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Chromium(VI) removal from aqueous solution by untreated rubber wood sawdust

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Abstract

The ability of untreated local rubber wood sawdust (RWS) to remove Cr(VI) was carried out under a bench-scale shaking condition by varying parameters such as initial Cr(VI) concentrations, adsorbent dosage, pH, temperature and eluting agent. Complete Cr(VI) removal was achieved at pH less than 2, initial Cr(VI) of 100 mg/L and RWS dosage of greater than 1.5 % (w/v). The point of zero charge (pH_{PZC}) of 4.90 explained the decrease in Cr(VI) removal capacity by RWS when pH (3–9) and initial Cr(VI) concentrations (200–500 mg/L) were increased. Shorter time was needed when 1 M HCl was used to recover Cr from RWS. FTIR analysis suggests the importance of functional groups such as amino, hydroxyl and carboxyl during Cr(VI) removal. Results suggest that the Cr(VI) removal by RWS is an endothermic process with positive entropy and occurs non-spontaneously.

Keywords: Sawdust; Chromium; FTIR; Removal; Point of zero charge

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1. Introduction

A wide array of technologies is available for the removal of chromium from wastewaters that include simply removing the chromium from wastewater to the recovery and use of the metal. In practical applications, the choice of one particular form of treatment depends on many factors including the form and concentration of chromium in the wastewater, other constituents present, extent of chromium removal targeted, environmental regulations, operating costs, amount of sludge and residues generated and their disposal cost. Selection of the most appropriate treatment system requires determination of the volume and characteristics of the effluent along with bench-scale treatability studies [1,2].

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Chemical precipitation is the most common Cr(VI) removal technique used. The chemicals most frequently used are lime, caustic soda and sodium bicarbonate. However, direct use of precipitation to remove Cr(VI) is not possible because Cr(VI) is highly soluble and does not precipitate out of solution at any pH [3]. Consequently, treatment of Cr(VI) waste usually consists of a two-stage process that is firstly the reduction of Cr(VI) to Cr (III), and secondly the precipitation of Cr (III). Other treatment technologies available for Cr(VI) include electrochemical reduction, sulphide precipitation, electrolytic ferrite treatment system, insoluble starch xanthate, cellulose xanthate, complexation with polygalacturonic acid, cementation, ion exchange, reverse osmosis, electrodialysis, electrolytic recovery, the chrome-apper system, solvent extraction, liquid membranes, evaporation, foam separation, freeze separation and activated carbon adsorption [2]. The use of chemical reducing agents such as sulphur dioxide (SO_2), sodium bisulphite ($NaHSO_3$) and sodium metabisulphite ($Na_2S_2O_5$) is the most widely practiced treatment method for the reduction of Cr(VI) to Cr (III) [4]. These Cr(VI) reduction and Cr (III) precipitation steps not only consume considerable amounts of acids and bases but also generate large volumes of sludge. The process also has a tendency to release obnoxious gases such as H_2S, which is toxic and detrimental to health. Also, a lot of money is spent on the chemical reducing agents used for Cr(VI) reduction and for the disposal of solid wastes generated from the precipitation process [1].

In view of this, substitute treatment technologies were developed as an alternative [5]. These substitute technologies offer lower operating costs by reducing requirement for operating equipment or operating expenses such as chemical reagent purchases and reduced sludge generation. Examples of substitute treatment technologies are sulphide precipitation, ion exchange [5], sodium borohydride, ozone oxidation, thermal oxidation [1], freeze crystallization, insoluble starch xanthase, sacrificial iron anodes, ultrafiltration, ferrous sulphate reduction and integrated treatment [2].

The use of cheap and readily available industrial waste as an alternative to currently practiced Cr(VI) treatment techniques is gaining importance lately. Industrial waste/ biomass such as coconut shells [6], *Eucalyptus grandis* sawdust [7], spent tires [8] and even cow dung [9] have been used and proven to remove Cr(VI) from aqueous solutions. Agricultural waste such as rubber wood sawdust have been used for the preparation of activated carbons and for the removal of Cr(VI) from waste water. Together with its high surface areas and high concentration of active functional groups, the abundance and availability of rubber wood sawdust makes it economically feasible [10]. Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material. Wood sawdust, a solid waste product obtained from mechanical wood processing, can be used as a low-cost adsorbent of heavy metals, largely due to its lignocellulosic composition. It is mainly composed of cellulose (45–50%) and lignin (23–30%), both with a capacity for binding metal cations due to hydroxyl, carboxylic and phenolic groups present in their structure [11]. A number of publications have reported on the use of wood sawdust to remove Cr(VI) from solution [6, 8, 10, 11]. However, in most cases the biomass has to be converted into activated carbon first via physical, chemical or the combination of both techniques that will inevitably add to the cost during large-scale production of commercial activated carbon.

This paper reports on the use of untreated rubber wood sawdust of *Hevea brasiliensis* as a potential alternative to commercial activated carbon to remove Cr(VI) from aqueous solutions. The effect of Cr(VI) concentrations, adsorbent dosage, pH, temperature, adsorbent pretreatment and eluting agent are discussed.

