

Removal of Cr(VI) from industrial wastewaters by adsorption Part I: Determination of optimum conditions

Muradiye Uysal, Irfan Ar*

Gazi University, Department of Chemical Engineering, Maltepe 06570 Ankara, Turkey

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Abstract

Aim of this study is the determination of the Cr(VI) removal efficiency of treated pine sawdust and also to find out the thermodynamic and kinetic parameters of Cr(VI) removal process in batch systems. Sawdust has been treated with 1,5-disodium hydrogen phosphate before the adsorption experiments. The effects of initial concentration of Cr(VI) ion, temperature, amount of adsorbent and pH of the solution on adsorption have been investigated. Optimum conditions for adsorption were determined as $T=40\text{ }^{\circ}\text{C}$, sawdust dose = 4 g, pH 2, by using the results of these experiments and an additional set of experiments was performed under these optimum conditions in order to see the change in the adsorption efficiency. Removal of chromium ion was found as highly dependent on pH and initial Cr(VI) concentration of the solution.

In order to find out thermodynamic and kinetic parameters equilibrium adsorption models were applied. Although experimental data confirm with both Langmuir and Freundlich isotherm models, they suit most on Langmuir isotherms. Adsorption rate constant was determined from Lagergren equation. Equilibrium constants, adsorption free energy, enthalpy and entropy change values were also determined. It was found that adsorption process follows first order kinetic and adsorption of Cr(VI) on sawdust has the spontaneous nature.

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1. Introduction

Heavy metals are toxic and environmentally harmful substances. Especially those accumulated within the living organisms as well as in human body are more dangerous [1]. Therefore, they have to be removed from the wastewaters before they are given to the receiving medium.

A large number of studies on removal of heavy metals from wastewater have been reported in the literature [2]. As a result of these studies the methods used for the removal of chromium ions from wastewater can be divided into five main categories: (i) chemical reduction by using ferro sulfates, sodium metabisulfite, sodium sulfite, sulfur dioxide and similar chemicals, (ii) ion exchange by using anion exchange resins, and (iii) electrochemical reduction, (iv) recovery by evaporation and finally (v) adsorption. Matagi et al. [3] discussed the potential for heavy metal removal mechanisms by wetlands through reactions invol-

ving sedimentation, flocculation, absorption, co-precipitation, cation and anion exchange, complexation, precipitation, oxidation/reduction, microbial activity and plant uptake.

Hexavalent chromium Cr(VI) is one of the most dangerous heavy metal and a major pollutant in wastewaters, because it is a strong oxidizing agent which irritates plant and animal tissues and it is carcinogenic and mutagenic [4]. Cr(VI) can diffuse through cell membranes in the form of CrO_4^{2-} or HCrO_4^- [5] which do not form insoluble compounds. Therefore, direct precipitation cannot be used for the removal of chromium ions. On the other hand, reduction is the conversion of mobile and toxic Cr(VI) ions to the less mobile and less toxic Cr(III) ions [6,7] and it is not an effective method because of the incomplete reduction of Cr(VI) that may form a toxic sludge via the surface adsorption onto the Cr(III) hydroxide precipitate [8]. Another disadvantage of this method is the requirement of high cost chemicals for the reduction.

Adsorption is the accumulation of gas, vapor or liquid molecules on an interface. It is regarded as one of the most efficient methods for the removal of toxic and non-biodegradable compounds such as heavy metals [5,9]. All solid materials including

* Corresponding author. Tel.: +90 312 231 7400/2517; fax: +90 312 230 8434.
E-mail address: irfanar@gazi.edu.tr (I. Ar).

metals and plastics have the adsorption capacity whether they have the crystalline structure or not. However, the solids which have the high adsorption capacities are the ones having a porous structure like a sea sponge, and magnitude of their adsorption capacity is determined by the radius and number of these pores [10]. Various materials such as natural zeolites [11], clay minerals [12,13], lignocellulosic materials [14], waste tires [15], biomaterials [16], industrial wastes [17–19] and agricultural wastes [20] are used as adsorbent for the removal of heavy metals.

There are large numbers of studies in the literature in which various adsorbents are used [21–25]. Two recent reviews reported by Mohan and Pitman [26] and Kurniawan et al. [27] can be referred for the other possible adsorbents for the removal of heavy metals.

Adsorption depends on number of parameters such as physical and chemical properties of adsorbent and adsorbate, temperature, pH, concentration, pressure, etc., therefore, determination of adsorption mechanism and optimum operation conditions are generally a difficult task [23]. Although there are large number of studies in which sawdust is used as adsorbent for the removal of chromium ions [13,28–31], still there is need for experimental data in order to determine the adsorption mechanism of chromium ions on sawdust especially for the dilute solution [32]. Objectives of this study were to investigate the thermodynamic and kinetic parameters of removal of chromium ions from wastewaters by using pine sawdust treated with 1,5-disodium hydrogen phosphate, as adsorbent in batch system.

2. Materials and methods

2.1. Preparation of adsorbent and solutions

Pine sawdust was first screened (200 μm) and washed with distillate water three times and drained. Sawdust then immersed into 1,5-disodium hydrogen phosphate solution (20 mL solution per gram of sawdust) and mixture was left in a furnace that is maintained at 21 $^{\circ}\text{C}$, for 24 h. Dried sawdust was washed with distilled water in order to remove the excess phosphate and phosphate analysis of drained water was made by using sodium acetate and Fe_3Cl . Washed sawdust was dried to bring it to a constant weight in a drying-out cupboard maintained at 41 $^{\circ}\text{C}$. Then it was kept in a desiccator.

