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# Kinetics, thermodynamics, and isotherms studies of Cd(II) adsorption onto grape stalk

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ABSTRACT

In this study, the ability of grape stalk residue of wine production to remove Cd(II) from aqueous solution by adsorption has been investigated through batch experiments. The grape stalk was characterized in detail by Fourier transform infrared spectrophotometer, scanning electron microscopy, BET, particle size, and elemental analysis. The Cd(II) adsorption property of the grape stalk was evaluated as a function of pH, adsorbent dosage, particle size, initial Cd(II) concentration, and temperature. The adsorption kinetics was evaluated with the pseudo-first-order, second-order kinetics models, and intraparticle diffusion model. The equilibrium data were analyzed using Langmuir and Freundlich isotherms. The adsorption kinetics followed the second-order rate law. The adsorption of Cd(II) onto the grape stalk is fitted to the Langmuir isotherm, and the maximum adsorption capacity was 21.5 mg-Cd(II)/g. Thermodynamic parameters including the changes of enthalpy ($\Delta H$), free energy ($\Delta G$), and entropy ($\Delta S$) were evaluated. The calculated thermodynamic parameters showed that adsorption of Cd(II) was spontaneous and exothermic under examined conditions.

*Keywords:* Cadmium; Grape stalk; Adsorption kinetic; Thermodynamic; Isotherm

## 1. Introduction

Heavy metals and their compounds have many industrial uses such as alloying, electroplating, textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others. As a result of unregulated applications and inappropriate waste-disposal practices, heavy metal contamination of surface and ground water has become a significant environmental problem. Heavy metals tend to accumulate in living organism by joining the food chain, causing various toxic effect and diseases. Since they are not biodegradable, when they are released into the waters, most of them are strongly retained and their adverse effects can last for a long time. Thus, it is important to apply an effective treatment method to wastewaters polluted with heavy metals. The treatment methods for heavy metal-bearing wastewaters commonly include chemical precipitation, ion exchange, cementation, electrode position, membrane systems, solvent extraction, and adsorption. Among these methods, adsorption is a highly effective method in terms of initial cost, simplicity of design, and ease of operation, especially for wastewaters that contain low concentrations of metals and complex-forming substances [1]. Activated carbon is the most widely used adsorbent in the wastewater

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treatment. High cost of activated carbon limits its use as an adsorbent [2]. Therefore, the cost-effective alternative adsorbents for removal of heavy metals from aqueous solutions are needed.

Hundreds of studies on the use of low-cost adsorbents for heavy metal adsorption have been published up to now. Particularly, usages of the low-cost adsorbents such as agricultural residuals, metallurgical slags, fly ashes, and various minerals have been widely investigated. Kurniawan et al. [3], Mohan and Pittman [4], Demirbaş [5], Salam et al. [6], and Ahmaruzzaman [7] reviewed lots of these studies. Among these researches, the removal of heavy metals by adsorption onto agricultural wastes or residues has recently become the subject of considerable interest due to abundant availability and low cost. A lot of agro-based materials such as hazelnut shells [8], peanut hull [9], sawdusts [10], pinus bark [11], coconut husk [12], rice hulls [13], buckwheat [14], bagasse [15], apple wastes [16], tree leaves [17], banana and orange peels [18], *Raphanus sativus* peels [19], and maize leaf [20] were investigated. Grape stalk was also tried for heavy metal removal by Martinez et al. [21]; Fiol et al. [22]; Escudero et al. [23]; Valderrama et al. [24]. However, detailed data have not been reported adsorption kinetics, and particularly thermodynamics of Cd(II) from aqueous solutions by grape stalk. Grape stalk is a naturally abundant biomass with high content of lignin, cellulose, and hemicellulose, and waste produced in great amounts in the industrialization processes of grape. Starting from this point, in this study, it was investigated the possible use of grape stalk as an alternative adsorbent for removal of Cd(II) from aqueous solutions. Batch adsorption studies were carried out systematically in terms of process parameters such as pH, particle size, adsorbent dosage, contact time, initial Cd(II) concentration, and temperature. Langmuir and Freundlich adsorption isotherms were tested at various temperatures and adsorption kinetic and thermodynamic parameters were determined.

## 2. Materials and methods

### 2.1. Materials

Grape stalk used in the study was supplied from a wine plant, Malatya (Turkey). Grape stalk was rinsed three times with tap water and then dried in an oven at 85˚C. It was cut and ground with knife grinder and sieved. It was characterized by Fourier transform infrared spectrophotometer (FTIR), scanning electron microscopy (SEM), BET, particle size, and elemental analysis.