2. Experimental

2.1. Adsorbent

Rubber wood sawdust (RWS) used in this study was collected from the compound of a wood-finishing factory in Skudai, Malaysia. Sawdust collected originated from the rubber wood treated with the chromated copper arsenate (CCA). The specific surface area was determined using a surface area analyzer, ASAP 2010 (Micromeritics, USA). The RWS sample was degassed at a temperature of 473 K for 90 min to remove any contaminants that may be present on the surface. N_2 gas adsorption was performed at 77 K. The values for specific surface areas obtained by BET, Langmuir and single point (at $P/Po = 0.2002$) methods were 3.0025, 5.8345 and 1.9806 m^2/g respectively while the average pore diameter was 694.03 nm. Sugar-rich dried pineapple skin (PA) was obtained from the waste treatment section of one local pineapple processing premise, i.e. Lee Pineapple Sdn. Bhd. (Tampoi, Johor, Malaysia) while samples of the pulp-based egg carton (PEC) were collected from a local sundry facility. In this study, the RWS was used without any other physical or chemical treatment.

2.2. Preparation of stock Cr(VI) solution

Stock Cr(VI) solution (5000 mg/L) was prepared by dissolving 2.829 g $K_2Cr_2O_7$ (294.18 $gmol^{-1}$, Fluka) in 200 mL of deionised water (UHQII, Elgastat).

2.3. Batch adsorption studies

2.3.1. Effect of initial Cr(VI) concentration and contact time

A series of Cr(VI) solution (100, 200, 300, 400 and 500 mg/ L) were prepared by adding 4.0–20.0 mL of 5000 mg/L stock Cr(VI) solution into 200 mL volumetric flasks. The Cr(VI) solutions were then transferred into 2 L Erlenmeyer flasks and the pH was adjusted to 2.0 using 1 M HCl. RWS, 3% (w/v) was then added to the flasks to initiate the reaction. The mixtures were shaken for 7 days at 200 rpm in room temperature (25 °C). Cr(VI) adsorption was evaluated by taking the difference between initial and final Cr(VI) concentrations in solution at different time intervals. Throughout the study, Cr(VI) was determined using the diphenylcarbazide (DPC) method as follows [12]; in a 10 mL volumetric flask, 1 mL of sample was mixed with 9 mL of 0.2 M H_2SO_4. Then 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added to the volumetric flask. The mixture was then vortexed (Maxi Mix-II Thermolyne) for about 15–30 s and let to stand between 10 and 15 min for full colour development. The red-violet to purple colour formed was then measured at OD_{540} using distilled water as reference. The instrument used was calibrated using 0.4–2.0 mg/L Cr(VI) prepared from Cr(VI) stock solution (1000 mg/ L). To monitor the speciation of Cr during the adsorption process, the experimental set-up as above was used but using a Cr(VI) concentration of 120 mg/L. Determination of Cr was made using an atomic absorption spectrometer, AAS (Perkin Elmer AAnalyst 400), whereas Cr(VI) was determined using the DPC method.

To assess the possibility of recovering adsorped Cr from the adsorbent (RWS), the adsorbent was first recovered from adsorbate solutions with different initial concentrations of Cr(VI) via filtration (Whatman No. 1). Then, 80 mL of 1 M HCl were added to each flask and shaken at 160 rpm for 24 h at room temperature. Concentration of Cr eluted in different time intervals was determined using AAS.

2.3.2. Effect of pH

Stock Cr(VI) solution (6 mL) was added to a series of 200 mL volumetric flasks containing deionized water to prepare a 150 mg/L Cr(VI) solution. The solutions were transferred into 2 L Erlenmeyer flasks and the pH was adjusted to

1.0–9.0 using 1 M HCl or 1 M NaOH. RWS 3% (w/v) was added to the flasks before shaking for 24 h, 150 rpm at room temperature. Cr(VI) was then determined using the DPC method. The point of zero charge (PZC) of RWS was determined using the batch equilibrium method [13]. The samples of RWS (0.5 g) were shaken in 250 mL Erlenmeyer flasks containing 100 mL of 0.1 M KNO_3 at pH values ranging from 2.0–11.0. Initial pH values were adjusted using either 0.1 M KOH or 0.1 M HNO_3 solutions in order to keep the ionic strength constant. The amount of H^+ or OH^- ions adsorbed by RWS was calculated from the difference between the initial and final concentrations of H^+ or OH^- ions. Possible involvement of functional groups from RWS during Cr(VI) reduction was elucidated using the Fourier transform infra-red (FTIR) analysis. The RWS sample (10 mg) was ground with 200 mg of KBr (spectroscopic grade) in a mortar before pressed into 10mm diameter disks under 6 tons of pressure. FTIR spectra were obtained on a Jasco FTIR-3500 spectrometer. The analysis conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400–4000 cm^{-1}.