One hundred milligrams per litre Cr(VI) stock solution was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in double distilled water whose conductivity and pH were controlled.

0.1 M HCl and 0.1 M NaOH solutions used for the pH adjustment were prepared by using concentrated HCl and NaOH (Merck, reagent grade) solutions, respectively.

2.2. Adsorption experiments in batch system

Adsorption experiments were performed in two steps. In the first step, preliminary experiments were performed in order to determine the rate of change of adsorption with time and also to determine the equilibrium concentration of aqueous solution.

In this group of experiments 500 mL of 100 ppm solutions were used. Ten grams of treated sawdust were added to the solutions and experiments were carried out at 100 rpm shaking rate for 6.5 h. Four millilitre samples were taken from the solutions in 10 min intervals in the first 1 h period and then 30 min intervals within the remaining 5.5 h. Samples were first filtered in order to remove the possible sawdust within the sample and they were kept in black, tightly closed sample holders.

Experiments that took place in the second step were designed to investigate the effects of operating conditions on the removal of Cr(VI) ion and to obtain data in order to evaluate the thermodynamic and kinetic parameters of chromium ion sorption on sawdust.

In order to see the effect of the concentration on adsorption efficiency, solutions with concentrations of 20, 40, 60, 80, 100 Cr(VI)/L were prepared by diluting the stock solution and 150 mL solutions were taken into Erlenmeyer from each solution. Two grams of sawdust were added to each sample and placed in to water bath which is maintained at 20 $^{\circ}\text{C}$. In this first group of experiments bath temperature was maintained at 20 $^{\circ}\text{C}$ but it was changed to 30, 40, 50 $^{\circ}\text{C}$ in second set of experiments in order to determine the effects of temperature.

The effect of adsorbent dose on removal efficiency was also investigated and 1, 2, 3, 4, 6 and 8 g of sawdust were added to six different solutions each having a volume of 150 mL. These solutions were placed into the water bath which was maintained at a temperature and shaking rate of 20 $^{\circ}\text{C}$ and 100 rpm, respectively.

Fourth group of experiments was carried out in order to see the effect of solution pH on removal efficiency by using 150 mL solution samples having the concentration of 60 mg/L at a bath temperature of 40 $^{\circ}\text{C}$. Four grams of sawdust was added to each solution sample whose pH values were 2, 3, 4, 7 and 9. In these experiments only initial pH values were adjusted but pH control was not made during the experiment.

Finally, a last set of experiments was performed in order to find out the maximum adsorption efficiency under the optimum experimental conditions. In these experiments 4 g of sawdust was added to each solution sample. Solution samples having concentrations of 20, 40, 60, 80 and 100 mg Cr(VI)/L at a pH of 2 were used. Water bath temperature and shaking rate were maintained at 40 $^{\circ}\text{C}$ and 100 rpm, respectively.

2.3. Measurement of Cr(VI) concentration in aqueous solutions

There are some components within the sawdust that may reduce the Cr(VI) to Cr(III). Therefore, oxidation of Cr(III) within the samples to Cr(VI) is necessary before the analysis of each sample. Cr ions within the samples were oxidized by using potassium permanganate in acidic medium. The violet color that forms as a result of the reaction between the Cr(VI) ions and 1,5-diphenyl carbazide in acidic medium, was measured by using Shimadzu UV/V double beam spectrophotometer at 540 nm. The lowest limit of this method is 0.01 mg/L and the best suitable measurement range is 0.5–5.0 mg/L. Therefore, in order to obtain the more reliable measurements some of the

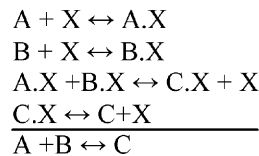
samples were diluted before the measurements and measured values were multiplied by the dilution factor.

2.4. Adsorption models

Adsorption isotherms are very powerful tool for the analysis of adsorption processes. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. But due to the complex nature of liquid-phase adsorption on the microporous substances there may not be a simple expression that is capable of describing the process. In order to avoid complexity in practical applications Langmuir and Freundlich models have been widely used to describe the behavior of adsorbent–adsorbate couples.

2.4.1. Langmuir isotherm

Langmuir isotherm is applicable for the adsorption on homogeneous surfaces and it depends on the assumptions which can be summarized as there are constant numbers of active sites having the uniform energy on adsorbent surface and adsorption energy is constant. Further, it is assumed that adsorption is a monolayer adsorption and the maximum adsorption occurs when molecules adsorbed on the surface of adsorbent form a saturated layer. Langmuir isotherm is valid for the cases where adsorption is a monolayer coverage processes, therefore, it is expected that adsorption value reach to a maximum value at high pressure or concentrations.



General expression of Langmuir isotherm is

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount of adsorbate adsorbed by a unit mass of adsorbent at equilibrium (mg/g adsorbent), C_e the concentration of adsorbate remaining in the solution at equilibrium (mg/L), K_L the constant related with adsorption net enthalpy, Q_0 amount of adsorbate adsorbed by unit mass of adsorbent that is required to cover adsorbent surface completely as a monolayer (mg/g).

In most of the cases linearized form of this expression is used.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (2)$$

or

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{K_L Q_0} \times \frac{1}{C_e} \right) \quad (3)$$

Constants Q_0 and K_L can be evaluated from the plot of either C_e versus C_e/q_e or $1/q_e$ versus $1/C_e$.

