Removal of Cr(VI) from aqueous solutions using modified red pine sawdust

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Abstract

The adsorption of Cr(VI) from aqueous solutions on sawdust (SD), base extracted sawdust (BESD) and tartaric acid modified sawdust (TASD) of Turkish red pine tree *(Pinus nigra),* a timber industry waste, was studied at varying Cr(VI) concentrations, adsorbent dose, modifier concentration and pH. Batch adsorption studies have been carried out. Sawdust was collected from waste timber industry and modified with various amount of tartaric acid (TA) (0.1–1.5 M). The batch sorption kinetics has been tested and the applicability of the Langmuir and Freundlich adsorption isotherms for the present system has been tested at $25 \pm 2\,^\circ C$. Under observed test conditions, the equilibrium adsorption data fits the linear Freundlich isotherms. An initial pH of 3.0 was most favorable for Cr(VI) removal by all adsorbents. Maximum Cr(VI) was sequestered from the solution within 120 min after the beginning for every experiment. The experimental result inferred that chelation and ion exchange is one of the major adsorption mechanisms for binding metal ions to the SD. Percentage removal of Cr(VI) was maximum at the initial pH of 3.0 (87.7, 70.6 and 55.2% by TASD, BESD, and SD, respectively). Adsorption capacities range from 8.3 to 22.6 mg/g for SD samples.
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Keywords: Tartaric acid; Pine sawdust; Adsorption; Batch mode; Cr(VI)

1. Introduction

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The problem of removing pollutants from water and wastewater has grown with rapid industrialization. The discharge of toxic metals into watercourses is a serious pollution problem, which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity. Less well-developed countries are expanding their industries, often with serious accompanying pollution. In recent years, removal of heavy metals in wastewater is normally achieved by advance technologies such as ion exchange, chemical precipitation, ultrafiltration, or electrochemical deposition which do not seem to be economically feasible for such industries because of their relatively high costs. Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economic, and can be used by such industries.

Chromium, in its hexavalent form, is one of the undesirable heavy metals because it affects human physiology accumulates in the food chain and cause several ailments. Chromium exists in different oxidation states in aqueous solutions. Although Cr(III) is an essential element for humans, water soluble Cr(VI) is highly irritating and toxic to humans and animals [1–3]. The process of adsorption implies the presence of an 'adsorbent': solid that efficiently binds molecules by means of physical attractive forces, ion exchange or chemical binding. A number of literature reports in biosorption have recently expanded sharply; the methods, metals adsorbed and biomaterials used are diverse. Such systems may be based on biomasses derived from waste products from wood industries or low-cost material harvested for the purpose of biosorption. It is recommended that the adsorbent is available in large quantities, of free or very low cost and easily regenerable.

Many methods have been used to remove the dye component, oil pollutants, and heavy metals as well from the textile effluent, namely, membrane filtration, coagulation, adsorption,

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oxidation, ion exchange, precipitation, etc. have been reported in the literature, but few of them were accepted due to cost, low efficiency, and inapplicability to a wide variety of pollutants. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water, but the high cost of activated carbon inhibits its large-scale use as adsorbent. Consumptive processes, such as chemical precipitation, entail large capital and operating costs [4–12].

The lignocellulosic waste materials are accomplished requirements for good adsorbent, they possess some adsorption capacities, and they are locally available and have a low cost. Several natural adsorbents, including algal biomass [13–16], banana pith [17], rice bran, soybean and cottonseed hulls [18], hazelnut shell [5], peat moss [19], humic acids [20], bark of trees [21–24], sugar beet pulp [25,26], leaves [27,28], leaf mould [29], moss peat [30], green algae [31], activated carbon fibers [32], coconut waste [33], wood [34], sawdust [35], straw [36] have been investigated for their ability to sequester metal ion from water. However, limited information exists on the removal efficiency of anions [37]. New economical, easily available and highly effective adsorbents are still needed.