Cd(II) solution was prepared by dissolving appropriate amount of $Cd(NO_3)_2{\cdot}4H_2O$ in distilled water. pH adjustments were made by using $HNO_3$ and NaOH solutions. All reagents used in the study were in the analytical reagent grade.

### 2.2. Adsorption experiments

Adsorption experiments were carried out in the batch reactors (250 mL Erlenmeyer) containing various amounts of adsorbent and 100 mL of Cd(II) solutions having different concentrations and pH. The batch reactors were shaken at 200 rev/min by using a flask shaker (GFL 1083) for contact times ranging from 5 to 180 min. From the obtained results, optimum pH, adsorbent dosage, particle size of adsorbent, and contact time were selected for further studies. For the adsorption isotherm studies, reactors containing Cd(II) solutions of different concentrations in the range of 25–400 mg/L were shaken at the conditions of pH, adsorbent dosage, and contact time optimized.

At the end of the predetermined contact period, reaction mixtures were filtered and then the final pH of the filtrates was measured by a pH meter (Orion 4 star). The filtrates were acidified with 1 mL of $HNO_3$ solution to prevent the precipitation of Cd(II) and then they were analyzed for Cd(II).

The experiments were performed in duplicate and mean values were taken into account.

### 2.3. Methods of analysis

Grape stalk used in the study was characterized FTIR (ATI Unicam Mattson 1000 Fourier Transform Infrared Spectrophotometer), SEM (JEOL/JSM-6510 LV), BET (Quantrachrome Instruments Nova 4000E), particle size (Malvern Master Sizer 3000), and elemental analysis (LECO CHNS 932). Cd(II) analysis in the solutions was made by Perkin Elmer AAnalyst 800 atomic absorption spectrophotometer. In order to explain the Cd(II) uptake mechanism, FTIR and SEM analyses were performed with free and Cd(II)-loaded grape stalks.

## 3. Results and discussion

### 3.1. Characterization of grape stalk

In order to determine the type of functional groups on the grape stalk, the sample was subjected to FTIR analysis. Fig. 1(a) shows the FTIR spectra of the grape stalk. The broad band at 3,340/cm indicates hydroxyl groups. The peaks observed at 2,921 and 1,620/cm

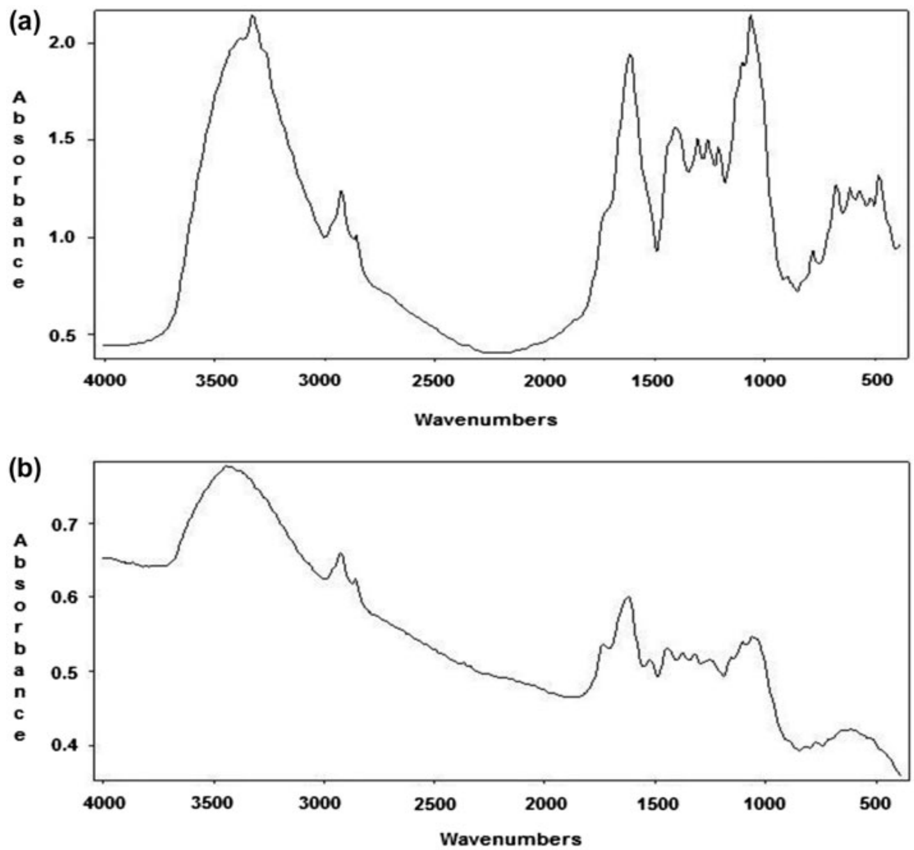


Fig. 1. FTIR spectra of grape stalk (a) and grape stalk loaded with Cd(II) (b).

can be assigned to the C–H group and C=C stretching, respectively. The region between 1,610 and 1,500/cm is associated with C–C stretching in aromatic rings. These groups are present on the lignin structure [25].