2.4.2. Freundlich isotherm

Although Freundlich isotherm is generally used for the adsorption from liquid solutions, it is used for the gas adsorption as well. This model expresses a special case in which adsorbent surface energy is heterogeneous and energy related term K_L in Langmuir isotherm changes as a function of surface coverage q . According to this model, initially amount of adsorbed compound increases rapidly, this increase slow down with the increasing surface coverage. This change is expressed as;

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and $1/n$ constants depend on temperature and properties of adsorbate and adsorbent. They are measure of adsorption capacity of adsorbent and measure of adsorption intensity, respectively. Linearized form of this model is,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Langmuir and Freundlich isotherms mathematically characterize the adsorption in dilute solutions, therefore, adsorption data confirm with both of these models when studies are carried out in medium concentration range [33–35]. In this study, both of these two isotherms were applied to the experimental data.

2.5. Kinetics and thermodynamics of adsorption

Mechanism of batch adsorption can be given as [15,36]



$$\begin{aligned} \frac{dC_B}{dt} - \frac{dC_A}{dt} &= \frac{C_{A0} dX_A}{dt} = k_1 C_A - k_2 C_B \\ &= k_1 (C_{A0} - C_{A0} X_A) - k_2 (C_{B0} + C_{A0} X_A) \end{aligned} \quad (11)$$

where C_A is the concentration of remaining metal in the solution, C_B the concentration of metal on the adsorbent, C_{A0} and C_{B0} the initial concentrations of metal in solution and on adsorbent surface, respectively, X_A the conversion fraction of metal, and k_1 and k_2 are the first order reaction rate constants.

At equilibrium;

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0 \quad (12)$$

$$X_{AC} = \frac{(K_C - C_{B0}/C_{A0})}{(K_C + 1)} \quad (13)$$

$$K_C = \frac{C_{BC}}{C_{AC}} = \frac{C_{B0} - C_{A0} X_{AC}}{C_{A0} - C_{A0} X_{AC}} = \frac{k_1}{k_2} \quad (14)$$

where K_C is the equilibrium constant and C_{BC} and C_{AC} the metal concentration on adsorbent and in solution, respectively.

Adsorption free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be evaluated as follows;

$$\Delta G^\circ = -RT \ln K_C \tag{15}$$

and Van't Hoff Equation;

$$\log K_C = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{16}$$

For an adsorption process that obeys the first order rate law, adsorption rate constant can be found from Lagergren equation [20,37]. These equations are especially applicable to the reactions that obey the first and second order kinetics. Starting from the amount of adsorbate adsorbed by a unit mass of adsorbent, adsorption rate constant can be obtained. If the expression given for a first order kinetics,

$$\frac{dq}{dt} = k_{ADS}(q_e - q) \tag{17}$$

is integrated

$$\log(q_e - q) = \log q_e - \frac{k_{ADS,t}}{2.303} \tag{18}$$

is obtained.

In this study, it was tried to obtain the reaction and adsorption parameters using above expressions.

3. Results

In this study, effects of initial metal concentration, temperature, pH and amount of adsorbents on adsorption of Cr(VI) ions on sawdust were investigated in batch systems. Also adsorption efficiency, equilibrium isotherms and kinetic parameters were investigated by performing a set of experiments under the experimentally determined optimum conditions.

3.1. Determination of optimum operating conditions

Change in the amount of adsorbed metal ion with time at different concentrations is given in Table 1. According to data in Table 1, amount of adsorbed Cr(VI) ions increases with the increasing initial concentration except the solution whose initial concentration was 100 mg/L. Baral et al. [36] explained this

Table 1
Variation of amount of adsorbed metal with time at different initial chromium concentrations (sawdust = 2 g)

t (min)	Amount of metal adsorbed by sawdust at 20 °C				
	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L
30	0.797	2.272	4.061	2.799	4.325
60	1.533	3.462	5.441	7.902	6.341
90	2.544	3.902	7.203	9.020	7.008
120	2.778	5.863	10.414	11.547	10.655
150	2.885	6.355	10.536	12.876	11.874
180	3.090	6.846	10.689	12.965	11.876
210	3.099	6.490	10.678	12.969	11.875
240	3.099	6.492	10.692	12.972	11.877
270	3.10	6.489	10.689	12.970	11.877

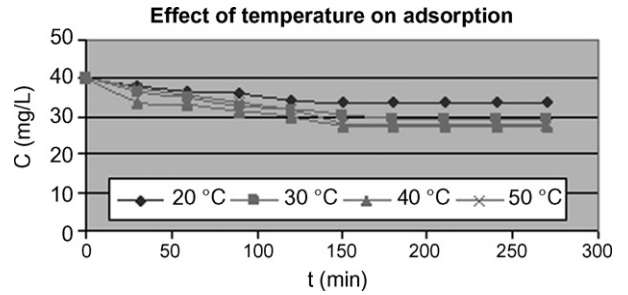


Fig. 1. Effect of temperature on adsorption ($C_0 = 40$ mg/L, sawdust = 2 g, pH uncontrolled).

behavior by the increase in the number of chromium ions available for the adsorption in the solution and also by the fact that, higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr(VI) ions and active sites. Results of some studies reported in the literature [37–40] for the effect of initial adsorbate concentration, confirm very well with the results obtained in this study. It has been observed that initial adsorption rate is initially very high for all initial concentrations. But it decreases with time due to the coverage of the active sites by the metal ions. Adsorption process almost completed within 2 h and no significant change was observed at the end of 3 h. Change in the solution concentration with time was calculated by using these values. The concentrations of solutions did not change after 200 min which are called as equilibrium concentrations (C_e). Other important observations were that the smallest equilibrium value was obtained for the initial concentration of 20 mg/L and values of equilibrium concentrations increase with the increasing initial concentrations.