2.3.3. Effect of temperature

Adsorption studies were carried out at different temperatures, i.e. 298.15, 303.15, 310.15, 318.15 K (Certomat-H, B. Braun) to obtain the equilibrium isotherms. Cr(VI) solutions (50, 100, 150 and 200 mg/L) were prepared from stock Cr(VI) solutions (2.0–8.0 mL) in 200 mL volumetric flasks. The pH was adjusted to 2.0 using 1 M HCl before transferred into 2 L Erlenmeyer flasks. RWS 3% (w/v) was then added to the flasks prior to shaking at 150 rpm for 3 h at the respective temperatures. Cr(VI) was determined using the DPC method and was evaluated using the Langmuir adsorption isotherm as shown in Eq. (1) [14].

$$q_e = Q_o bc / 1 + bc \qquad (1)$$

where q_e is the Cr(VI) adsorped at equilibrium condition (mg/g cell dry wt.), Q_o is the maximum Cr(VI) adsorped (theoretical), b is the constant for adsorption energy coefficient and c is the Cr(VI) concentration at equilibrium.

2.3.4. Adsorbent dosage

Cr(VI) solution (150 mg/ L) was prepared by adding 6 mL of stock Cr(VI) solutions into deionised water in 200 mL volumetric flasks. The pH was adjusted to 2.0 using 1 M HCl before being transferred into 2 L Erlenmeyer flasks. The concentration of adsorbent (RWS) was varied between 1.0–7.0% (w/v). The mixture was shaken for 24 h at 150 rpm in room temperature before determination for Cr(VI) adsorption using the DPC method. The efficiency of RWS to remove Cr(VI) from solution was compared with other potential Cr(VI) adsorbents i.e. the sugar-rich dried PA and the PEC.

Cr(VI) solutions (10 mg/L) were prepared by adding 0.5 mL of stock Cr(VI) solution into deionised water in 50 mL volumetric flasks. The pH was adjusted to 2.0 using 1 M HCl before transfer into 500 mL Erlenmeyer flasks. Then, 4.0% (w/v) adsorbent (RWS, PA, PEC) was added to the respective flasks and shaken for 2.5 h and 150 rpm at room temperature. Cr(VI) adsorption was determined using DPC.

3. Results and discussion

3.1. Effect of initial Cr(VI) concentration and contact time

The amount of Cr(VI) adsorbed at different times for different initial Cr(VI) concentrations onto RWS is shown in Fig. 1. The adsorption of Cr(VI) was rapid in the early stage but decreased gradually with time. After 3 h of contact time, around 69% of Cr(VI) was removed from initial Cr(VI) of 100 mg/L followed by 200 mg/L (42%), 300 mg/L (34%), 400 mg/L (22%) and

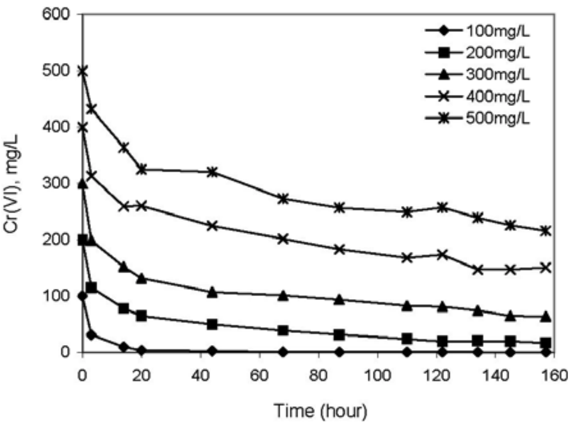

Fig. 1. Effect of initial Cr(VI) concentration and contact time on Cr(VI) adsorption by 3% (w/v) RWS at pH 2.0.

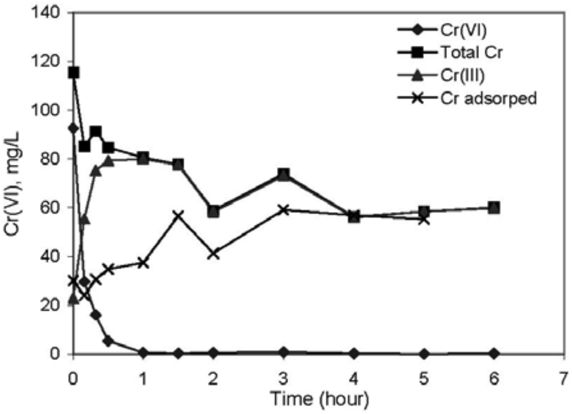

Fig. 2. Cr species present in solution during the removal of 120 mg/L Cr(VI) by 3 % (w / v) RWS.

500 mg/L (14%). The use of pH 2.0 during the experiment ensures all Cr(VI) species in solution were in the highly soluble, negatively charged, dichromate ($Cr_2O_7^{2-}$) form with a Keq of 1.2–4.2×10^{14} [15]. Cr(VI) removal was dependent on the initial Cr(VI) concentration where the amount adsorbed decreased with increasing initial Cr(VI) concentration. Complete Cr(VI) removal was only achieved for initial Cr(VI) of 100 mg/L after 68 h of contact time. Incomplete Cr(VI) removal was observed for the other Cr(VI) concentration even after 168 h of contact time i.e. 92% for 200 mg/L, 79% (300 mg/L), 62% (400 mg/L) and 57% (500 mg/L). One possible explanation can be derived from the negligible volume of micropores available (based on average pore diamater of 694 nm) and low surface area of the RWS as described earlier. At low initial Cr(VI) concentrations, the ratio for surface area of RWS to the initial Cr(VI) concentration is large, therefore increasing the possibility of interactions between positively-charged groups on RWS with Cr(VI). However, the ratio is lower when initial Cr(VI) concentrations increases, hence increasing the competition amongst Cr(VI) species for positively charged groups on surface area of RWS. This results in reduced Cr(VI) removal by RWS.

