].

Rye husk (RH) contains several types of organic compounds such as about 26% cellulose, 16% hemicellulose, 13% lignin, 17% starch, 10% protein, and 7% fat [29]. The Cr(VI) anion in the aqueous solution is not a simple monovalent anion, but it can be found in the different forms according to the pH and concentration of the medium. Cr(VI) exists in the form of $HCrO_4^-$ and CrO_4^{2-} in the solution at low concentrations and near neutral pH values. When the solution phase is acidic, $HCrO_4^-$ is the main species in the aqueous phase [30]. In this study, RH was applied to aqueous systems as an efficient adsorbent for removing Cr(VI) ions in batch reactors by changing some parameters such as pH, concentration, time, and adsorbent dosage. This material is cheap and cultivated on a large scale in many parts of Turkey.

2. Experimental

2.1. Materials

Mili-Q filtered deionized water was used for dilutions and all of solutions used in the experiments were prepared from analytical grade chemicals. Cr(VI) stock solution used in the adsorption procedures was prepared by dissolving of $K_2Cr_2O_7$ (from Merck) and 0.1 M KNO_3 was used to adjust the ionic strength in the bulk solution for the adsorption [31]. The various concentrations of NaOH and HCl were used for fine adjustment of pH of the medium, as required.

2.2. Preparation of RH

The RH used throughout the experiments was collected at the time of harvesting from agricultural fields in the vicinity of Konya (Turkey). Husks were left in the open air for a long period of time to dry and then all the water inside of them was evaporated. Dried RH was converted into to a powdered form by grinding in a ball mill and consequently was sieved to obtain the product in 100 μm particle size. After that, the RH powders were washed several times using deionized water and dried in oven at 100˚C for a day.

2.3. Apparatus

Shells were grounded using with a Retsch RM 100 model grinding machine for the batch adsorption. During the experiment, the pH measurements were controlled with Orion 900S2 Model pH meter and a thermo stated shaker of GFL 3033 model and IKA-MAG-RO15 model magnetic stirrer were used for mixing of the bulk solutions in adsorption experiments. The analysis of Cr(VI) remained in the solution phase (except Cr(III) passed into the solution) was realized with the 1,5 diphenyl carbazide using a UV–vis spectrophotometer (Shimadzu UV-1700) (λ: 540 nm) [32]. The total chromate species will be represented as Cr (VI) because some Cr(III) was oxidized with potassium permanganate to Cr(VI) when measuring with UV–vis spectrophotometer.

The different functional groups present in the adsorbent were determined with an IR spectrometer (Perkin Elmer 1600) by preparing a KBr disk from the adsorbent. Elemental analysis of adsorbent was carried out using an elemental analyzer, TUBITAK Test and Analysis Laboratory in Ankara, Turkey (Perkin Elmer Elemental Analyzer Model 240). The elemental composition of RH was identified by regarding carbon, hydrogen, nitrogen, and oxygen content.

2.4. Adsorption studies

The adsorption studies of Cr(VI) ion by RH was completed in a batch plastic reactor. The following method was used to remove the Cr(VI) ion from solution phase: 0.5 g RH was equilibrated with 50 ml of 5.0 mM Cr(VI) solution in a plastic reactor at 25˚C and then put into the shaker. The initial pH of the solution in the reactor was controlled in the range of 2–9 by adding 0.1 M HNO_3 or 0.1 M NaOH. The mixture was stirred at 250 rpm to maintain the adsorbent in the suspension form. The suspension was separated by filtration and RH was washed with deionized water and then Cr(VI) ions which remained in the solution phase measured using UV–vis spectrometer. The filtrate containing the residual concentration of Cr(VI) was determined spectrophotometrically at 540 nm and the residue in filtrate has not any chromium. The mass balance of adsorbed amount of chromium, q_t (mmol g^{-1}), can be calculated by the mass balance:

