CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš
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ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870192

Sawdust Bio sorption of Chromium (VI) Ions from Aqueous Solutions

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In the present study, the Cr (VI) ion removal from synthetic wastewater utilizing sawdust as a rather inexpensive adsorbent studied by the batch adsorption technique. The sawdust physiochemical characterizations done through employing FTIR and BET analyses. Experiments performed at temperature range of 25-65 ºC with 0.5-5 g/L of sawdust dosage. Moreover, these conditions applied to separate Cr (VI) ion concentrations of 1-6 ppm in the pH range of 3-10. The adsorption parameters determined using both an A-Priori Langmuir and a heterogeneous surface displayed by the Freundlich isotherm models. Thermodynamic standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) calculated for predicting the nature of adsorption. Experimental results revealed the maximum adsorption yield achieved at pH of about 3. Furthermore, the temperature and adsorbent dosage led to positive effects upon adsorption yield as well. On the other hand, the adsorption efficiency increased through enhancing the Cr (VI) ion initial concentration up to 4 ppm. Nonetheless, further increase of this concentration lowered the mentioned separation efficiency.

1. Introduction

The importance of water quality preservation and improvement considered necessary and continuously increasing in life. In view of these facts, all water regulatory authorities and agencies acted very conscious on the pollution of water resources. Amongst these pollutants, heavy metal ions known as very dangerous due to their toxic and carcinogenic nature. Moreover, some metal ions considered not biodegradable or bio-transformable hence; existed in environment for a long time. In view of this point, attempts made to review the removal of these toxic metal ions from wastewater. A number of industries such as metal planting facilities, mining operations and tanneries often discharges heavy metals as waste. These led to contamination of fresh water resources and marine environment. One of these heavy metals known as Chromium. This species in its hexavalent form, considered as one of the undesirable heavy metals because it affected human physiology, accumulated in the food chain and caused several ailments (Verma et al., 2006). Generally, techniques employed for heavy metal removal included adsorption, screening, centrifugation and filtration (e.g.; micro- and ultra-filtration) to name a few. Adsorption technique for the treatment of water known as the best method due to its wide range of applications as well as; efficient and ease of operations. On the other hand, the use of activated carbon and ion exchange resins might not be suitable for developing countries due to their high capital and operational costs. This encouraged researchers towards developing materials being both efficient and economically wise. (Md.Juned and Ahmaruzzaman, 2016).In general, an adsorbent assumed as ‘low cost’ if it required small extent of processing, being abundant in nature or a by-product or waste material from industry. The lingo-cellulosic waste materials accomplished these criteria. They possessed reasonable adsorption capacities, were locally available while inexpensive. Several natural adsorbents investigated for their ability to sequester metal ions from water. These included; wheat straw (Chun et al., 2004), rice bran (Oliveira et al., 2005), cotton ball (Ozsoy and Kumbar, 2006), red pine sawdust (Gode et al., 2008) and green algae (Jalali-Rad et al., 2004). Moreover, eucalyptus bark (Sarin and Pant, 2006), activated carbon (Radjenovic and Medonic, 2015), Holga leaves (Moniruzzaman et al., 2017), Coffee grounds (Patterer et al., 2017), reed biochar (Yang and Chen, 2017) pine needles, olive cake, wool, almond and soya cake (Dakiky et al., 2002) also understudied for this purpose. However, limited information existed upon the removal efficiency of anions. New economical,

Please cite this article as: Sirusbakht S., Vafajoo L., Soltani S., Habibi S., 2018, Sawdust bio sorption of chromium (vi) ions from aqueous solutions , Chemical Engineering Transactions, 70, 1147-1152 DOI:10.3303/CET1870192

easily, available and highly effective adsorbents still needed. There existed methods available for contacting sorbent materials with solutions containing metal ions. Batch contacting process for example employed to investigate the performance of the raw sawdust in removing Cr (VI) from aqueous solution. Lignocelluloses resources and the cell walls of sawdust mainly consisted of polyphenolic compounds, hydroxyl groups such as tannin and lignin acting as active sites for attachment of heavy metal cations (Srivastava et al., 1994). Sawdust considered a waste by-product of the timber industry used either as a fuel for cooking or as a packing material. Moreover, sawdust known as a solid waste produced in large quantities at sawmills. If this material utilized as an absorbent, related contaminated streams cleaned-up and a new market opened-up to it (Mohanty et al., 2005). In this direction, possible involved mechanisms included; ion exchange, physical sorption, chemisorption, chemical reaction and/or lone pair electron sharing (Harmita et al., 2009). This research aimed at gaining a fundamental understanding of the chemical and physical phenomena associated with the binding of Cr (VI) to untreated the sawdust obtained as a by-product from a local carpentry shop.