There are methods available for contacting sorbent materials with solutions contacting metal ions. Batch contacting process has been employed to investigate the performance of the modified sawdust in removing Cr(VI) from aqueous solution. Lignocelluloses resources and the cell walls of SD mainly consist of polyphenolic compounds, hydroxyl groups such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations [6]. All those components are active ion-exchange compounds. The lignin content of woods is usually in the range of 18–35%. Tannins are complex polyhydric phenols that are soluble in water and they occur chiefly in hardwoods, and are present in many barks, including softwoods barks. Lignin molecule is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three-carbon side chain. Natural tannins are classified as either hydrolysable or condensed tannins. The hydrolysable tannins are esters of glucose with one or more polyphenolic acids, commonly gallic, digallic, or ellagic acid.

(SD) is a waste by-product of the timber industry that is either used as cooking fuel or a packing material. Sawdust is a solid waste produced in large quantities at sawmills. It contains lignin and cellulose. If sawdust could be used, as an absorbent, contaminated streams would be cleaned, and a new market would be opened for the sawdust. Various chemical treatments of sawdust might improve the heavy metal binding capacity of these materials [38–40]. The mechanism may be due to ion exchange, physical sorption, chemisorption, chemical reaction, lone pair electron sharing [1]. Bryant et al. showed adsorption of hexavalent chromium by the sawdust to take place primarily on components such as lignin or tannin rather than onto the cellulose backbone of the sawdust [35].

The Langmuir and Freundlich isotherms were both used to describe observed sorption phenomena of various metal ions on sawdust materials [8,9,34]. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. For a single solute, it is given by the Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, was also used to explain the observed phenomena of metal adsorption on sawdust materials. The sorption data of Cr(VI) have been correlated with Langmuir and Freundlich models (Eqs. (1) and (2)).

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{1}$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of adsorbed material at equilibrium (mg/g), b the "affinity" parameter or Langmuir constant (L/mg), and Q_0 is the "capacity" parameter (mg/g).

Freundlich equation:

$$q = K_f \times C_e^n \tag{2}$$

where n is Freundlich constant and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid. Taking logs and rearranging Eq. (2), Eq. (3) was obtained.

$$\log q = \log K_f + n \log C_e \tag{3}$$

The purpose of this research was aimed to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of Cr(VI) to untreated and treated sawdust obtained as by-product from locally used wood. The modification of red pine sawdust (RPS) by tartaric acid with the highest sorption capacity was subsequently investigated for its potential as a sorbent for the removal of Cr(VI) from aqueous solutions. The Cr(VI) retention study on the sawdust of pine tree pre-treated with alkaline and tartaric acid has been carried out batchwise where the influence of physico-chemical key parameters such as the solution pH, the initial concentration, and the ionic strength has been considered. A desorption study for the solid support regeneration has also been included.

2. Materials and methods

2.1. Preparation of base and tartaric acid treated sawdust

Sawdust of red pine collected from Nalti Timber Industry in the northern part of west Anatolia (Isparta-Turkey) was dried in sunlight and ground to a fine powder. SD was washed with distilled water, activated at 80 °C in a hot air oven for 24 h, and then the resulting material was ground followed by sieving in the size range of 80–100 mesh ASTM. The material was placed in an airtight container for further use.

BESD was prepared by stirring 50 g of (SD) in 1000 mL of 0.1 M NaOH at room temperature at 180 rpm. The product was filtered, washed with four-time larger volume of distilled water than volume of solution for modification was, and was dried at 50 °C, overnight. Drying at 50 °C was choosen because high drying temperature might cause a decrease of the number of cellulose based OH⁻ groups on the lower SD moisture content. Modification with tartaric acid (TA) was carried out using the method reported by Wong et al. (2003). 0.1 g (SD) and 0.7 mL of

1.2 M TA was mixed in a container. TA modified sawdust samples were dried 80 °C for 24 h then the material was heated at 90 °C for 90 min and rinsed with distilled water in a ratio of 0.1 g TASD to 5 mL distilled water. The adsorbents were further modified by changing the tartaric acid concentration (0.1–1.5 M). One g of TASD was suspended in 75 mL of 99.9% methanol and 0.6 mL of concentrated HCl then suspension was continuously agitated for 48 h. The modified sawdust was then washed to neutral pH and dried at 50 °C 40 h. Fig. 1 shows the uptake of Cr(VI) using red pine sawdust modified with various tartaric acid concentrations. The results show that 1.2 M TASD has the highest sorption capacity (22.6 mg/g TASD) for Cr(VI) among all the other concentrations. 1.2 M tartaric acid has been chosen as optimum concentration of acid for the modification.