$$q_t = ((C_o - C_t)V)/m \tag{1}$$

where q_t is the removed Cr(VI) ions (mmol/g adsorbent) from the solution phase by the RH, m is the weight of RH (g), V is the volume of solution (L), C_o is the initial Cr(VI) concentration (mmol/L), and C_t is the Cr(VI) concentration (mmol/L) at equilibrium. When the equilibrium reached between Cr(VI) ion and RH after certain time, the amount of Cr(VI) ion adsorbed, q_e, can be calculated using Eq. (1). Time dependent experiments were carried out by shaking the adsorption mixture at various predetermined intervals (5–240 min) and analyzing the Cr(VI) ion content at the end of the contact time. RH (0.5 g) was added into the Cr(VI) solution having different initial pH (2–9) values and were agitated then left for settle. The initial pH (pH_i) of the solutions was roughly adjusted between 2 and 9 by adding both 0.1 M HNO_3 or 0.1 M NaOH and all pH measurements were done with an Orion 900S2 model digital pH meter. Initial pH (pH_i) of the solutions was accurately noted with the pH meter. The final pH (pH_f) of the equilibrium was also measured and noted. The difference between the initial pH (pH_i) and final pH (pH_f) values ($pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with abscissa gave the pH_{PZC}. A pH increase was slightly observed in the acidic medium from 2.0 to 3.0. At higher initial pH, there are no changes in the pH of the solution. Equilibrium isotherms were carried out with different initial chromium concentrations varying from 1.0 to 10.0 mM with a constant adsorbent mass (0.5 g) at 25˚C. The adsorbent mass was varied from 0.1 to 1.0 g in order to determine the effect of adsorbent amount in adsorption.

3. Results and discussions

3.1. Characterization of RH

Surface area of RH was determined as 3.5 m^2 g^{-1} by Brunauer–Emmett–Teller using nitrogen as a surface occupying gas. The results obtained for functional groups of RH are presented in Table 1. As observed in this table, the RH is consists of carbon, hydrogen, oxygen, nitrogen, and sulfide. This composition is like to that of the other agricultural residues such as coconut coir and wheat husk [14,29].

The IR spectrum of RH was recorded in a range of 4,000–1,000 cm^{-1}. The FT-IR spectrum of RH is shown in Fig. 1. The peak at about 3,447 cm^{-1} is due to the stretching hydrogen-bonded O–H. The hydrophilic tendency of RH was reflected in the broad absorption band (3,050–3,750 cm^{-1}), which is related to the –OH groups present in aliphatic or aromatic alcohol. The peak obtained at about 2,922 cm^{-1} is due to the C–H stretching from aliphatic saturated compounds. A peak at 1,734 cm^{-1} in the spectrum is assigned to the C=O stretching of the acetyl and uronic ester groups of hemicellulose or to the ester linkage of carboxylic group of the ferulic and p-coumaric acids of lignin in the double bond region [29]. The peak at 1,653 cm^{-1} for RH was reflected for amide group and this band represents 80% of the C=O stretching of the amide group, coupled to in-plane N–H bending and C–N stretching modes [33]. The peaks around 1,508 cm^{-1} are due to the C–C stretching that can be attributed to the aromatic C–C bond. The bands in the range 1,450–1,370 cm^{-1} were assigned to the C–H deformations. The bands appearing at 1,246 and 1,038 cm^{-1} represent, C–N from amine, C–O from carboxylic acid and S=O from sulfoxide [25]. The peak at 670 cm^{-1} can be assigned to bending modes of aromatic compounds [20].

3.2. Effect of contact time on the removal of Cr(VI)

The initial metal concentration of the solution was 5.0 mM Cr(VI) and the concentration of Cr(VI) remaining in the solution phase was plotted against time. Equilibrium time depends on of many factors, such as number and kind of adsorption sites, size, and form of RH. The plots drawn for Cr(VI) adsorption (%) vs. time for RH (Fig. 2) indicates that the equilibrium was

Table 1
Elemental composition of RH

Rye husk (weight percentage (%))	RH
C[a]	43.290
H[a]	6.858
O[a]	48.311
N[a]	1.120
S[a]	0.421
O/C (atomik)[a]	0.837

[a] Dry and ashless (900˚C).