Taking the adsorption mechanism into account, FTIR analysis is considered to be a useful technology for exploring the adsorption behaviors of metal ions on adsorbents. In order to further confirm the adsorption mechanism of grape stalk for Cd(II), the changes of characteristic absorption peaks in adsorbents, before and after adsorption, were investigated by FTIR. A peak verified is observed at 1,610/cm (Fig. 1(b)). This situation may be attributed to the grape stalks that were loaded with Cd(II). A considerable decrease in the intensity of this band was observed after contact with Cd(II) solutions. Thus, when the grape stalks were loaded with Cd(II), the intensity of this band was strongly influenced by structures bordering on the aromatic nuclei.

The SEM images of free grape stalk and grape stalk loaded with Cd(II) showed different surface characteristics (Fig. 2(a) and (b)). The surface of free grape stalk appeared to be rough in nature, while some occlusions were observed on the surface after Cd(II) adsorption, probably due to the formation of a cadmium–grape stalk complex, involving carboxyl, hydroxyl, and amino groups (Fig. 2(b)).

The specific surface area and average particle size of grape stalk was determined to be 0.316 $m^2/g$ and 50.15 μm, respectively. Elemental analysis of the material showed that it contains 41.58% C, 4.91% H, 1.182% N, and 0.163% S.

### 3.2. Effect of pH

Adsorbate structure and functional groups on the adsorbent surface are significantly affected by pH. Therefore, pH is one of the most important parameters that control the adsorption process during the transition of absorbate from liquid phase to solid surface. Especially in heavy metal adsorption processes, any change in pH value can cause hydrolysis, precipitation, and complex ion or complex compound forming. Therefore, pH has top priority in parameters to be optimized in the adsorption processes. The effect of pH on Cd(II) adsorption from aqueous solution onto

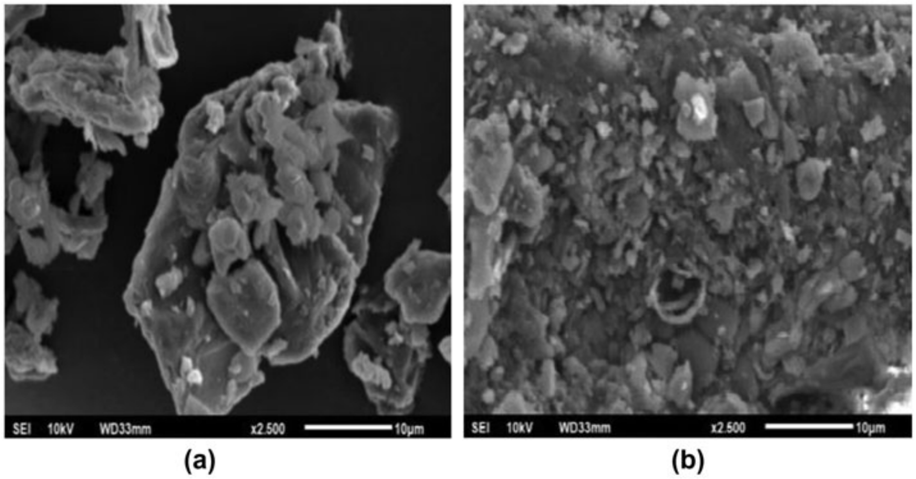


Fig. 2. SEM micrographs of grape stalk (a) and grape stalk loaded with Cd(II) (b).

grape stalk was investigated at pH range of 2–8 by taking into account precipitation pH value of Cd(II) [26]. Fig. 3 shows the percentages of Cd(II) sorbed from solution onto grape stalk vs. solution pH. The adsorption percentages of Cd(II) were low at low pH, because the hydrogen ($H^+$) ions having higher concentration at low pHs cause an increase in positive surface charge that weakens electrostatic force of attraction for Cd(II) by competing with Cd(II) at sorption sites. Similar results have been also reported for cadmium ions with some indigenous adsorbents [27,28]. However, as the pH increases, more negatively charged adsorbent surface becomes available thus facilitating greater metal uptake. The adsorption yields were sharply increased up to pH 6 and maximum value was reached at this pH. At the higher than pH 6, it almost remained constant. Therefore, it can be concluded that the pH of 6 is more reasonable for Cd(II) adsorption onto grape stalk. This pH is in agreement with the results of some earlier studies [29,30], thus, and subsequent experiments were carried out at pH 6.