Effect of temperature on adsorption capacity of sawdust was investigated at two initial concentrations by using 2 g of sawdust at the temperatures of 20, 30, 40 and 50 °C. Data obtained from these experiments are given in Figs. 1 and 2. Change in solution concentration with time was similar in these two figures; initially there is a rapid decrease in concentration and then it starts to slow down and finally there is no significant change after 2 h. Solution concentration decreases more rapidly, i.e. amount of adsorbed ions increases when temperature was increased from 20 to 50 °C. Adsorption is considered as an exothermic process; therefore, it is expected that the equilibrium concentration increases (i.e. amount of adsorbed material decreases) with increasing

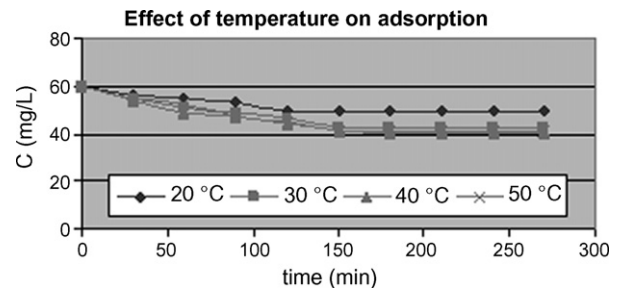


Fig. 2. Effect of temperature on adsorption ($C_0 = 60$ mg/L, sawdust = 2 g, pH uncontrolled).

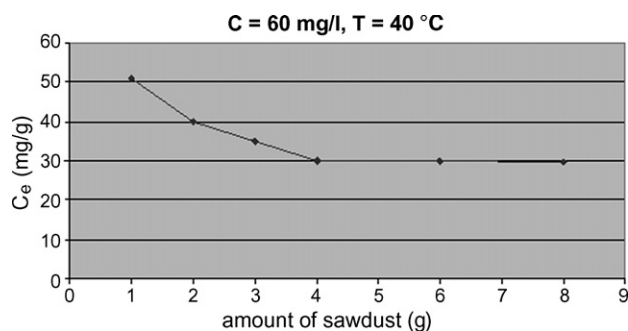


Fig. 3. Equilibrium concentrations as a function of dose of sawdust.

temperature. But some chemical adsorption processes are endothermic processes; therefore, increase in temperature leads to increase both in adsorption rate and amount of adsorbed materials [19]. Since this trend was observed in this study, adsorption of Cr(VI) on sawdust is possibly a chemical adsorption process.

An interesting point which can be observed from both Figs. 1 and 2 is that there is a slight increase in equilibrium concentration when temperature is changed from 40 to 50 °C. Kinetic energies of chromium ions were low at low temperatures. Therefore, it is very difficult and time-consuming process for ions to reach the active sites on the adsorbent. Increase in temperature causes increase in the mobility of the ions. If temperature is further increased, the kinetic energies of chromium ions become higher than the potential attractive forces between active sites and ions [37,41,42]. Decrease in equilibrium concentration when temperature was increased from 20 to 40 °C and slight increase in it when temperature was raised from 40 to 50 °C may be explained as a result of this phenomenon.

Effect of amount of sawdust on the adsorption efficiency was investigated by using six different solutions having the same properties except the dose of adsorbent. Amounts of adsorbent within these solutions were different such as 1 g in first solution, 2 g in second one, 3 g in third one, 4 g in fourth, 6 g in fifth and finally 8 g in the sixth solution. Results obtained from these experiments are given in Fig. 3 in which equilibrium concentrations are plotted as a function of dose of sawdust. Experimental results showed that the equilibrium concentration decreases (i.e. amount of chromium ion adsorbed increases) with the increasing amount of adsorbent up to 4 g. After this dose of adsorbent no significant change was observed. This behavior of equilibrium concentration may be explained by the increase in adsorption surface area and hence the active sites with the increasing dose of adsorbent [8,35,40]. Since amount of initial Cr(VI) is constant, they can occupy only a certain amount of active sites. Therefore, further increase in the number of active sites does not affect the amount of adsorbed ions. In other words, for each ion concentration there is a corresponding adsorbent dose at which adsorption equilibrium was established.