Smooth and continuous plots obtained also suggested the possible monolayer adsorption of Cr(VI) on the surface of RWS as suggested by Karthikeyan et al [10]. It was also noted from Fig. 1 that the rate of percent chromium removal is higher at the beginning. This is largely due to the larger surface area of the RWS being available at beginning for the adsorption of metals. With time, the surface adsorption sites become exhausted where at this point, the uptake rate can be regarded to be controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [16]. The equilibrium between Cr species in solution during the Cr removal process was also monitored and the result obtained is shown in Fig. 2.

A good equilibrium was obtained for Cr(VI) and Cr (III) species in solution throughout the Cr(VI) removal process by 3% (w/v) RWS. Complete Cr(VI) removal was achieved after 1 h of contact time. At this point, Cr (III) and total Cr concentrations reaches maximum indicating total conversion of Cr(VI) to Cr (III) by RWS. A point to note is that an unexpected reduction of total Cr concentration was observed at the end of the contact time. Total Cr concentration was observed to decrease by 46.61% from 118 mg/L initially to 63 mg/L. This can be attributed to the spontaneous adsorption of Cr(VI) species or the complexation of Cr (III) ions by the positively charged groups on the RWS surface. It is imperative to analyze for total Cr concentration, i.e. the sum of Cr(VI) and Cr (III), to justify simple mass balance for Cr species present in the system. Cr (III) concentration is calculated from the difference between total Cr and Cr(VI) concentrations. For example, if 90% of 100 mg/L Cr(VI) was reduced, it is expected that 10 mg/L Cr(VI) can be detected using the DPC method while 100 mg/L of total Cr can be determined via AAS analysis. Provided that less than 100 mg/L total Cr analyzed, this difference should be attributed to Cr uptake by the RWS via adsorption or complexation. This situation is clearly shown in this work (Fig. 2) from the difference between initial and final total Cr concentrations as stated earlier.

Cr(VI) can be removed from the aqueous solution by nonliving biomass via two mechanisms [17]. The first mechanism involves direct reduction of Cr(VI) to Cr (III) in the aqueous phase by contact with the electron-donor groups on the biomass having lower reduction potential values than +1.3 V, i.e. that of Cr(VI) [15]. It was established that when Cr(VI) comes into contact with organic substances or reducing agents in an acidic medium, the Cr(VI) is easily or spontaneously reduced to the Cr (III) [18–20].

The second mechanism consists of three steps starting with the binding of anionic Cr(VI) ion species to the positively charged groups present on the biomass surface. Then Cr(VI) reduction to Cr (III) takes place by the adjacent electron-donor groups. Finally, Cr (III) ions will be released into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr (III) ions, or the complexation of the Cr (III) with adjacent groups capable of Cr-binding such as oxygen. Oxygen is an important heteroatom for Cr(VI) adsorption which commonly occurs in the form of carboxylic acid, phenolic hydroxyl and quinone carbonyl groups [21]. If there are a small number of electron-donor groups in the biomass or protons in the aqueous phase, the chromium bound on the biomass can remain in the hexavalent state [22]. At any given time, these two mechanisms would occur concurrently depending on the parameters involved such as pH, temperature, biomass concentration, functional groups present on the biomass and Cr(VI) concentration [17]. Hence, it is rather inappropriate to address the mechanism occurring during the contact between Cr(VI) and RWS simply as “adsorption” or “reduction” because both reactions occur at the same time. Therefore, the term “removal” or “removed” will be used hereafter with reference to Cr(VI) adsorption by RWS. The recovery of chromium from RWS was carried out using 1 M HCl and result obtained is shown in Fig. 3.

Complete Cr recovery was achieved for RWS removing initial Cr of 500 mg/L after 17 h of contact time followed by 24 h for initial Cr of 400 mg/L and 42 h for 200 and 300 mg/L. It should be mentioned that all of Cr desorbed from RWS was in the Cr (III) form. Other mineral acids such as 0.2 M H_2SO_4 can be used to recover Cr from adsorbent [23].