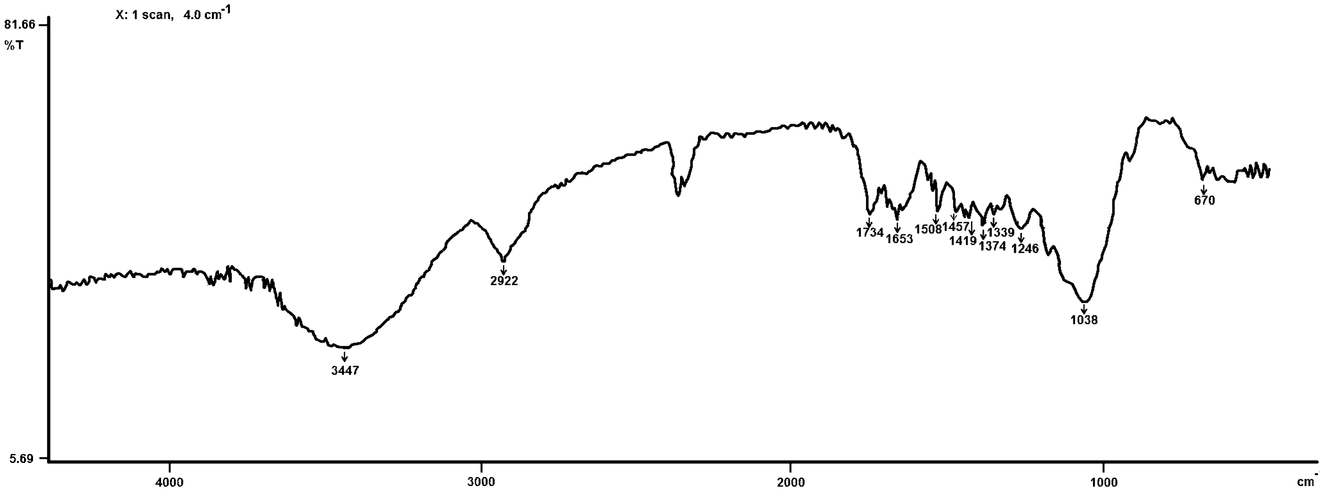

Fig. 1. IR spectra of RH.

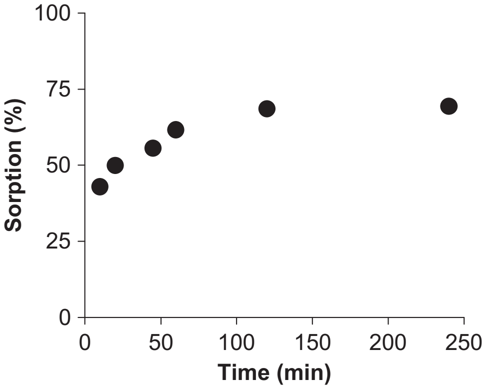

Fig. 2. Effect of contact time on the sorption of Cr(VI) by RH. Adsorption conditions; initial concentration of Cr(VI): 5 mM, 0.5 g adsorbent, 50 mL of adsorption medium, temperature: 25 ± 1˚C, pH 3.

reached in 140 min and, the uptake of Cr(VI) was rapid at the beginning of the reaction and then continued at a much slower rate. The Cr(VI) concentration in the solution phase decreased rapidly within 20–80 min and the adsorption event was continued between 120 and 140 min. Fig. 2 indicates that the adsorption reaction can be considered in two stages: initially the adsorption rate is very high in the beginning of the reaction between Cr(VI) ions and RH (69% of adsorbent capacity was reached in a contact time of 140 min), and secondly adsorption rate is very slow at the equilibrium.

3.3. *Effect of pH on Cr(VI) adsorption*

There are different explanations in describing the interaction of Cr(VI) ions with RH. Major adsorption mechanisms for binding Cr(VI) ions to RH are electrostatic attraction between RH surface and Cr(VI) ions in the solution phase, physical adsorption, ion exchange, and surface complexation. The electrostatic interaction (attraction or repulsion) between Cr(VI) and RH is one important mechanism of the existing reaction. Therefore, the increase in Cr(VI) adsorption on the surface of RH at acidic pH values is due to the electrostatic attraction of the anion $HCrO_4^-$ which is the dominant species at low pH values to the positively charged groups of the RH surface. The decrease in electrostatic attraction causes the decrease in the adsorption when the pH of solution increasing. The competitiveness between the chromium anionic species ($HCrO_4^-$ and CrO_4^{2-}) and OH^- ions in the bulk solution for the adsorption on active sites results in low adsorption. It can be suggested that physical adsorption mechanism and electrostatic interaction could be predominant mechanism for the Cr(VI) removal by RH.