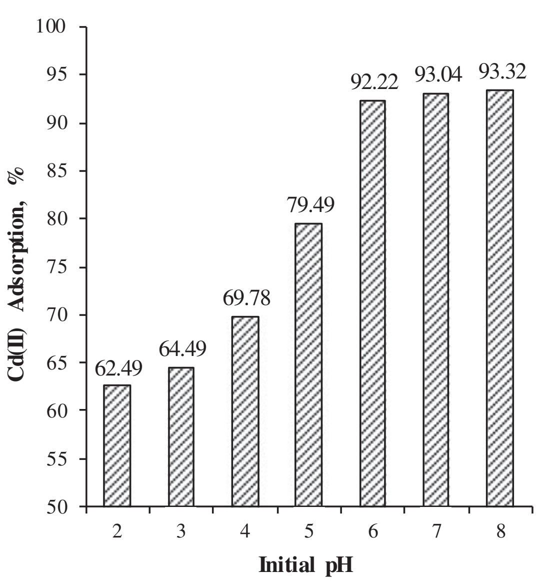


Fig. 3. The effect of pH on the Cd(II) adsorption by grape stalk [Cd(II) concentration: 10 mg/L; adsorbent dosage: 10 g/L; contact time: 60 min; particle size: −100 + 140 mesh; and temperature: 25˚C].

### 3.3. Effect of particle size

Surface area, particle size, and pore structure are the other important parameters that affect adsorption process. Since adsorption is an event occurring on the solid surface, an adsorbent with smaller particle size, a larger surface area, and more porous is preferred. In the study, effect of the particle size of grape stalk on the Cd(II) adsorption was investigated with grape stalks having different particle sizes. The obtained results are presented in Fig. 4. The increase in percentage removal of Cd(II) with the decrease in particle size of the adsorbent was very small (less than 8%). On reducing the particle size from −50 + 80 mesh (about 0.177–0.3 mm) to −200 mesh (0.075 mm), the removal percentage of Cd(II) increased from 84.11 to 92.63%. Among the particle sizes tried in the experiment, the percentage removal was maximum for the particle size range from −100 + 140 mesh to −200 mesh. Since a reduction of the particle size does not lead to a higher total number of active sites available, the reduction of

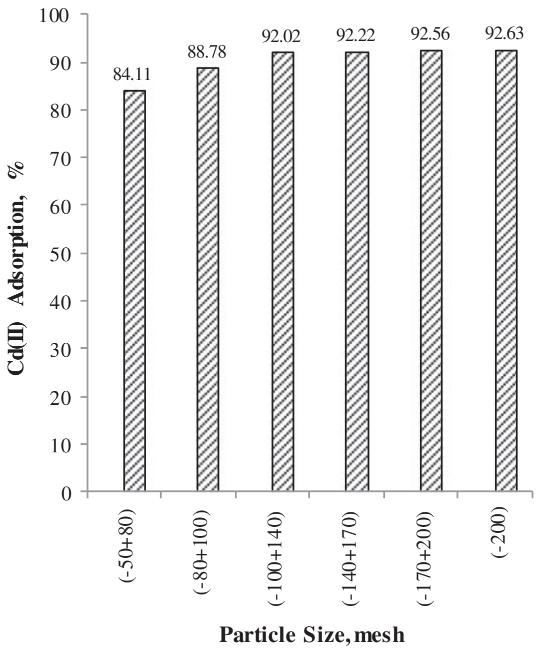


Fig. 4. The effect of particle size on the Cd(II) adsorption by grape stalk [Cd(II) concentration: 10 mg/L; adsorbent dosage: 10 g/L; pH 6; contact time: 60 min; and temperature: 25℃].

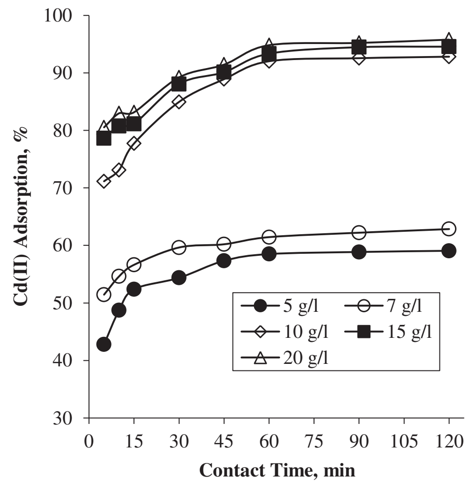


Fig. 5. The effects of adsorbent dosage and contact time on the Cd(II) adsorption by grape stalk [Cd(II) concentration: 10 mg/L; pH 6; particle size: −100 + 140 mesh; and temperature: 25℃].