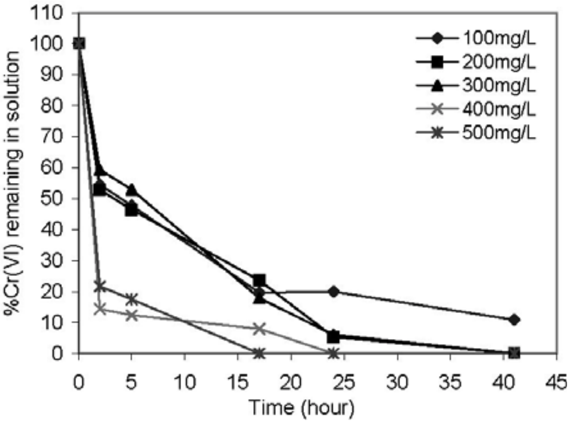

Fig. 3. Percentage of Cr recovery from RWS at different time using 1 M HCl; Legend: — initial Cr(VI) concentration.

3.2. Effect of pH

The profile for the removal of 150 mg/L Cr(VI) by RWS at different initial Cr(VI) pH is shown in Fig. 4. Complete removal of Cr(VI) was achieved at pH less than 2.0. This can be explained as follows; at initial pH of less than 2.0, the surface of RWS is highly protonated which allows the electrostatic interaction with the predominant anionic form of Cr(VI), i.e. $HCrO_4^-$ [24]. In the acidic range, $HCrO_4^-$ ions have a greater affinity towards the hydrogen ions present on the surface of the RWS [25]. Furthermore, there is the presence of a large number of H^+ ions, which in turn neutralize the negatively charged functional groups on the RWS adsorbent surface thereby reducing hindrance to the diffusion of dichromate ions. However, the percentage of Cr(VI) removal by RWS decreased gradually as the pH increases. At pH more than 7.0, i.e. 8.0 and 9.0, the percentage of Cr(VI) removal was 21.23% and 27.41% respectively. With the increase in pH from 3.0 to 9.0, the degree of protonation on RWS surfaces reduced gradually and hence removal was decreased. As the pH increases, concentration of OH^- ions on RWS surfaces and in the solution increases, hence increasing the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of RWS. The above finding can also be supported from the pH_{PZC} value of 4.90 for RWS (Fig. 5).

It is shown that Cr(VI) removal decreases with increasing initial pH and can be explained as follows; as the initial pH increases, more of the H^+ available from the protonated (due to pH 2.0 used) surface of RWS will be deprotonated, hence reducing the capacity of RWS to adsorped the negatively charged Cr(VI) ions (Fig. 4). A PZC value of 4.90 was reached at initial pH of 7.0. This justifies complete Cr(VI) removal at pH less than 2.0 where during this condition, the surface of RWS should be completely protonated, hence suitable to adsorp the anionic Cr(VI) species. KNO_3 was used as the aqueous solution because it has been reported to be independent of ionic strength [13].

The pH of the system determines the adsorption capacity due to its influence on the surface properties of the RWS and different ionic forms of the chromium solutions. At pH 1.0, the chromium ions exist in the form of H_2CrO_4, while in the pH range of 1.0–6.0 different forms of chromium ions such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$

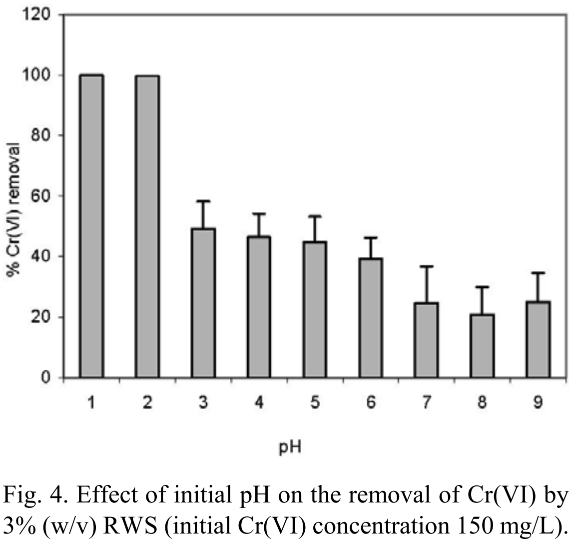

Fig. 4. Effect of initial pH on the removal of Cr(VI) by 3% (w/v) RWS (initial Cr(VI) concentration 150 mg/L).

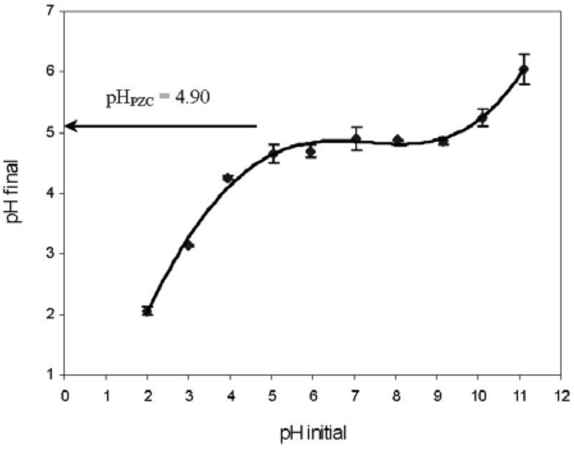

Fig. 5. Determination of pH_{PZC} (pH final where common plateau is obtained) of RWS in 0.1 M KNO_3 solution (indicated by arrow).