The pH of the system is an important variable and by simply regulating the solution pH, the adsorbent surface properties and ionic forms of Cr(VI) ions can be changed. Batch adsorption experiments were carried out over a large pH range of 2.0–9.0. At low pH values at about 2 the carboxyl groups will be protonated [24]. The surface of adsorbent is protonated at initial pH of less than 3.0, and permits the electrostatic interaction with the anionic form of Cr(VI). The RH can adsorb Cr(VI) ions, likely due to the presence of functional groups as alcohol and carboxyl groups. From Fig. 3(a), in all cases the adsorption of Cr(VI) is pH-dependent and showed a maximum adsorption at equilibrium pH values between 2.0 and 3.0. The adsorption of Cr(VI) takes place at a pH below the

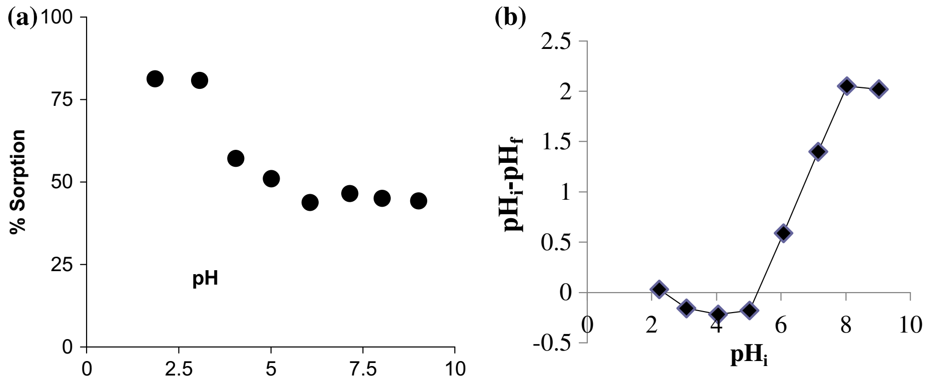

Fig. 3. (a) Effect of pH on the adsorption of Cr(VI) using the RH. Adsorption conditions; initial concentration of Cr(VI): 5 mM, 0.5 g adsorbent, 50 mL of adsorption medium, temperature: 25 ± 1˚C, contact time: 140 min, pH 2–9. (b) Point of zero charge.

pHpzc that was found to be about 5.2 (Fig. 3(b)) and the similar result is found by Baran et al. [34]. There was subsequently a sharp decrease in percent adsorption of Cr(VI) ion with increase in pH of the aqueous solution. Cr(VI) removal decreased when pH was increased from 3 to 9. Maximum adsorption of Cr(VI) was at pH 3.0 for further adsorption experiments and the pH influence on Cr(VI) removal onto the matrix of the RH is related to the type and ionic state of the functional groups that presents on it.

As the pH of the solution is changing, the equilibrium between Cr(VI) and RH will alternate and then reestablish again after a certain time. In the pH range of 2–6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are in equilibrium and at lower pH values; $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species of chromium are appeared in the solution phase. Increasing the quantity H^+ ion on the RH surface, the electrostatic attraction between positively charged surface and negatively charged chromate ions occurs. The adsorption of Cr(VI) at $pH \geq 6$ is less because of double competition of both anions (CrO_4^{2-} and OH^-) to be adsorbed on the RH surface. More adsorption of Cr (VI) on RH lattice can cause more reduction of the Cr (VI) ion to Cr(III) in acidic region. Cr(III) is small in size and can easily be replaced by the positively charged species. In some studies, the removal of Cr (VI) was successfully realized by different adsorbents and the optimum pH was recorded in the range of 2.0–3.0 [12,13,35]. According to Sharma and Forster [12], oxo groups (C_xO) of the carbonaceous material release hydroxyl ions into the solution by following Eq. (2). During Cr(VI) adsorption experiments at initial acidic $pH < 3.5$, a rise in pH can exist and proton consuming reduction reactions effects as Eq. (3).

$$C_xO + H_2O \leftrightarrow \{C_xOH\}^+ + OH^- \tag{2}$$

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \tag{3}$$

The adsorption mechanism based on ionic equilibrium between Cr(VI) and Cr(III) is complicated for RH. One possibility can be that the surface complexation reactions with protonated sites can affect the adsorption. The direct and indirect reduction of Cr(VI) to Cr(III) is proposed in Cr(VI) adsorption on the surface of RH. Cr(VI) ions can directly be reduced to Cr (III) by electron-donor groups exist on the surface of RH and the reduced to Cr(III) and form complexes with the RH.