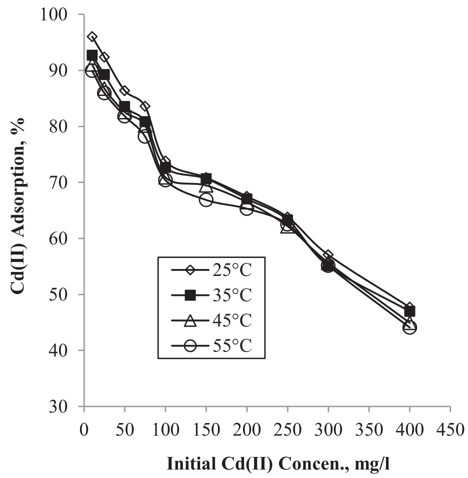


Fig. 6. The effects of initial Cd(II) concentration and temperature on the Cd(II) adsorption by grape stalk [adsorbent dosage: 10 g/L; contact time: 60 min; and particle size: −100 + 140 mesh].

particle size does not improve the percentage removal much. Therefore, it can be stated that the optimum particle size of grape stalk for Cd(II) adsorption may be considered as −100 + 140 mesh.

### *3.4. The effects of the grape stalk dosage and contact time*

Generally, an adsorbent quickly adsorbs the molecules or ions in the liquid film surrounding. Therefore, the adsorption rate is higher at the time of first contact, but a decrease is observed with increasing contact time and it remains constant after the adsorbents surfaces are saturated with metal ions. In order to determine this situation, the effect of the grape stalk dosage on the removal of Cd(II) was studied depending on contact time by varying the adsorbent dosage in the range of 5–20 g/L. The results are presented in Fig. 5.

In all cases, the Cd(II) adsorption yield increases with the increasing adsorbent dosage. Grape stalk dosage of 10 g/L has the most effective adsorption yield. The adsorption yield also increases with contact time and attains a maximum value at 60 min, thereafter, it remains almost constant. Therefore, it can be concluded that the adsorbent dosage of 10 g/L and contact time of 60 min are more reasonable for Cd(II) adsorption onto grape stalk.

### *3.5. Effects of initial Cd(II) concentration and temperature*

The effect of initial Cd(II) concentration on the adsorption was investigated by changing the initial Cd(II) concentration in the range of 10–400 mg/L under the optimized conditions (initial pH of 6; contact time of 60 min; adsorbent dosage of 10 g/L; and temperature of 25℃). The Cd(II) adsorption percentage and calculated adsorption densities depending on initial Cd(II) concentration are presented in Fig. 6. The Cd(II) adsorption yield decreases with the increasing initial Cd(II) concentration. When the initial Cd(II) concentration was increased from 10 to 400 mg/L, the adsorption percentage decreased from 96.02 to 47.7%. However, amount of the Cd(II) sorbed per g grape stalk, which is adsorption density, increases. For example, while the adsorption percentages for initial Cd(II) concentration values of 50, 100, and 400 mg/L were found to be 86.38, 73.82, and 47.7%, adsorption density values of them were found to be 4.32, 7.38, and 19.08 mg-Cd(II)/g grape stalk, respectively.

Fig. 6 also shows the Cd(II) adsorption percentages as a function of temperature. It can be seen that the Cd(II) adsorption percentage slightly decreases with the increasing temperature. This decrease in Cd(II) adsorption yield by the increasing temperature suggests that the adsorption process is exothermic. In the some investigations carried out with agro-based adsorbents, similar results have also been reported that the adsorption yields decrease with the increasing temperature and these adsorption processes are physical [31].

### 3.6. Adsorption kinetics

The adsorption kinetics that describes the solute uptake rate governing the contact time of the adsorption is one of the important characteristics that define the efficiency of the adsorption. Adsorption kinetics gives important information for designing adsorption systems. Although there are various kinetic models used to describe the uptake of metals on different adsorbents, pseudo-first-order, second-order, and intraparticle diffusion kinetic models have been widely used [32]. In order to analyze the adsorption rate of Cd(II) onto the grape stalk, all three models were employed to interpret the experimental data. In addition, in order to determine the rate constant ($k$) of adsorption, kinetic analyses were made at various temperatures depending on contact time by using following first-order rate expression of Lagergren (Eq. (1)) and second-order kinetic model (Eq. (2)) and intraparticle diffusion model given by Weber Morris (Eq. (3)):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \tag{2}$$

$$q_t = k_{id} t^{1/2} + c \tag{3}$$

where $q_e$ and $q_t$ (both in mg/g) are amount of Cd(II) adsorbed per gram grape stalk at equilibrium and any time, $C_t$ and $C_0$ are concentrations of Cd(II) in the solution any time and initial, $k_1$ (min), $k_2$ (L/mg min), and $k_{id}$ (mg/g min$^{1/2}$) are the first-order, second-order, and intraparticle diffusion rate constants of adsorption, respectively.