Fourier transform infrared spectroscopy (FTIR) of the unmodified SD, BESD, and TASD were recorded using a Perkin-Elmer 1600 Series FTIR Spectrometer. A weight of sample (2 mg) was mixed with 100 mg of FTIR-grade KBr. The samples were scanned 20 times at $4 \, cm^{-1}$ resolution in the $4000–400 \, cm^{-1}$ range and then averaged. Some of chemical characteristics and the FTIR spectra of the studied SDs are given in Fig. 2. The region corresponding to high wavenumbers shows a broad band centered at $3600–3400 \, cm^{-1}$. The broad region around $3400 \, cm^{-1}$ can be assigned to –OH stretching the surface hydroxyl groups. The band at $2930 \, cm^{-1}$ is assigned to symmetric vibration of CH_2 especially alkenes, $2360 \, cm^{-1}$ is stretching vibrations of N–H or C=O groups probably due to amines and ketones, $1626 \, cm^{-1}$ is an indication of COO, C=O, and can also indicate the bending vibration of adsorbed water, $1259 \, cm^{-1}$ is assigned to carboxylic acids vibration, $1029 \, cm^{-1}$ is stretching vibration of C–O–C and O–H of polysaccharides, and $582 \, cm^{-1}$ shows the characteristic band of $–SH_2$ and $–PO_4$ functional groups. The content of carboxyl groups was determined by separation of the bands in the $1800–1500^{-1} \, cm$ spectral region. The band at around $1420 \, cm^{-1}$ is assigned to symmetric COO–

stretching motions and to the bending vibrations of aliphatic groups. The band at $1615 \, cm^{-1}$ is assigned to aromatic carbonyl and carbonyl motion in carboxyl groups. The band appearing at approximately $1270 \, cm^{-1}$ can be attributed to the C–O stretching of phenolic groups. FTIR spectrums also show that SDs constituents mainly composed of polymeric OH groups, CH_2 and COO groups, and OH groups of polysaccharides. It has been known that all these groups have affinity of Cr(VI) ion adsorption.

2.2. Preparation of Cr(VI) solution

An accurately weighed quantity of the $K_2Cr_2O_7$ (purchased from Merck Company) was dissolved in double-distilled water to prepare a stock solution (1000 mg/L). Experimental solutions of the desired concentrations were obtained by successive dilutions (1×10^{-4} to 1×10^{-3} mol/L). 0.1 M NaCl solution is used for ionic strength. All chemicals used were of analytical reagent grade.

2.3. Adsorption experiments

The sorption mixture was consisted of 0.1 g of sorbent in 20 mL of chromium solution from 1×10^{-4} to 1×10^{-3} mol/L $K_2Cr_2O_7$ for 2 h at 25 ± 2 °C. After equilibration, the sorbent-solution passed through a filter and was analysed for metal ion content using an atomic adsorption spectrometer (Perkin-Elmer AA800 Model). The sorbent dosage was changed in the range of 0.025–0.4 g. The chromium concentration (1×10^{-4} to 1×10^{-3} mol/L) was adjusted in the batch experiments. The temperature of the Cr(VI) solution was adjusted in the range of $25–65 \pm 2$ °C using a thermostatic shaking water bath (Memmert WB29 Model). Contact time adsorption experiments were conducted at 25 ± 2 °C in a well-mixed pyrex glass vessel with a cover. Cr(VI) removal is built up, equilibrium conditions are attained after nearly 2 h.

To study the effect of pH on sorption, the pH of the chromium solution was adjusted to values in the pH range of 3–10 by the addition of 0.1 M HCl or 0.1 M NaOH prior to experiment. All pH measurements were performed with a Crison Basic 20 Model pH meter. Time dependent experiments were carried out by shaking the adsorption mixture at various predetermined intervals and analyzing the Cr(VI) content at the end of the contact time.