The adsorption of Cr(III) ion on the surface of RH is not possible at pH 3.0 and the adsorption–reduction of Cr(VI) to Cr(III) can take place on the RH surface. Cr(VI) can be eliminated from aqueous phase with two reduction mechanisms [36]: in the first mechanism, the reduction of Cr(VI) to Cr(III) exists in the solution by contact with the electron-donor groups that have lower reduction potential values than that of Cr(VI). Remaining Cr(III) in the solution phase makes complexes with the Cr-binding groups that exist in the matrix of the RH. The second mechanism is by the binding of anionic Cr(VI) to the positively charged groups in the RH surface such as carboxyl groups and the reduction of Cr(VI) to Cr(III) by joined electron-donor groups. After that, it releases Cr(III) into solution phase due to repulsion between positively charged Cr(III) and positively charged groups in the RH surface, or complexation of Cr(III) with joined groups can be suggested [11,37].

3.4. *Effect of ionic strength*

Ionic strength of equilibrium solution is one of the significant factor affecting equilibrium [31]. The effect of the interfering KNO_3 ion on the adsorption of Cr(VI) was investigated by changing amount of salt concentration. The electrostatic attraction at low-ionic strength suggested that the low-salt concentration seems to play an unimportant role in the adsorption of Cr(VI). The result shows that the removal of Cr(VI) ion was changed slightly for the range of 0.01–0.05 M KNO_3.

3.5. *Effect of adsorbent amount*

Keeping other parameters (pH-3.0, Cr(VI) concentration-5.0 mM, temperature-25˚C, stirring rate-250 rpm, and contact time-140 min) constant, the adsorption of Cr(VI) was studied by changing the amount of RH between 0.1 and 1.0 g (Fig. 4). The removal efficiency of the RH mainly increases with increasing the amount of RH for a certain Cr(VI) concentration. This result was obtained because at a certain initial Cr(VI) concentration, increasing the amount of adsorbent results in greater surface area (or adsorption sites) of the RH. The addition of adsorbent for definite time (0.5–1.0 g RH/50 mL) did not changed the adsorption % of Cr(VI) further. The maximum removal of Cr(VI) was about 68% for 0.5 g/50 mL of RH dose at 5.0 mM Cr(VI).

3.6. *Cr(VI) adsorption isotherms as a function of concentration*

The equilibrium isotherms describe the interaction between Cr(VI) and RH and so are important in optimizing the adsorption process. The effect of Cr(VI) concentration on the adsorption of RH was evaluated by changing the Cr(VI) concentration (1.0–10.0 mM) at pH value of 3.0 for 140 min of equilibrium (Fig. 5). When the initial Cr(VI) concentration increased, the amount of Cr(VI) ions adsorbed per unit mass of the RH increased as expected and saturated of RH at low concentrations indicates strong binding for Cr(VI). The isotherm plot in Fig. 5 shows a steep slope in the initial concentration range for pH 3.0 and it implies efficient uptake of Cr(VI) by RH in dilute Cr(VI) solution. The initial concentration of Cr(VI) was increased from 1.0 to 10.0 mM to reach the saturation of interaction with Cr(VI) ions on the RH as well as to obtain the maximum sorption capacity for them. At the higher concentrations, more Cr(VI) ions cannot adsorbed and remained in the aqueous phase due to the saturation of binding sites.

Equilibrium isotherm which is the most important parameter for adsorption system provides information on the RH capacity. The adsorption process of Cr(VI) ions on RH is characterized using a number of isotherm models such as Langmuir, Freundlich, Scatchard, and D–R (Dubinin–Radushkevich) isotherms [38]. These isotherms describes Cr(VI) ion uptake per unit weight of the adsorbent, q_e, and the equilibrium Cr(VI) ion concentration in the aqueous phase, C_e.