Straight lines will be obtained of the left-hand sites the three equations vs. $t$ for Eqs. (1) and (2), and $t^{1/2}$ for Eq. (3) suggest the applicability of these kinetic models (Fig. 7). Data obtained in this study were well fitted to the second-order rate expression. The correlation coefficient values ($R^2$) for the rate expression were found greater than 0.98 for all temperatures studied. The values of $k_2$ at 25, 35, and 45℃ were calculated to be 0.0164, 0.0137, and 0.0109/min from the slopes of the straight lines, respectively. The decrease in rate constants depending on temperature shows that the rate-limiting step is surface adsorption and the process is exothermic.

The Arrhenius Equation (Eq. (4)) expresses rate constant of the adsorption reaction as a function of temperature and the activation energy of the process is calculated from the Eq. (4).

$$k = A.e^{-E_A/RT} \tag{4}$$

where $k$ is rate constant at temperature of $T$ (K), $A$ is frequency factor, $R$ is universal gas constant (8.314 J/g mol K), and $E_A$ (J/g mol) is activation energy for the adsorption process. The magnitude of activation energy may give an idea about the type of adsorption. There are two types of adsorption; physical and chemical. In the physical adsorption, the equilibrium is rapidly attained and reversible. Since the effective forces for this type of adsorption are weak, its activation energy value is low. On the contrary, chemical adsorption has higher activation energy value and it is specific. Also, the rate in chemical adsorption varies with increasing temperature [33]. In order to determine adsorption type of Cd(II) adsorption onto grape stalk, Arrhenius Equation was used. For this purpose, ln $k_2$ values were plotted vs. $1/T$ and activation energy value was calculated to be 16.08 kJ/g mol from the slope of the line. Low activation energy value indicates that physical forces govern the adsorption process.

### 3.7. Adsorption isotherms

Adsorption isotherms are commonly used for describing adsorption equilibrium for wastewater treatment. Langmuir and Freundlich adsorption isotherms are classical models to describe the equilibrium between metal ions adsorbed onto adsorbent and metal ions in solution at a constant temperature. These