3. Results and discussion

3.1. Effect of pH on Cr(VI) removal

The interactions of metals with SD surface molecules are complex, dominated by adsorption, ion exchange and chelation. Hunt notes as a generalization the binding of metal ions involved two mechanism, the first of these being simple ion exchange and the second through the formation of complexes, which may be chelates [41]. According to the mechanism and the discussion of pH effect, the adsorption will lead to a decrease in pH as equivalent H^+ will be released along with the adsorption. Hexavalent chromium existing as negative species in solution may
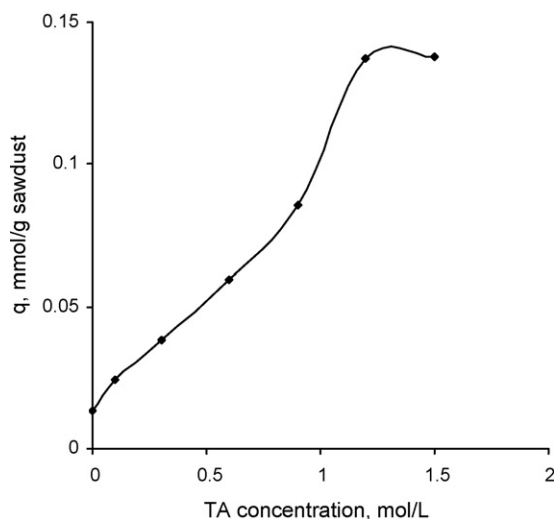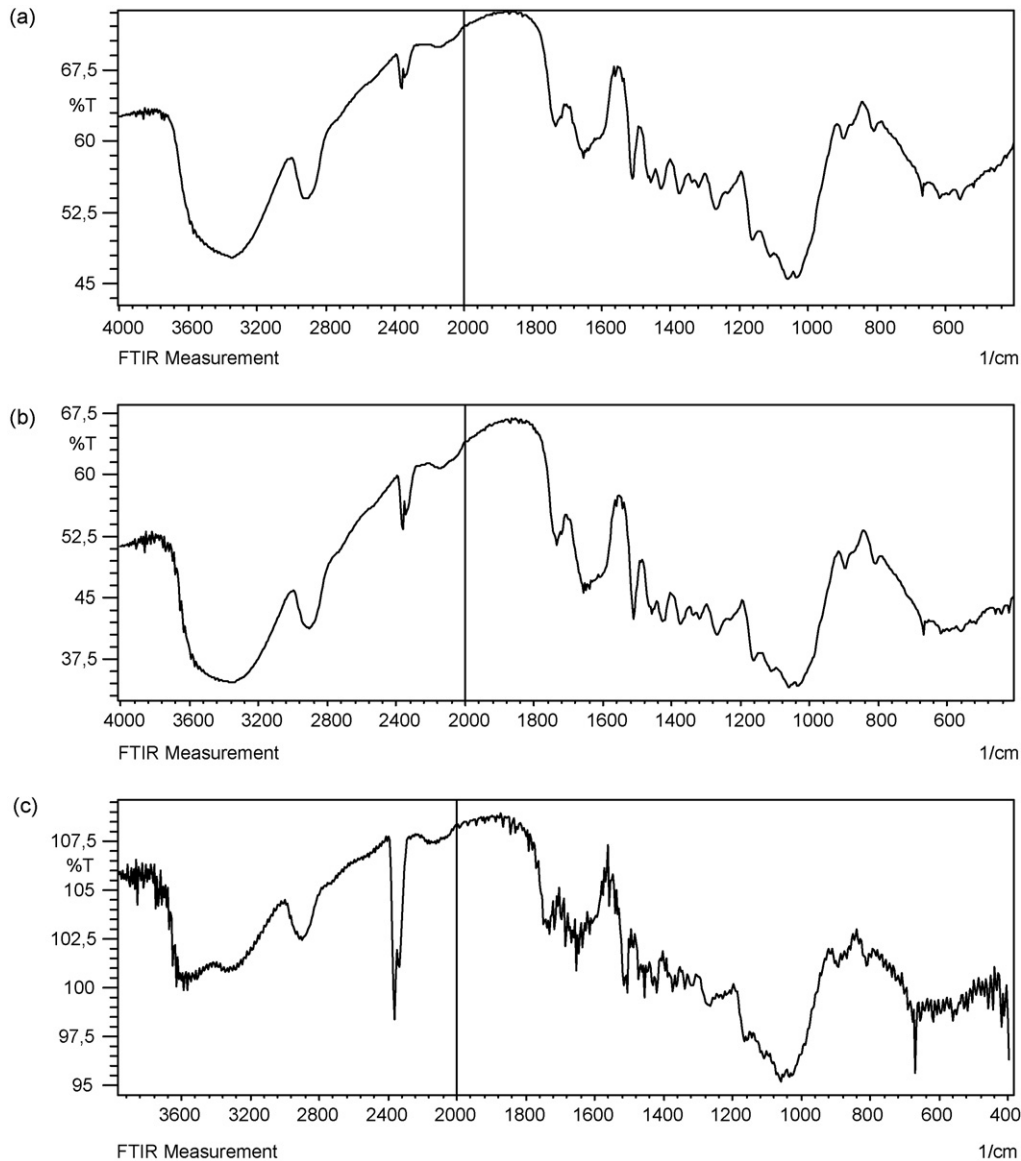