2. Materials and methods

2.1 Sawdust treatment

The Pinewood sawdust obtained commercially treated to prepare an adsorbent. One washed it with distilled water to remove surface impurities and dried under sunlight for 24 h. sawdust activated at 80 °C in a hot air oven for 6 h. Then the resulting material ground followed by sieving in a size range of 80–100 mesh, and kept in the desiccator to prevent moisture absorption. The sawdust physiochemical characterizations done through employing FTIR (Fourier transform infrared spectroscopy) and BET (Brunauer-Emmett- Teller) analyses. The moisture content determined using 'oven drying method'. A clean empty porcelain capsule over dried at 105 ºC, and then quenched in a desiccator. 2 g of sawdust weighted then dried at 100 ºC to a constant weight for 3 h. the percentage moisture content calculated using equation 1 below. The value of moisture content percentage tabulated in table 1.

$$\%\ \mathrm{moisture} = \frac{\mathrm{weight\ loss}}{\mathrm{sample\ weight}} \times 100 \tag{1}$$

2.2 Preparation of Cr (VI) solution

An accurately weighed quantity of the $K_2Cr_2O_7$ (purchased from the Merck Company) dissolved in double-distilled water to prepare a stock solution (1000 mg/L). All chemicals used were of analytical reagent grade.

2.3 Adsorption experiments

Batch process employed for adsorption studies. Pre weighted sample of the adsorbent and a measured volume of Cr (VI) solution placed in a 250 mL Pyrex glass vessel with a cover. The mixture agitated at 150 rpm for 120 min to ensure equilibrium attained. Then it filtered through Whatman 45 filter paper and analyzed for metal ion content using an atomic adsorption spectrophotometer (Shimadzu AA6300) operating with an air-acetylene flame. Four standard solution with concentration of heavy metal ions in the linear range of the instrument used to construct each calibration curve. All measurement repeated in triplicates and those results in which the standard deviation found greater than 0.1 mg/L rejected. The equilibrium condition reached after nearly 60 min. The adsorption capacity (q_e) of the adsorbent determined through a mass balance upon the sorbate in a system with solution volume V often used to acquire the experimental adsorption isotherms. The adsorption capacity of the sawdust calculated using the following equation:

$$\mathrm{q_e}\ (\mathrm{mg.g^{-1}}) = \left(\frac{\mathrm{C_i} - \mathrm{C_e}}{\mathrm{M}}\right) \times \mathrm{V} \tag{2}$$

Where C_i and C_e stood for the initial and final concentration of chromium in the solution (mg/L), respectively. V was the volume of solution (L) and M referred the mass of adsorbent (g) used.

Next, one studied the effect of pH, adsorbent dosage, temperature and initial concentration upon sorption extent (Sirusbakht, 2018). The latter quantity changed in the range of 1-1.5 g while the initial chromium concentration adjusted in the range of 1-6 ppm. Moreover, the temperature of the Cr(VI) solution varied in the range of 25-65 ± 2 ºC and the pH on the chromium solution adjusted to values of 3 to 10 by addition of HCl (0.1 M) or NaOH (0.1 M) prior to experiment. To obtain the optimal values of these parameters, several experiments performed. D-Optimal design in RSM (Response Surface Methodology) by Design Expert Version 11- 0-0 (State Ease, USA) used to optimize the understudied adsorption process. Nonetheless, due to the page wise limitations imposed upon this paper, only the ultimate results presented.