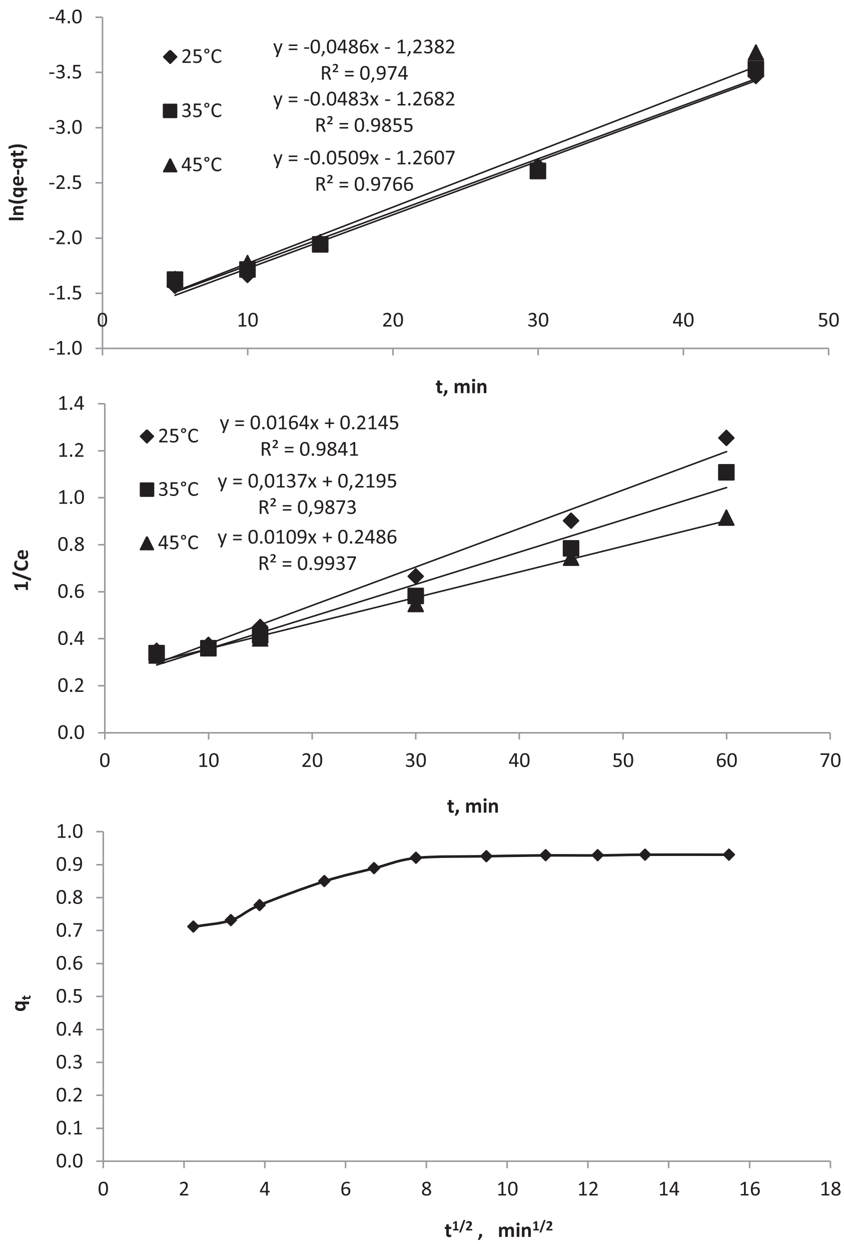


Fig. 7. Lagergren's pseudo-first-order and second-order kinetic model for the adsorption of Cd(II) onto grape stalk [Cd(II) concentration: 10 mg/L; initial pH 6; adsorbent dosage: 10 g/L].

models were applied for Cd(II) adsorption onto grape stalk in this study. For this purpose, the experimental data obtained under the various concentrations and temperatures were plotted in linearized forms of Langmuir (Eq. (5)) and Freundlich (Eq. (6)) adsorption isotherms.

$$\frac{C_e}{x/m} = \frac{C_e}{q_e} = \frac{1}{bQ^\circ} + \frac{C_e}{Q^\circ} \tag{5}$$

$$\ln\frac{x}{m} = \ln q_e = \ln k_f + n \ln C_e \tag{6}$$

where $C_e$ is equilibrium concentration of Cd(II) (mg/L), $x/m$ is amount of Cd(II) adsorbed at equilibrium (mg/g), $Q^\circ$, $b$, $k_f$, and $n$ are isotherm constants. $Q^\circ$ and $k_f$ are defined as adsorption maxima or adsorption capacity (mg/g) for Langmuir and Freundlich isotherms, respectively.

Langmuir and Freundlich adsorption isotherms of Cd(II) on grape stalk are shown in Fig. 8. The isotherm constants and correlation coefficients ($R^2$) calculated at different temperatures are also tabulated in Table 1. Experimental data were fitted to both the isotherms. But, the correlation coefficients of Langmuir adsorption isotherm showed that the Langmuir isotherm yielded the best fitted to experimental data. As seen from Table 1, Langmuir adsorption capacity values slightly decreased by the increasing temperature. The other Langmuir parameter $b$ shows a similar trend. This situation confirms the finding that physical forces govern the adsorption process.

It has been determined that the Cd(II) maximum adsorption capacity ($Q^\circ$) of grape stalk is 21.5 mg/g at 25˚C. In the earlier studies related to Cd(II) adsorption, it has been determined that the adsorption capacities of spent grain [34], rice husk [35], sugar beet pulp [36], and peanut hull [37] are 17.3, 8.58, 24.3, and 6 mg/g, respectively. When taking into consideration, Cd(II) adsorption capacities of the adsorbents mentioned above and the values obtained from the present study to be 21.5 mg/g, it can be seen that the Cd(II) adsorption efficiencies of the agro-based adsorbents mentioned decrease in the order of sugar beet pulp > grape stalk > spent grain > rice husk > peanut hull.

### 3.8. Adsorption thermodynamics

The decreasing adsorption efficiency with increasing temperature can be explained on the basis of some thermodynamic parameters such as the changes in Gibbs free energy ($\Delta G^\circ$), standard enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$), which can be calculated using equations (7–9);

$$\ln\frac{1}{b} = \frac{\Delta G^\circ}{RT} \tag{7}$$

$$\ln b = \ln b_o - \frac{\Delta H^\circ}{RT} \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