Fig. 1. The uptake of Cr(VI) using SD modified with various tartaric acid concentrations. Adsorption conditions: initial concentration of Cr(VI), 1×10^{-3} mol/L; amount of SDs, 1.0 g; volume of adsorption medium, 30 mL; temperature, 25 ± 2 °C; stirring time, 300 rpm.

Fig. 2. Fourier transform infrared (FTIR) spectrum of (a) SD; (b) BESD; (c) TASD.

release hydroxide (OH−) instead of proton (H+) when they are adsorbed by SD, and therefore result in an increase in pH [34]. This is the case for most metal adsorption, but there is always exception. Because of the complexity of most biomaterials, it is very likely that both of these processes of binding will take place in a system at the same time. The following Eq. (4) describes the chemical adsorption involving exchange with hydroxyl ions:

$$R\text{–}CO + H_2O + HCrO_4{}^- \leftrightarrow R\text{–}COHO_3Cr^+ + 2OH^- \qquad (4)$$
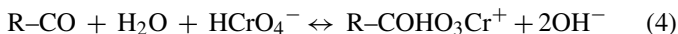
The effect of pH is presented in Fig. 3. The effect of pH on adsorption of Cr(VI) was studied at room temperature be varying the pH of metal solution–SD suspension from 3.0 to 10.0. The percent adsorption decreases in the pH range of 3.0–10.0, showing the maximum adsorption at pH 3.0. The Cr(VI) removals were mainly governed by physico-chemical adsorption onto the SDs. The pH dependence of adsorption may suggest that metal

ions are adsorbed according to the ion-exchange mechanism, and deacetylation dependence of adsorption may indicate the chelation mechanism. The pH increase was lesser at lower initial pH values. It may be due to hydrolysis of the adsorbent in water, which will create positively charged sites [42]. Percentage removal of Cr(VI) was maximum at the initial pH of 3.0 (87.7, 70.6 and 55.2% by TASD, BESD, and SD, respectively) and decreased at lower and higher initial pH values (Fig.3). As described in Eq. (4), hydroxyl species are released from the process of Cr(VI) adsorption instead of hydrogen ions. In this case, decreasing the pH will favor the Cr(VI) adsorption on sawdust but not help strip Cr(VI) ions from sawdust [34,43].