3. Results and discussion

3.1 FTIR analysis

Fourier transform infrared spectroscopy of the raw sawdust recorded using a Shimadzu 8400 Series FTIR Spectrometer employing a KBr pellet method on the wavenumber in the range of 400 - 4,000 cm^{-1}. Some chemical characteristics and the FTIR spectra of the understudied sawdust before and after adsorption presented in Figures 1a and 1b. The region corresponding to high wave numbers showed a broad band centered at 3,300 – 3,500 cm^{-1}. The broad region around 3,400 cm^{-1} assigned to the –OH stretching the surface hydroxyl groups. The band at 2,930 cm^{-1} assigned to symmetric vibration of CH$_2$ especially alkenes. The one at 1652 cm^{-1} considered an indication of –COO and C=O indicating the bending vibration of adsorbed water. The band at 1,030 - 1,083 cm^{-1} considered indicative of stretching vibration of C=O=C and OH of polysaccharide while the one at 420.45 cm^{-1} revealed characteristic band of disulfides group. The content of carboxyl groups determined by separation of the bands in the 1,500 - 1,800 cm^{-1} spectral region. The band at 1,612 cm^{-1} assigned to aromatic carbonyl and carbonyl motion in carboxyl groups. Moreover, the ones at 2,700 - 2,770 cm^{-1} assigned to aldehydes and the band at 500-600 cm^{-1} showed characteristic band of alkyl halide groups. Polymeric OH groups, CH$_2$ and COO groups as well as the OH groups of polysaccharides all revealed affinity for the Cr (VI) ion adsorption.

3.2 BET (Brunauer-Emmett-Teller) specific surface area measurement

The specific surface area of sawdust determined via the nitrogen adsorption multipoint BET method using SAP^{TM} micromeritics model. The values of surface area of sawdust presented in table1.