It was shown in Table 2 that the correlation coefficient obtained from the Freundlich adsorption isotherm was 0.985. It was higher than it in Langmuir sorption isotherm. It can be concluded that the Freundlich adsorption isotherm was more appropriate for explaining equilibrium than Langmuir adsorption isotherm with Cr(VI) sorption capacity of

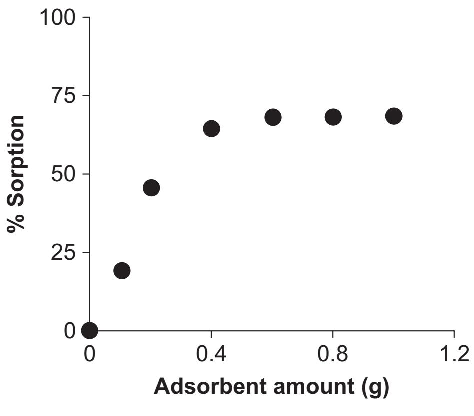

Fig. 4. Effect of adsorbent dosage on the sorption of Cr(VI) on RH. Adsorption conditions; initial concentration of Cr (VI): 5 mM, 0.10–1.0 g adsorbent, volume 50 mL of adsorption medium, temperature: 25 ± 1˚C, pH 3, contact time: 140 min.

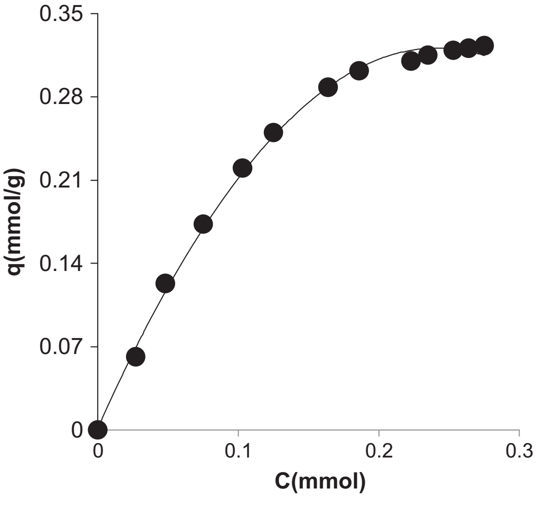

Fig. 5. Sorption isotherm of Cr(VI) ion on RH as a function of initial Cr(VI) concentration (1.0–10.0 mM) and 50 mL of Cr(VI) solution at pH 3.0; 0.5 g adsorbent, temperature: 25 ± 1˚C, contact time: 140 min.

Table 2
Freundlich, Langmuir, Scatchard, and D–R adsorption isotherm parameters

Freundlich isotherm			Langmuir isotherm			Scatchard isotherm			D–R isotherm			
k[a]	n	R^2	K[b]	A_s[a]	R^2	K_s	Q_s[a]	R^2	X_m[a]	K[c]	E	R^2
1.31	0.82	0.99	57.94	0.44	0.96	43.79	0.63	0.69	0.12	0.01	6.48	0.99

[a](mmol/g) dry adsorbent.
[b](L/mol) dry adsorbent.
[c]($\text{mol}^2\ \text{kJ}^{-2}$).

0.435 mmol/g for RH (Table 2). Since the Langmuir adsorption isotherm constant does not explain clearly the physical or chemical properties of the adsorption, Scatchard, and D–R adsorption isotherms were also investigated for Cr(VI) adsorption with RH. The average adsorption energy (E) calculated from the D–R isotherm and correlation coefficient (R^2) found as 0.693 from Scatchard isotherm gives important information [38]. For $E < 8\ \text{kJ mol}^{-1}$, the physical adsorption predominates. The adsorption energy was calculated as $6.482\ \text{kJ mol}^{-1}$ for Cr(VI) (Table 2). If E is between 8 and $16\ \text{kJ mol}^{-1}$, ion exchange can be the dominant factor and if $E > 16\ \text{kJ mol}^{-1}$, the adsorption is dominated by particle diffusion [20]. In the Cr(VI) interaction with RH, the electrostatic attraction is main mechanism for the adsorption process.