Another important parameter for the adsorption is pH of the solution. In order to determine the effect of pH on the adsorption, five solutions with different pH (2, 3, 4, 7 and 9) but having same concentration (60 mg/L) and containing 4 g of sawdust were prepared and placed into water bath maintained at 40 °C. Change of equilibrium concentration as a function of pH is given

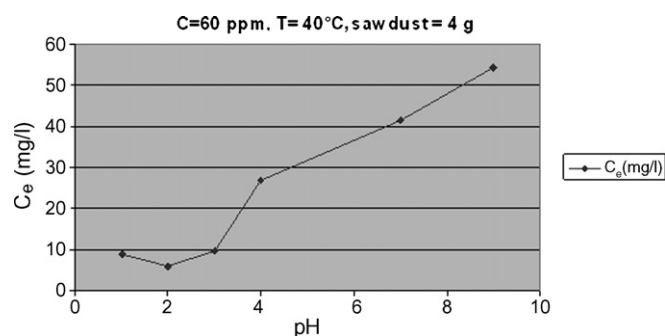


Fig. 4. Change of equilibrium concentration as a function of pH.

in Fig. 4. Experimental results given in Fig. 5 show that increase in the initial pH of the solution from 2 to 9 caused to increase in equilibrium concentration of Cr(VI) ions. Starting from this point it may be concluded that 2 is the best initial pH value for the adsorption of chromium ions on sawdust. Although Malkoç et al. [19], Garg et al. [44] and Kiran et al. [45] used different adsorbents in their studies, they also found that pH 2 is the optimum pH value. Similar behavior was observed by El-Shafey who investigated the removal of chromium ions from wastewaters by using modified rice husk as adsorbent [46] and also by Karthikeyan et al. [29]. For each metal ion, there is a specific pH value at which the maximum adsorption of that ion takes place. This pH takes place in basic region (i.e. at high pH values) for the cationic metals; it takes place as an exceptional case at the low pH values for the anionic metals. Adsorption of chromium ions was around 95% at pH 2, and it decreased to 84%, 55% and lower values with the increasing pH values. This may be explained by the influence of solution pH on the surface charge distribution which is strongly related with the metal ions removal [5].

The dominant chromium compound within the solution at pH 2 is HCrO_4^- (CrO_4^{2-} and also $\text{Cr}_2\text{O}_7^{2-}$ exist). Removal of Cr(III) at pH 2 is zero while its removal percentage is very high at pH 5 whereas removal percentage of Cr(VI) is significantly low. This shows that pH of the solution is very important parameter for the removal of Cr(VI) which is the toxic form of the chromium metal. At pH 2, due to the excess amount of H^+ ions within the medium, the active site on the sawdust is positively

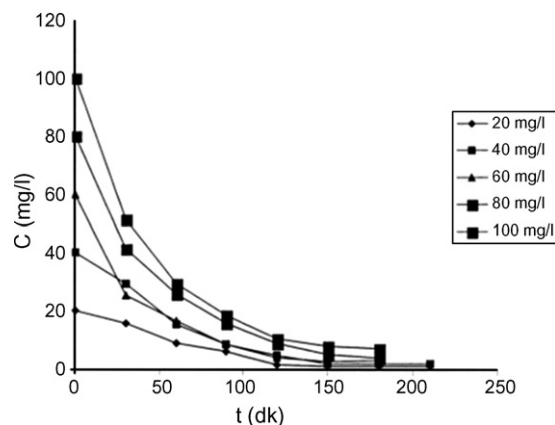


Fig. 5. Adsorption experiments at optimum conditions.

Table 2

Comparison of experimental results obtained under the optimum conditions with the ones obtained from the experiments carried out by using 2 g of sawdust

C_0 (mg/L)	q_e (mg/g ads.)				
	$T=20^\circ\text{C}$	$T=30^\circ\text{C}$	$T=40^\circ\text{C}$	$T=50^\circ\text{C}$	At optimum conditions
40	0.486	0.800	0.933	0.88	1.42
60	0.801	1.326	1.499	1.42	2.14
	% Adsorb.				
40	16.222	26.678	27.56	29.41	94.75
60	17.815	29.480	33.32	31.65	94.98

charged. This causes a strong attraction between these sites and negatively charged HCrO_4^- ions [45,46];



At low pH values active sites are positively charged. Therefore, negative metals adsorption increases significantly. When pH value increases, surface of the adsorbent becomes the neutral and a decrease in the adsorption is observed. When adsorbent surface is negatively charged, adsorption decreases significantly. This behavior is specific for the chromium ions and it is different for the divalent metals. Chromium ions release hydroxide ions to the solution instead of proton [36].

A last set of experiments was performed under the optimum conditions ($T=40^\circ\text{C}$, sawdust dose = 4 g, pH 2) determined as a result of above experiments. Results of these experiments are presented in Fig. 5. Concentration of chromium ion in the solution decreases (i.e. amount of adsorbed ion increases) with time and rate of this decrease increases with the increasing temperature. Rate of adsorption is initially very high at all adsorption temperatures but it starts to slow down after about 50 min and it ceases approximately after 150 min. This behavior may be explained by the availability of the active surfaces for the adsorption. Initially, number of active sites available for the adsorption on the adsorbent surface is high but this number starts to decrease with the progress of the adsorption. Finally, adsorption finishes when all active surfaces are covered with the metal ions. This implies that chromium ions adsorbed on sawdust possibly by chemical adsorption because chemical adsorption takes place as a monolayer coverage rather than multilayer adsorption as in the case of physical adsorption. Initial adsorption rate is very high because of the large surface area of the sawdust available for the adsorption. But after the coverage of this surface area by the adsorbed metal ions as a monolayer its adsorption capacity was exhausted and rate of adsorption controlled by the diffusion rate of adsorbate from external sites to the internal sites [48].