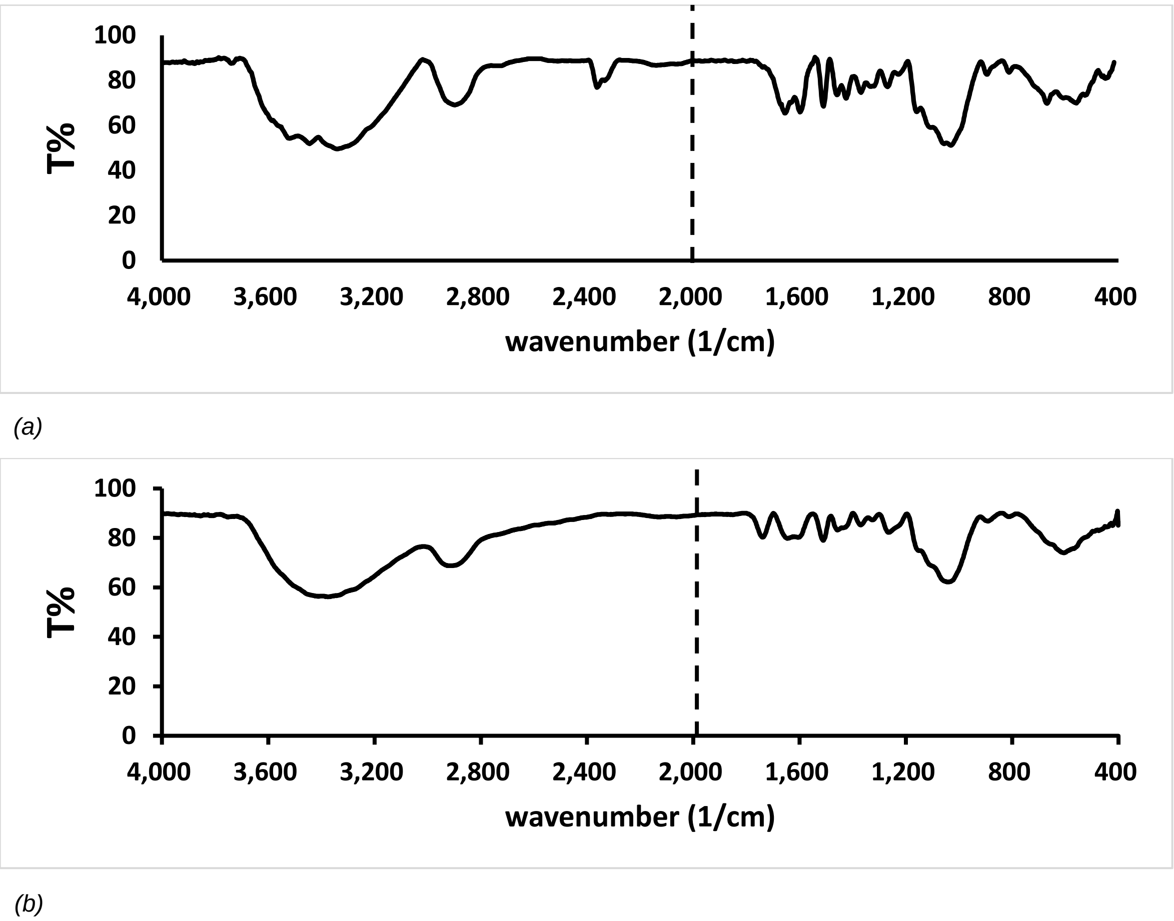

Figure1 :(FTIR) spectrum of sawdust: (a) before adsorption and (b) after adsorption

Table1. BET analysis data

Single point surface	BET Surface Area	Langmuir Surface Area	Average pore width	Average pore diameter	Moisture content (%)
0.300-0.565 m²/g	0.434 m²/g	0.880 m²/g	1.592 nm	4.726 nm	6-7

3.4 Adsorption isotherms

The adsorption parameters determined using both an A-Priori Langmuir and a heterogeneous surface displayed by the Freundrich isotherm models. The Langmuir treatment based on the assumption that a maximum adsorption corresponded to a saturated monolayer of solute molecules upon the adsorbent surface. In addition, the energy of adsorption considered constant while no transmigration of adsorbate upon the surface considered. These represented by the following equation: (El-Qada et al., 2006)

$$q_e = \frac{a.bC_e}{1+bC_e} \tag{3}$$

Where q_e stood for amount of heavy metal ions adsorbed per unit mass of adsorbent (mg.g^{-1}) “a” and “b” known as Langmuir constants indicating adsorption capacity and energy, respectively. The plot of q_e^{-1} versus C_e^{-1} at room temperature found linear, this indicated the applicability of the Langmuir model to the system understudied. The statistical significance of the correlation coefficient (R^2) for this linear plot was the criteria by which the fitting of data to Langmuir isotherm tested. The essential characteristic of the Langmuir isotherm also evaluated by dimensionless adsorption intensity R_L provided by the following relationship:

$$R_L = \frac{1}{1+bC_0} \tag{4}$$

Where C_0 (in mg.L^{-1}) was the initial concentration of Cr (VI) and b (in L.mg^{-1}) was the Langmuir constant. R_L values led to the IUPAC type of isotherms and its value fell between 0 and 1 indicating favorable adsorption. Parameters a, b and R_L calculated for this study and results tabulated in table2.

The Freundlich equation widely used for isothermal adsorption. This considered a special case for heterogeneous surface energies in which the energy term (b) in the Langmuir equation varied as a function of surface coverage (q_e) strictly due to variation in heat of adsorption. The Freundlich equation has the general form:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

Where qe stood for amounts of heavy metal ion adsorbed per unit mass of adsorbent (mg.g^{-1}) at equilibrium, C_e was the equilibrium concentration of heavy metal ion (mg.L^{-1}), K_F and n were Freundlich’s constants. These related to adsorption capacity and intensity, respectively. If the plot of log ($q_{e)}$ versus log (C_e) at room temperature become linear, the applicability of the Freundlich model to the understudied system emphasized. The intercept of the resulting line roughly considered as an indication of the adsorption capacity and the slope indicated the adsorption intensity. The resulting values provided in Table 2. One reiterated that the Langmuir isotherm corresponded to a dominant ion exchange mechanism while the Freundlich isotherm revealed adsorption-complex formation reactions taking place in an adsorption process.