3.7. Modeling of adsorption kinetics

Experiments were also carried out to explain the kinetics of Cr(VI) by RH. The adsorption of Cr(VI) ions in aqueous phase is attributed to follow reversible first-order kinetics, when the Cr(VI) ions are adsorbed on the surface of RH. An important physicochemical parameter used to explain the adsorption phenomena is the kinetic of the adsorption reaction. Accordingly, the kinetic of Cr(VI) removal was investigated to understand the adsorption behavior of RH. The adsorption of Cr(VI) onto RH followed reversible first-order rate kinetic. The adsorption of Cr(VI) onto the adsorbent may be expressed as [3]:

$$A \underset{k_2}{\overset{k_1}{\leftrightarrow}} B \tag{4}$$

where k_1 and k_2 are reaction rate constants. These constants were calculated using the kinetic equations numbered (2)–(17) in Ref. [3]. The overall rate constant k was obtained by determining the slope of straight lines and using Eqs. (7) and (9) in Ref. [3]. The equilibrium constant K_C, forward and backward rate constants k_1 and k_2 were calculated and the forward rate constant for first-order reversible adsorption (0.0221) for Cr(VI) removal was much higher than the backward rate constant (0.0097) namely, the desorption.

The adsorption kinetics was also explained by pseudo-second-order equation [15] is given as:

$$\frac{dq}{q} = k_2(q_e - q)^2 \tag{5}$$

where q_e is the amount of Cr(VI) adsorbed per unit amount of RH at equilibrium state (mg/g), q is the amount of Cr(VI) adsorbed per unit amount of RH at any time t (mg/g) and k_2 is the rate constant in g/mg min. Integration of Eq. (5) for the boundary conditions $t = 0$ to $t > 0$ and $q = 0$ to $q > 0$ and linear form is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t_1}{q_e} \tag{6}$$

$h = k_2 q_e^2$, where h is the initial adsorption rate in mg/g min. The values of k_2 and h are determined from the intercept of second order graph and was calculated as 0.0653 and 0.1575, respectively. The greater correlation coefficient (0.9733) obtained from the first-order reversible kinetics is still better than the correlation coefficient of the pseudo-second-order kinetics (0.9686).

The diffusion of ions, one of the important properties of the reaction, influences the adsorption. The diffusion kinetic is supported by a convex adsorption isotherm, a high concentration of Cr(VI) and a large particle diameter of RH. The region describes the Cr (VI) adsorption displayed gradually rising curve, which shows the internal diffusion transport mechanism in the skeleton of RH.

3.8. Desorption studies

Desorption, the reverse of adsorption process gives some information on the adsorption mechanisms because of the fact that biomaterials can be decomposed under either basic or acidic conditions. Desorption studies give an idea of an alternative possibility of adsorbents reuse and the recovery of Cr(VI) metal resources. In the experiment, NaOH solution was used to remove Cr(VI) ions from the RH. Maximum desorption was observed at a pH range of 12–14. At pH value 12, 85% of Cr(VI) was removed. 90% of Cr(VI) is recovered under strong alkaline condition at pH 14. The desorption of Cr(VI) is enhanced by the increase in pH. This demonstrates that adsorbed Cr(VI) can be desorbed from the RH using 1 M NaOH and shaking for 24 h.

4. Conclusions

In this research, RH has been shown to be an effective adsorbent for Cr(VI) removal from aqueous solutions in a wide range of concentration. IR analysis suggests the importance of functional groups such as amino, sulfoxide, hydroxyl, and carboxyl during Cr(VI) removal. The adsorption of Cr(VI) by RH is found to depend on the adsorbent amount, pH of the solution, contact time, and the initial concentration of Cr(VI) ions. The maximum adsorption took place at around pH 3 and the adsorption of Cr(VI) increased with increase in the contact time and reached equilibrium after 140 min. The kinetic study revealed that increases in the initial Cr(VI) concentration affected the decrease in reaction rate. Adsorption data was analyzed using Langmuir, Freundlich, Scatchard, and D–R adsorption isotherms to understand the process of adsorption. The adsorption capacity of RH was found to be 0.435 mmol Cr(VI) per gram of RH from Langmuir isotherm. The amount of free energy in Cr(VI) adsorption by RH was 6.482 kJ/mol based on the Dubinin–Radushkevich (D–R) model. The adsorption kinetics can be explained by the first-order reversible kinetics rather than the pseudo-second-order kinetics.

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