Comparison of experimental results obtained under the optimum conditions with the ones obtained from the experiments carried out by using 2 g of sawdust is given in Table 2. The highest adsorption values were obtained at the optimum conditions for all temperature and concentration values. For example, the highest removal efficiency achieved by using 2 g of adsorbent at an initial concentration of 40 mg/L, was 29.41% whereas this value for the same solution was 94.75% at the optimum condi-

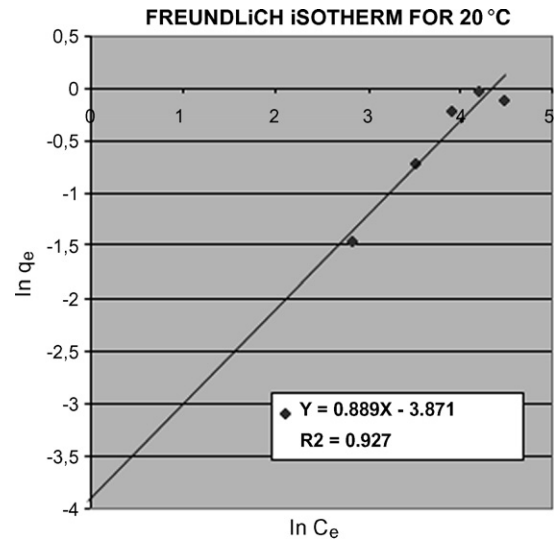


Fig. 6. Application of Freundlich model to the experimental data.

tions. For the solution with an initial concentration of 60 mg/L the highest removal percentage is 31.65%, whereas 94.98% removal efficiency was obtained under the optimum conditions.

3.2. Kinetic and thermodynamic parameters

Adsorption equilibrium data were used for the determination of kinetic and thermodynamic parameters. Adsorption equilibrium isotherms are very helpful tools for this purpose. The widely used adsorption isotherms are Langmuir and Freundlich isotherms which are given by Eqs. (1) and (4), respectively. The linearized forms of these equations (Eqs. (3) and (5), respectively) were applied to experimental data given in Figs. 6–9. Although experimental data confirm both of these adsorption models, values of regression coefficient, R^2 (see Table 3), indicate that adsorption of chromium ions on sawdust obeys the Langmuir type isotherm as reported in the literature [4,28,49,50]. This result implies that adsorption is a monolayer coverage for this system. One of the important assumptions in the development of Langmuir isotherm is the homogeneity of

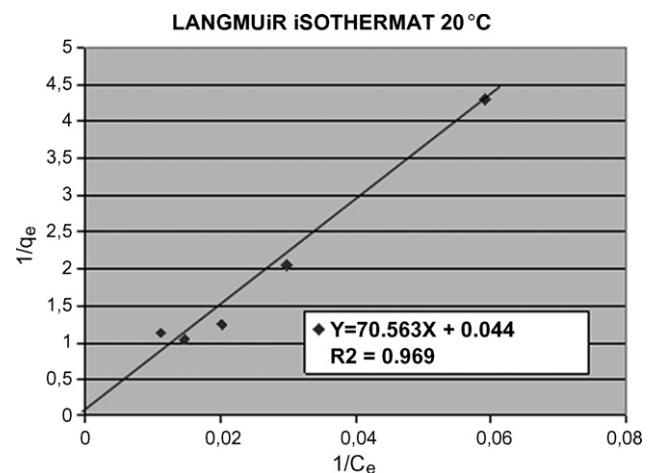


Fig. 7. Application of Langmuir model to the experimental data.

Table 3
Adsorption isotherm constant values for Langmuir and Freundlich models

		Uncontrolled pH, $T=20\text{ }^\circ\text{C}$, sawdust = 2 g	R^2	At optimum conditions (pH 2, $T=40\text{ }^\circ\text{C}$, sawdust = 4 g)	R^2
Langmuir isotherm constants	Q_0	30.488	0.98	121.95	0.991
	K_L	4.63×10^{-4}		54.13×10^{-4}	
Freundlich isotherm constants	$1/n$	0.887	0.924	0.882	0.964
	K_F	0.021		0.7203	

FREUNDLICH ISO THERM FOR OPTIMUM CONDITION DATA

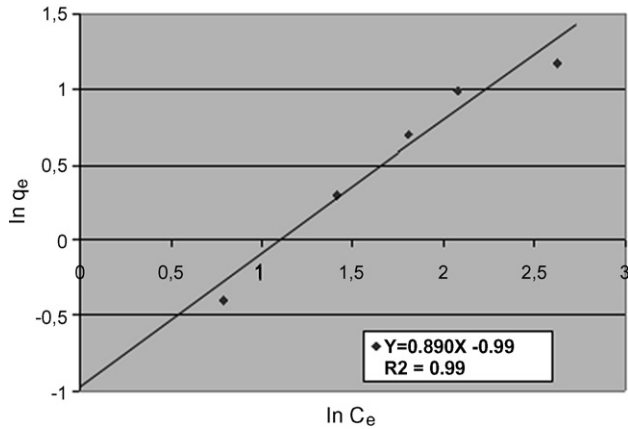


Fig. 8. Application of Freundlich model to the experimental data obtained at optimum conditions.

the adsorbent surface. Therefore, it may be regarded that sawdust has a homogeneous surface in surface charge distribution aspect [19,51].

Adsorption isotherm constants obtained from these figures are given in Table 3. Langmuir isotherm constant Q_0 indicates the amount of metal ions required for the monolayer coverage of the surface, in other words shows the monolayer capacity. Value of Q_0 in optimum conditions increased four times with respect to the value obtained when $T=20\text{ }^\circ\text{C}$, sawdust = 2 g and without pH control. This change in the monolayer adsorption capacity of the sawdust with the changing conditions is a very good improvement.