Table 2: Langmuir and Freundlich isotherms data

Langmuir isotherm parameters				Freundlich isotherm parameters		
a(mg/g)	b(L/mg)	R^2	R_L	K_f	n	R^2
45.25	0.91	0.99	0.52	25.63	1.23	0.99

3.5 Thermodynamic parameters

Changes in thermodynamic parameters such as free energy (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) calculated from the variation of the thermodynamic distribution coefficient, K_C, as a function of temperature. (Gaballah and Kilbertus, 1998)

$$K_c = \frac{C_{Ae}}{C_e} \tag{6}$$

Where C_{Ae} was the equilibrium concentration (mg.L^{-1}) of the Cr (VI) ion on the sawdust and C_e was its counterpart (mg.L^{-1}) in the solution.

The linear variation of the log K_c versus T^{-1} considered well proven due to the Arrhenius theory. ΔG^0, ΔH^0 and ΔS^0 calculated from a plot of log K_c vs T^{-1} (Figure 3) and Eq(7-9). (Jain, 2001)

$$\Delta G = -RT\ln K_c \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

$$\log K_c = \frac{\Delta S}{2.303\ R} - \frac{\Delta H}{2.303\ RT} \tag{9}$$

Results shown in Table 3 revealed the endothermic nature of the sorption process. The negative values of ΔG^0 indicated the spontaneous nature of it. On the other hand, the positive value of ΔS^0 pointed out toward the increased randomness at the solid/solution interface during the adsorption process.

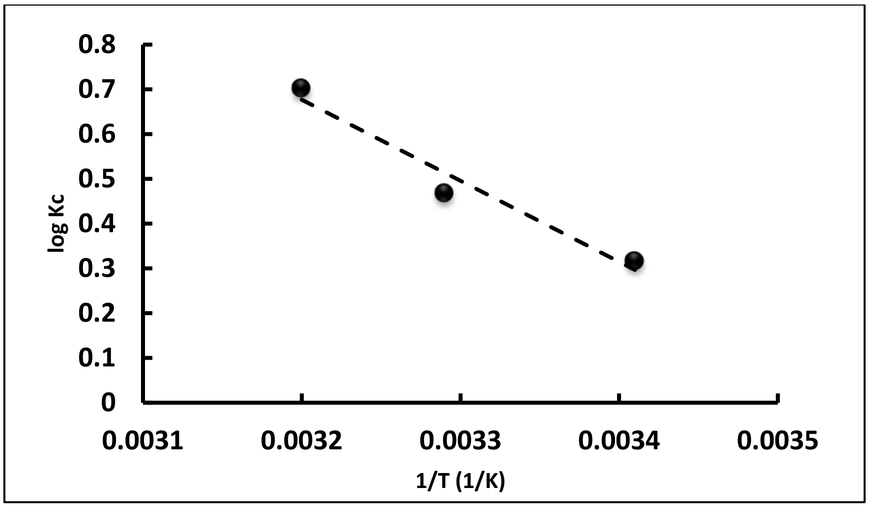

Figure3: The Vant-Hoff data

Table3: Thermodynamic parameters

T(°C)	Kc (dimensionless)	ΔG (kJ/mol)	ΔS (kJ/mol.K)	ΔH (kJ/mol)
20	2.071	-1.7743	0.1243	
30	2.094	-2.7180	0.1233	34.67
40	5.046	-4.2140	0.1241	

Conclusions

The removal of toxic hexavalent chromium ions from aqueous solution by their adsorption on a raw sawdust investigated. The adsorption was relatively rapid and equilibrium attained within 60 minutes under the investigated conditions. The equilibrium data fitted to the Langmuir and Freundlich isotherm models. The adsorption process was spontaneous and a positive value of the standard enthalpy change showed the endothermic and physical nature of the adsorption. The adsorption capacity enhanced with temperature while decreased with the pH of the system. Moreover, this variable increased upon enhancement of the adsorbent dosage. On the other hand, the adsorption capacity increased through enhancing the Cr (VI) ion initial concentration up to 4 ppm and then after lowered with increasing this initial concentration up to 6 ppm. In general The above results indicated the sawdust employed performed rather competitively and even better than other adsorbents such as more commonly used carbon based materials (e.g.; CNT's). This conclusion reached upon due to the adsorption activation energies and yields determined for this process.

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