Table 1
Comparison between initial and final pH of 150 mg/L Cr(VI) solution (initial concentration 150 mg/L) after contact with 3% (w/v) RWS for 24 h

Initial pH	Final pH
1.00	1.22
2.00	3.67
3.00	6.30
4.00	6.37
5.00	6.40
6.00	6.61
7.00	7.01
8.00	6.96
9.00	7.17

coexist of which $HCrO_4^-$ predominates [15]. As pH increases this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$ [17,25]. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [26]. The effect of pH on adsorption is also governed by the development of an electrical double layer on the adsorbent. The double layer at the surfaces causes the change in polarity from positive to negative as the H^+ changes from acidic to basic region. This accounts for the downfall in the sorption of chromium as chromate at increased pH [27]. Table 1 shows the comparison between the initial and final pH of 150 mg/L Cr(VI) after contacted with 3% (w/v) RWS for 24 h.

The pH increase was insignificant at pH less than 2. This was due to the hydrolysis of the RWS in water, which will create positively charged sites. Upon adsorption of $HCrO_4^-$, a net production of hydroxide ions will occur as shown in Eq. (2) [28]:

$$OH_2^+ + HCrO_4^- \leftrightarrow OH_2^+(HCrO_4^-) \quad (2)$$

In addition, increased in pH was also observed that can be attributed to the presence of oxo groups such as C_xO and C_xO_2 on the surface of the RWS [28]. These groups hydrolyze water molecules, thus provoking the release of OH^- ions into the solution and the formation of positively charged groups on the surface of adsorbent [29]. The FTIR spectra of RWS (before and after) contacted with 150 mg/L Cr(VI) is shown in Fig. 6.

Possible involvement of two or more functional groups from RWS during Cr(VI) binding is shown in Fig. 6c. This is evident from bands appearing at 3421 cm^{-1} (N-H amine and amide stretching), 2854 and 2925 cm^{-1} (C-H stretching and O-H from carboxylic acid), 1637 cm^{-1} (N-H bending, C=O amide), 1376 cm^{-1} and 1459 cm^{-1} (CH_3 bending), 1262 cm^{-1} and 1054 cm^{-1} (sulfonyl chloride, C-N from amine, C-O from carboxylic acid, S=O sulfoxide). Hence, suggesting the important role of amino (NH_2), carboxyl (C=O) and hydroxyl (O-H) groups during Cr(VI) reduction. The fact that more compounds were detected after RWS was contacted with Cr(VI) (Fig. 6c) as opposed to before (Fig. 6b) was due to protonation of groups such as COO^- to COOH and NH_2 to NH_3^+ that can interact with the negatively charged Cr(VI) ions. The sharp peak observed at 2924 cm^{-1} for RWS (Fig. 6b and 6c) can be attributed to the background correction effect as evident from the KBr spectra shown in Fig. 6a.

3.3. Effect of adsorbent dosage

Complete removal of Cr(VI) was achieved at RWS concentration greater than 1.5% (w/v). The percentage removal increased with the increase in adsorbent dose (Fig. 7). The percent removal increased from 10.14% for adsorbent dose of 0.2% (w/v) to 100% at 1.5% (w/v) adsorbent. Increase in Cr(VI) removal with adsorbent dose can be attributed to increased surface area and the availability of more adsorption sites [26, 30]. The efficiency of RWS to remove Cr(VI) from solution was compared with two other potential adsorbents namely the PEC and the PA (Fig. 8).