LANGMUIR ISO THERM FOR OPTIMUM CONDITION DATA

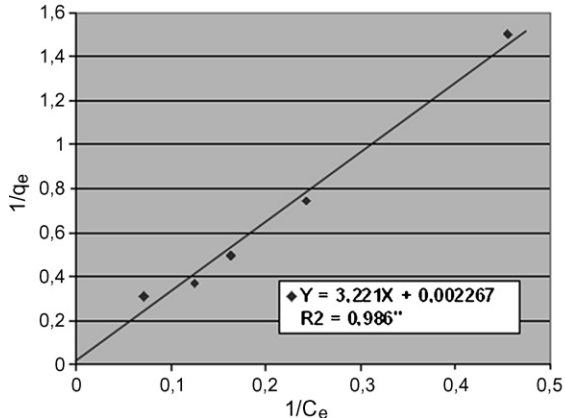


Fig. 9. Application of Langmuir isotherm to the experimental data obtained under optimum conditions.

Other Langmuir isotherm constant K_L also increased with the changing operation conditions. This constant can be used in the calculation of heat of adsorption. The values of constant R_L which shows the preferrability of the adsorbent, were calculated by using the K_L values from the following formula and they have been given in Table 4.

$$R_L = \frac{1}{1 + K_L C_0} \tag{20}$$

If value of R_L takes place between 0 and 1.0, adsorbent is a preferred one [43].

Freundlich adsorption constant $1/n$ shows the intensity of adsorption and if its value takes place between 0 and 1.0 it is regarded that the adsorbent is a preferred one. On the other hand, value of K_F increased from 0.021 to 0.7203 when experimental conditions were replaced by the optimum conditions. Since K_F is the measure of the adsorption capacity of the adsorbent, it indicates the improvement of adsorption due to change in the experimental conditions.

Adsorption rate constants were evaluated by using Lagergren equations which are used for the first and second order reactions. Lagergren equation given for a first order reaction kinetics (Eqs. (17) and (18)) was used in order to obtain the reaction rate constant in this study.

An example of $\log(q_e - q)$ versus t plot is given in Fig. 10. This plot gives a straight line, which indicates that the experimental data obey the Lagergren equation given for the first order kinetics. Slope of this line gives the rate constant.

The rate constants calculated in this manner are given in Table 5. Adsorption rate constants change with temperature but no increase or decrease proportional with temperature (i.e. no general tendency depending on the temperature) was observed. This implies that adsorption rate constants were affected from the parameters other than temperature.

Equilibrium constant K_C values were determined from Eq. (14) and given in Table 6. The big differences between the K_C

Table 4
 R_L values obtained for different metal initial concentration

C_0 (mg/L)	R_L (uncontrolled pH, $T=20\text{ }^\circ\text{C}$, sawdust = 2 g)	R_L (under the optimum conditions pH 2, $T=40\text{ }^\circ\text{C}$, sawdust = 4 g)
20	0.991	0.902
40	0.822	0.822
60	0.754	0.754
80	0.698	0.698
100	0.649	0.649

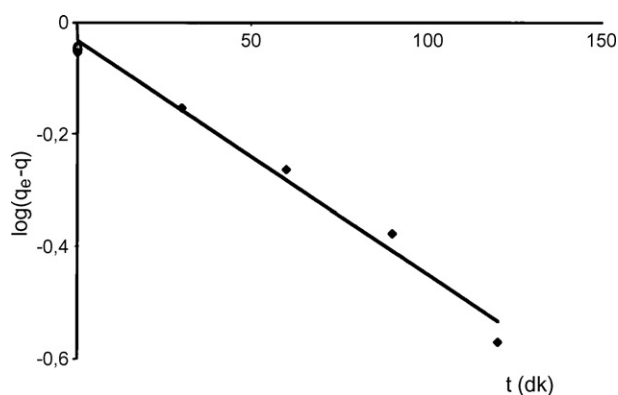


Fig. 10. Plot of $\log(q_e - q)$ vs. time to determine the rate constant ($T = 50^\circ\text{C}$, $C_0 = 40\text{ mg/L}$, pH 2).

Table 5
Adsorption rate constants obtained by using Lagergren equation

C_0 (mg/L)	$k_{\text{ads}} \times 10^2$ (min^{-1})				
	20 °C	30 °C	40 °C	50 °C	At optimum conditions
40	2.418	1.519	2.372	0.960	2.279
60	3.150	1.243	1.680	1.330	3.062

Table 6
Equilibrium constant (K_C) values

C_0 (mg/L)	20 °C	30 °C	40 °C	50 °C	At optimum conditions
40	0.193	0.363	0.451	0.416	18.047
60	0.216	0.418	0.499	0.463	18.933

values obtained from the data of experiments carried out under the optimum conditions and the ones obtained from the data of other experiments can be seen very clearly. Since equilibrium constants for endothermic reactions increase with the increasing temperature, data in Table 6 suggest that adsorption of Cr(VI) ion is endothermic. Increase in the K_C values also indicates the increase within the amount of adsorbed metal ion.