At initial pH of 3.0, the adsorbent surfaces might be highly protonated which favor the uptake Cr(VI) in the predominant anionic form (HCrO4−) [44–46]. With increase in pH from 3.0 to 10, the degree of protonation of carbon surfaces reduced gradually and hence removal was decreased. The rate of adsorption
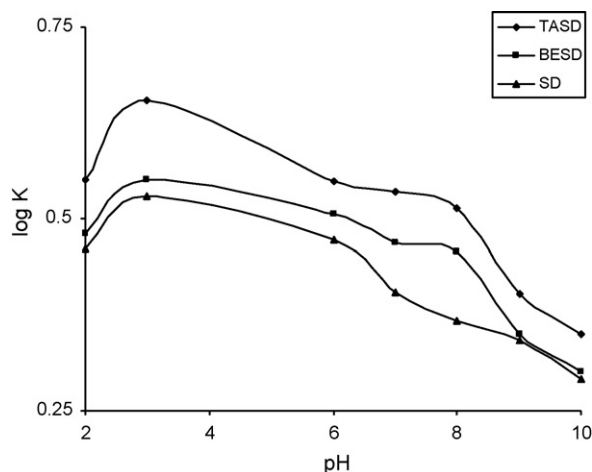
Fig. 3. Effect of pH on the adsorption of Cr(VI) using the SDs. Adsorption conditions: initial concentration of Cr(VI), 1×10^{-3} mol/L; amount of SDs, 1.0 g; volume of adsorption medium, 30 mL; temperature, $25 \pm 2\,^{\circ}$C; stirring time, 300 rpm.
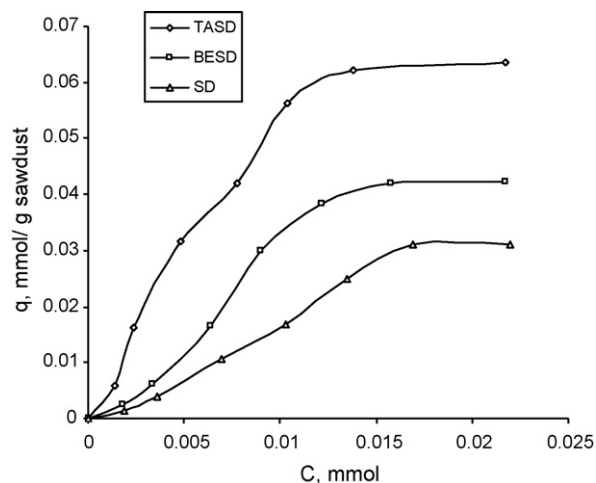

Fig. 4. Sorption isotherm of Cr(VI) ion on SDs as a function of initial chromium concentration 1×10^{-4} to 1×10^{-3} M and volume of Cr(VI) solution, 30 mL at pH 3.0; amount of SDs, 1.0 g; temperature, $25 \pm 2\,^{\circ}$C; stirring time, 300 rpm.

of Cr(VI) ion on sawdust was great for pH changes from 3 to 6 for Cr(VI) ion. An increase in pH above pH 3 shows a slight decrease in adsorption in which the surface of the adsorbent is negatively charged. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes. At below pH 3, part of residual chromium ions in the solution existed as trivalent state, while above pH 3, chemical reduction of Cr(VI) to Cr(III) occurred to lesser extends and anionic chromium species, $HCrO_4{}^{-}$, is the major species throughout the pH range studied.

3.2. Effect of initial Cr(VI) concentration

The effect of sorbate concentration is shown in Fig. 4. In the case of low Cr(VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The amount of Cr(VI) ions adsorbed per unit mass of the SD increased with the initial metal concentration as expected. To obtain maximum sorption capacities or reach the plateau values that represent saturation of the active groups which are available for interaction with Cr(VI) ions on the SD, the initial concentration were increased from 1×10^{-4} to 1×10^{-3} mol/L Cr(VI) for all SDs. The sorption capacities

were 8.3, 15.2 and 22.6 mg of Cr(VI) per g of SD, BESD and TASD, respectively.