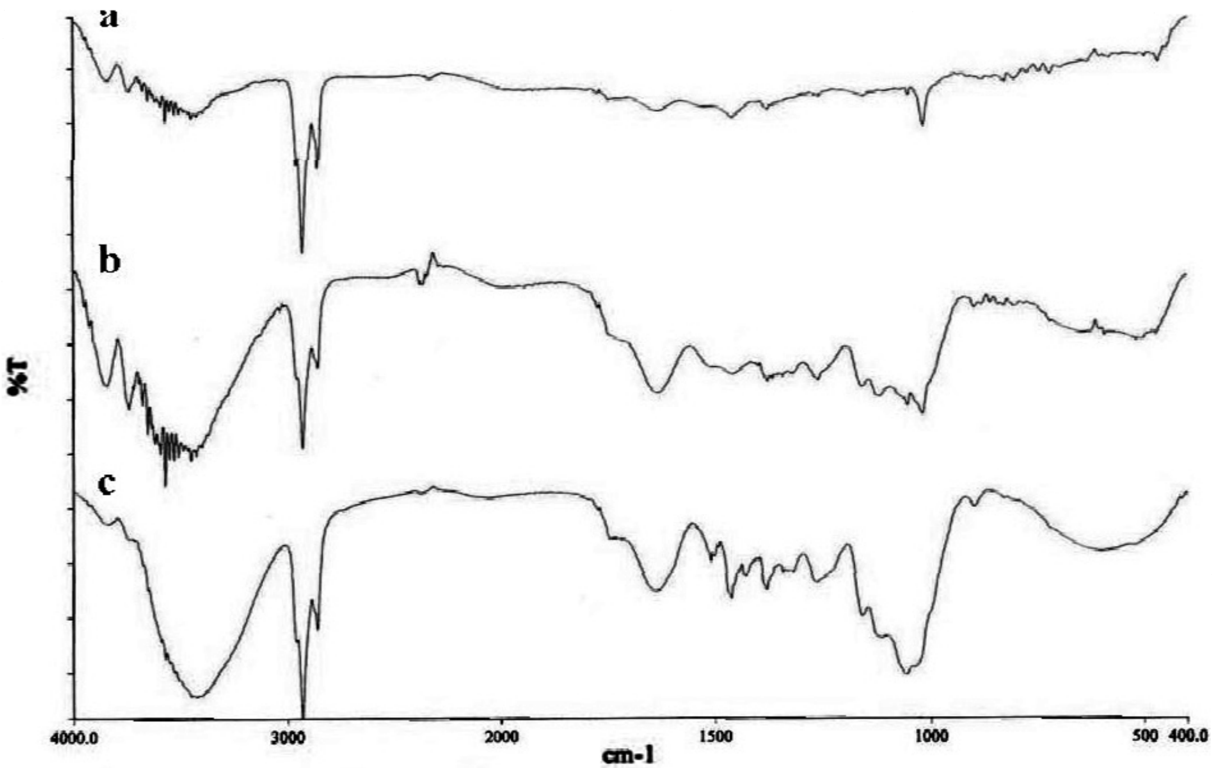

Fig. 6. FTIR of (a) KBr only, (b) RWS, and (c) RWS after contact with 150 mg/L Cr(VI).

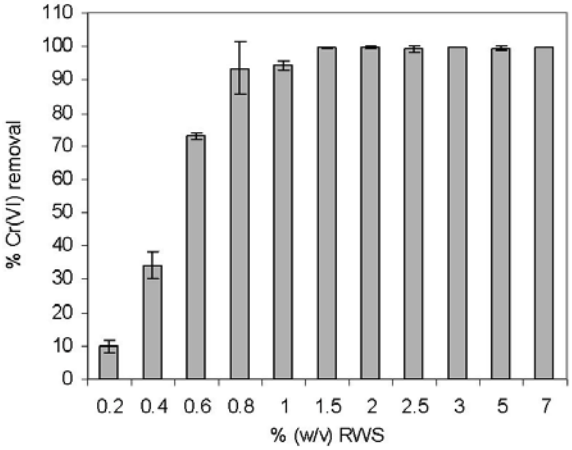

Fig. 7. Removal of Cr(VI) by different concentration of RWS (initial Cr(VI) concentration 150 mg/L).

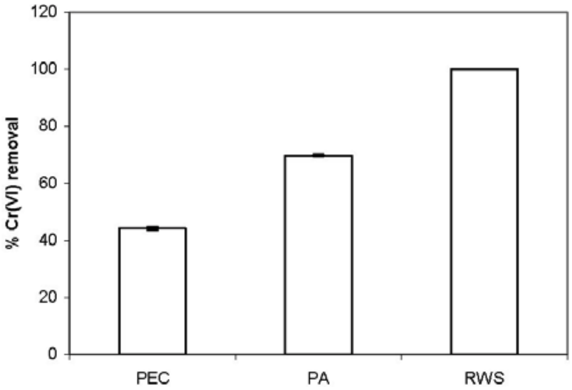

Fig. 8. Percentage of Cr(VI) removal by different adsorbents. PEC, pulp-based egg carton; PA, dried pineapple skin; RWS, rubber wood sawdust.

It is evident from Fig. 8 that the efficiency of RWS to remove Cr(VI) was the highest among the other adsorbents used. The variation in the sorption capacity between the various adsorbents could be related to the type and concentration of surface groups responsible for interaction with

Table 2
Cr(VI) removal capacity of different sources of sawdust

Source of sawdust	Treatment	pH	Initial Cr(VI), mg/L	Cr removed, mg/g	Ref.
Teak (*Teclona grandis Linn. f*)	None	5.72	184.90	0.89	[31]
Sal tree (*S. robusta*)	Physicochemical	3.5	40	9.55	[32]
Rubber wood	Chemical	3.0	40	158.7	[22]
Maple	None	6.0	10	5.1	[33]
Rubber wood (*Hevea brasiliensis*)	None	2.0	150	4.87	This study

the metal ions [28]. The selected adsorbents are cellulose-based plant fibers, with many hydroxyl groups that may bind the Cr(VI) ion. However, the presence of a particular functional group or binding site does not necessarily guarantee its accessibility as a sorption site, due to the possible coexistence of steric, conformational, or other types of barriers [28]. The utilization of sawdust for the treatment of Cr(VI) from aqueous solution is gaining importance as a useful, simple yet effective alternative method for commercial activated carbon. Various sources of sawdust have been used with varying Cr(VI) removal capacity (Table 2).