Table 9
Comparison of results reported in the literature for the removal of Cr(VI) with the values obtained in this study

Adsorbent	Lagergren rate constant	Adsorption isotherms constants				Equilibrium constant, K_C	Free energy, ΔG° (kJ/mol)	
		Langmuir		Freundlich				
		Q_0	K_L	K_F	$1/n$			
Wool	3.96×10^{-2}	41.15	7.15×10^{-3}	2.23	0.43	2.46	-2.26	
Olive paste	8.99×10^{-3}	33.44	4.70×10^{-3}	0.48	0.63	1.45	-0.94	
Sawdust	9.00×10^{-3}	15.82	9.17×10^{-3}	0.87	0.44	2.29	-2.02	30 °C
Pine needle	1.8×10^{-4}	21.50	5.44×10^{-3}	0.27	0.69	0.95	0.13	pH
	8.80×10^{-3}	10.61	5.46×10^{-3}	0.14	0.68	0.34	2.73	2
Coal	7.44×10^{-3}	6.78	11.5×10^{-3}	0.21	0.59	0.37	2.50	
Cactus	6.80×10^{-3}	7.09	6.13×10^{-3}	0.09	0.70	0.33	2.80	
Pine sawdust ^a	3.15×10^{-2}	30.48	4.62×10^{-4}	0.02	0.88	0.21	3.72	20 °C, uncontrolled pH
Pine sawdust ^a	3.06×10^{-2}	121.95	5.41×10^{-3}	0.72	0.88	18.93	-7.65	40 °C, pH 2
Biogas sludge	1.28×10^{-2}	5.87	–	1.50	0.49	2.73	-2.53	30 °C, pH 2
Rubber sawdust	1.50×10^{-2}	–	–	9.39	0.53	2.28	-2.14	40 °C, pH 2

^a This study.

Table 7
Adsorption free energy change (ΔG°) values

C_0 (mg/L)	ΔG° (kJ/mol)				
	20 °C	30 °C	40 °C	50 °C	At optimum conditions
40	3.999	2.546	2.296	2.350	-7.528
60	3.724	2.197	1.804	2.067	-7.653

Table 8
Adsorption enthalpy (ΔH°) and entropy (ΔS°) values

C_0 (mg/L)	ΔH° (J/mol)	ΔS° (J/mol K)
40	20.143	56.494
60	19.689	55.975

Free energy values were calculated by using Eq. (15) and results are presented in Table 7. Negative value of free energy indicates that adsorption is a spontaneous process. It is worthwhile that free energy values calculated from the uncontrolled pH experiments data are negative whereas they are positive for the experiments carried out under the optimum conditions. This indicates the importance of the conditions of adsorption medium beside the physical and chemical properties of adsorbent and adsorbate.

Adsorption enthalpy and entropy were calculated starting from Eq. (16) and drawing $\log K_C$ versus $1/T$ plot. Results are given in Table 8.

Positive value of adsorption enthalpy shows that process is endothermic. Increase in equilibrium constant with increasing temperature, positive value of adsorption enthalpy and its magnitude (magnitude of a chemical adsorption enthalpy is nearly equal to that of a chemical reaction) imply that adsorption of Cr(VI) on sawdust is a chemical adsorption [28,37,49]. Further the positive value of adsorption entropy supports the above conclusion withdrawn by considering the negative value of free energy change that process is spontaneous [50,52].

Results reported in the literature [47,50,53] for the adsorption of chromium ions on natural materials have been presented in Table 9 together with the values obtained in this study for comparison purposes.

Values presented in the tables were obtained by using the same procedure used in this study, therefore, they can be compared directly. Comparison of the reaction rate constants obtained by using Lagergren equation showed that the adsorption rate achieved in this study is higher than the reported values. Values of equilibrium constants calculated from experimental results obtained at optimum conditions showed that amount of adsorbed chromium ion in this study is higher than the ones obtained in the other studies. In other words, removal percentage in this study is better than those obtained in other reported studies. Of course this difference is essentially due to the difference between the physical and chemical properties of the adsorbents used in these studies.

On the other hand, operation conditions are very important. ΔG° value obtained under the uncontrolled pH conditions was negative whereas it was obtained as positive when studied at optimum conditions. This kind of a change in the sign of free energy occurs only due to change in the adsorption mechanism. This change in the mechanism may be expressed by the change in the surface charge distribution of the adsorbent that arises from the change in the pH of the solution.

4. Conclusions

Comparison of experimental values and Langmuir and Freundlich isotherms showed that Langmuir isotherm confirms very well with the experimental data. Regression coefficient values also support this observation. This observation suggests that the adsorption of chromium ion on pine sawdust treated with 1,5-disodium hydrogen phosphate is a monolayer adsorption.

It was concluded from the comparison of Q_0 value obtained in this study with the ones reported in the literature that, sawdust can be used as an efficient adsorbent material for the removal of chromium ion from wastewaters.

Value of Q_0 was obtained as 30.488 at 20 °C under the uncontrolled pH conditions by using 2 g of sawdust. This value increased four times when operation conditions adjusted to the optimum conditions. Chromium(VI) is an anionic metal and its compounds change with the changing pH of the solution. On the other hand, charge distribution on surface of the sawdust depends on the pH of the solution. Therefore, it has been concluded that the reason of this increase in the Q_0 value is the adjustment of pH of solution to 2.

Application of Lagergren equation to the experimental data gave a straight line which shows that adsorption process obeys the first order rate law.

Other important conclusions withdrawn from values of thermodynamic parameters can be stated as, negative value of ΔG° and positive ΔS° show that adsorption of chromium ion on sawdust is a spontaneous process and negative value of ΔH° indicates that adsorption is endothermic and therefore it is possibly a chemical adsorption process.

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