The Freundlich model fit well in the pH range between 3.0 and 4.0. The Freundlich equation was more applicable than the Langmuir was although both described the sorption data adequately. We found the Freunlich isotherms, to have the highest correlation coefficients above 0.97 for initial pH values for all SDs (Table 1). It was found that more than 87% removal was achieved using these adsorbents. The adsorption data in the linear forms gave satisfactory correlation coefficients for a part of the covered concentration range. The comparison of the experimental adsorption capacity obtained in this study with the data in the literature for various adsorbents shows that sawdust is an effective sorbent of metal ions. A comparison of the maximum adsorption (mg/g) of SDs and other adsorbents has been made and is given in Table 2 [47,48]. Modified SDs exhibited good adsorption capacities for Cr(VI) ion from aqueous solution. A dosage of 0.1 g of modified SDs is sufficient to remove more than 87.7% of Cr(VI) ion from the 1×10^{-3} M Cr(VI) solution.

3.3. Effect of ionic strength

Ionic strength is one of the important factors, which influence the aqueous phase equilibrium. A number of scientists [34,46] have intensively investigated this effect. Generally, adsorption decreases with increasing ionic strength of the aqueous solu-

Table 1
Freundlich and Langmuir adsorption isotherm parameters

Adsorbents	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	Q_0	b	R^2	K_f	n	R^2
SD	0.019	44.865	0.828	5.504	0.779	0.983
BESD	0.017	73.669	0.945	10.102	0.772	0.971
TASD	0.154	51.270	0.949	10.715	1.293	0.988

b and n; constants. R^2; correlation coefficients.

Table 2
Comparison of the adsorption capacities of SDs with various low-cost adsorbents [47,48]

Adsorbent	pH	Temperature (°C)	Adsorption capacity (mg/g)
Grafted silica	5.5	20	16.57
Fly ash	6.5	30	1.39
Bagasse fly ash	4.0	30	2.40
Tree fern	–	20	13.90
Chitosan	3.5	–	2.83
Lemma minor L.	4.0	20	69.00
Prawn shell	6.0	25	92.40
River bed sand	6.5	25	0.15
Pumice	8.0	20	0.06
Pumice/composite	8.0	20	0.27
SD[a]	3.0	20	5.50
BESD[a]	3.0	20	10.10
TASD[a]	3.0	20	10.72

[a] This study.

tion. The effect of interfering ion sodium chloride has also been studied on the adsorption of two metal ions on the sorbents. The ionic strength for all adsorption experiments in this study was 0.1 M. The electrostatic attraction at low ionic strength appears to play a negligible role in the removal of Cr(VI) for SDs. The results indicate that, up to 0.1 M NaCl, there was no significant decrease in the removal of Cr(VI). However, increasing the ionic strength over 0.1 M results in a decrease about 20% removal for Cr(VI) ion.

3.4. Desorption studies

The reversibility of the process was also investigated. Desorption studied are helpful to explore the possibility of recycling the adsorbents and recovery of metal resource. The desorption of Cr(VI) which were previously deposited on the SDs back into the deionized water was observed only in acidic pH values during one day study period and was generally rather low. After three cycles of operation the adsorption capacity of TASD decreased from 87.7 to 65.2%. The desorption tests showed that only an insignificant amount of adsorbed Cr(VI) is desorbed. This further confirms that sorption of Cr(VI) on SD is adsorption and mostly complex formation in nature.

4. Conclusion

Sawdust both untreated and treated is effective in removal of heavy metals from water. All sawdust appears to be a promising adsorbent for removal of chromium from wastewater. Adsorption of Cr(VI) is dependent on its initial concentrations and pH of the metal solution. The results indicate that the optimum pH for the removal of Cr(VI) ions by SD, BESD and TASD is around 3. Cr(VI) removal is built up, equilibrium conditions are attained after nearly 2 h. Isothermal data of Cr(VI) sorption on sawdust can be modeled by both Freundlich and Langmuir isotherms. The data in the linearized forms (Freundlich equation) gave satisfactory correlation coefficients for a part of the covered concentration range. The sorption capacities were 8.3,

15.2 and 22.6 mg of Cr(VI) per gram of SD, BESD and TASD, respectively.

SD is easily available in Mediterranean mountainous forest, so can be used by industries having low concentrations of Cr(VI) in wastewater using batched reactors after modified with tartaric acid. At these adsorption levels, a process using sawdust for the removal of Cr(VI) is potentially more economical and all those add more credits to sawdust materials for removing pollutants from waste waters.

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