3.4. Effect of temperature

The removal of Cr(VI) by RWS increased with increasing temperatures (Fig. 9). When the temperature was increased from 298.15 to 318.15 K, the removal capacity increased from 0.92 to 4.87 mg/g for initial Cr(VI) of 150 mg/L. Similar trends were observed for 50, 100 and 200 mg/L Cr(VI). This is indicative of an endothermic Cr(VI) removal process by the RWS [11]. The enhancement in the adsorption capacity was due to the chemical interaction between adsorbate and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the adsorbent at higher temperatures [11,25]. A contact time of 3 h between RWS and Cr(VI) solution was sufficient to reach equilibrium based on result shown in Fig. 2 where complete removal of 120 mg/L Cr(VI) by RWS was achieved within 1 h of contact time. The standard Gibb's free energy (ΔG^0) and the equilibrium constants, K_c was evaluated via Eqs. (3) and (4) [11,23]:

$$\Delta G^0 = -RT \ln K_c \tag{3}$$

$$K_c = CA_e / C_e \tag{4}$$

where CA_e is the concentration of Cr(VI) adsorbed on RWS at equilibrium (mg/ L), C_e is the Cr(VI) concentration in solution at equilibrium (mg/ L), R is the ideal gas constant (J mol^{-1} K^{-1}) and T is the temperature (K). The enthalpy change ΔH^0 (kJ/mol) and the entropy change ΔS^0 (J mol^{-1} K^{-1}) were obtained from the Eq. (5):

$$\ln K_c = (\Delta S^0 / R) - (\Delta H^0 / RT) \tag{5}$$

ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the Van't Hoff's plot of $\ln K_c$ versus $1/T$ as shown in Fig. 10. The negative values of ΔG^0 suggest the feasibility of the process. It was observed that the values become more negative with increase in temperature.

A positive value of ΔH^0 indicates that the Cr(VI) removal process is endothermic where higher temperature makes the adsorption easier. It also reflects the binding energies of the solvated ion in the carbon channels. The endothermic process shows that diffusion from bulk solution to adsorbent interface may require

Table 3
Thermodynamic parameters of RWS at initial Cr(VI) 50 mg/L

T (K)	ΔG^0 (kJ / mol)	ΔH^0 (kJ / mol)	ΔS^0 (J/mol K)
298.15	− 8.414	4.534	43.39
303.15	− 8.774		
310.15	−10.522		
318.15	−11.225		

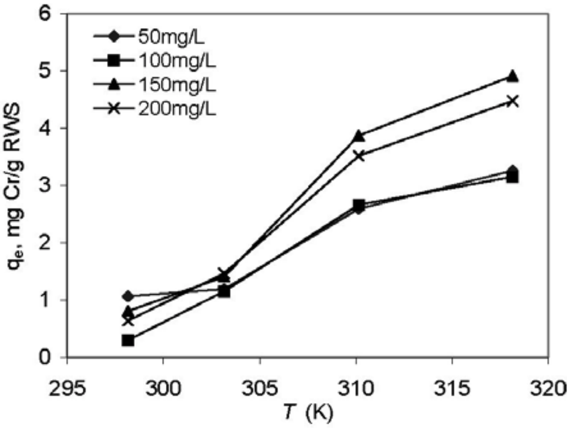

Fig. 9. Cr(VI) removal by 3% (w/v) RWS at different temperatures after 3 h of contact time. Legend, — initial Cr(VI) concentration.

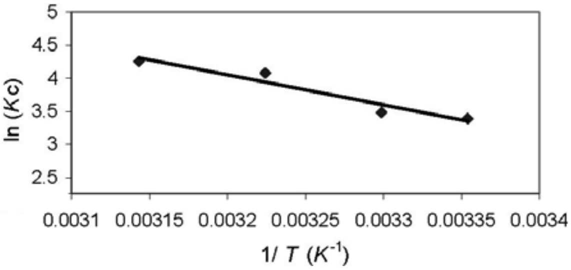

Fig. 10. Van't Hoff's plot for the removal of 50 mg/L Cr(VI) by 3% (w/v) RWS between 298–318 K.

energy to overcome interaction of dissolved ions with solvation molecules [34]. ΔS^0 indicates the disorderliness of the adsorption at a solid–liquid interface. A positive ΔS^0 value as obtained in this study (43.39 J/mol K) can be attributed to the redistribution of energy between the Cr(VI) as adsorbate and RWS as adsorbent. Adsorption is thus likely to occur spontaneously at normal and high temperatures because ΔH^0 and ΔS^0 are both greater than 0 [25]. The thermodynamic parameters of the Cr(VI) removal by RWS are shown in Table 3.

4. Conclusions

This study shows that untreated RWS can completely remove Cr(VI) from solution at the following conditions: pH less than 2.0, initial Cr(VI) of 100 mg/L and RWS dosage of greater than 1.5% (w/v). Decreased Cr(VI) removal was observed when the pH increases as RWS has a $\mathrm{pH_{PZC}}$ of 4.90. Shorter time was needed when 1 M HCl was used to recover Cr from RWS while FTIR analysis suggests the importance of functional groups such as amino, hydroxyl and carboxyl during Cr(VI) removal. Finally, this study has demonstrated the potential of untreated rubber wood sawdust as adsorbent to remove Cr(VI) from wastewater.

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