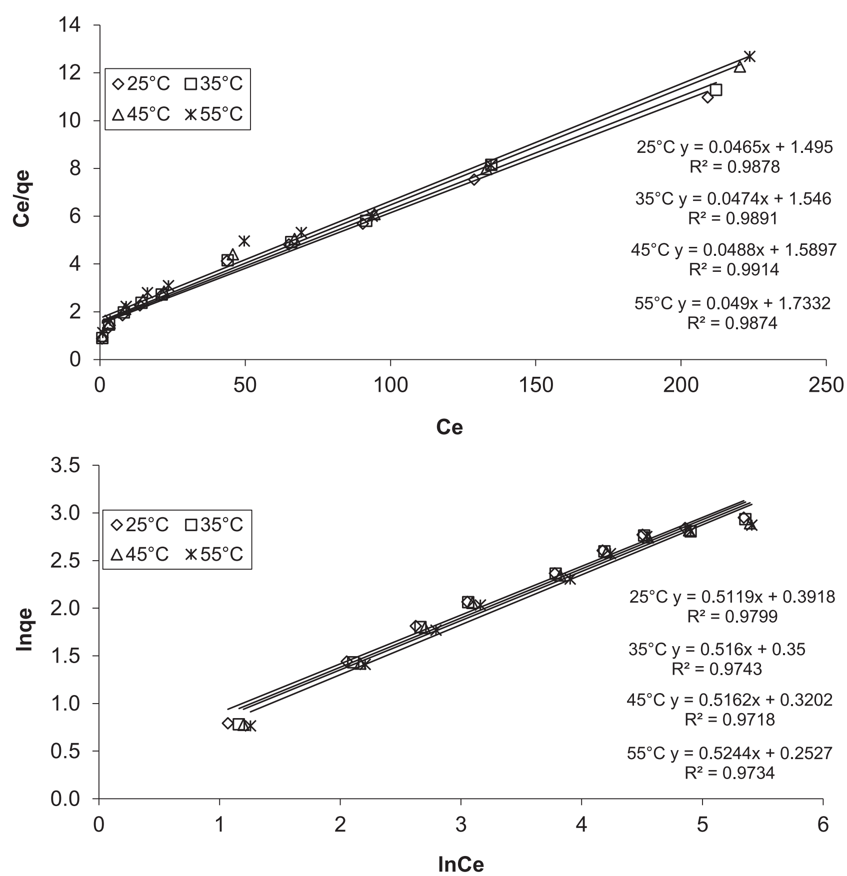


Fig. 8. Langmuir and Freundlich adsorption isotherm of Cd(II) by grape stalk.

Table 1
Correlation coefficients and isotherm parameters for Langmuir and Freundlich Isotherms of Cd(II) adsorption onto grape stalk

| | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| Temperature, ℃ | $k_f$ | $n$ | $R^2$ | $b$ (l/mg) | $Q^\circ$ (mg/g) | $R^2$ |
| 25 | 1.4796 | 1.9535 | 0.9799 | 0.0311 | 21.5053 | 0.9878 |
| 35 | 1.4191 | 1.9380 | 0.9743 | 0.0306 | 21.0970 | 0.9891 |
| 45 | 1.3774 | 1.9372 | 0.9718 | 0.0302 | 20.4918 | 0.9914 |
| 55 | 1.2875 | 1.9069 | 0.9734 | 0.0282 | 20.4081 | 0.9874 |

Table 2
Thermodynamic parameters for the adsorption of Cd(II) onto grape stalk

| Temperature, ℃ | $-\Delta G^\circ$, kJ/g mol | $\Delta S^\circ$, kJ/g mol K |
|---|---|---|
| 25 | −20.225 | $71.72 \times 10^{-3}$ |
| 35 | −20.862 | $71.46 \times 10^{-3}$ |
| 45 | −21.504 | $71.23 \times 10^{-3}$ |

where $b$ is Langmuir constant which is related with the energy of adsorption, $b_o$ is a constant, $R$ is ideal gas constant, and $T$ is temperature (K) [33].

The standard enthalpy change ($\Delta H^\circ$) of the Cd(II) adsorption onto grape stalk was determined to be −1.159 kJ/g mol from the $\ln 1/b$ vs. $1/T$. The negative values of $\Delta H^\circ$ suggest the exothermic nature of adsorption. The Gibbs' free energy ($\Delta G^\circ$) and entropy values ($\Delta S^\circ$) for the adsorption process were calculated from Eqs. (7) to (9) and tabulated in Table 2. The negative Gibbs' free energy values confirm that the adsorption is spontaneous. The increase in free energy change with the decreasing temperature shows an increase in feasibility of adsorption at lower temperatures.

## 4. Conclusions

In this study, Cd(II) was removed successfully from aqueous solution by adsorption on grape stalk. Maximum Cd(II) removal percentage of 92.06 was found at conditions of 6 pH value, 10 g/L adsorbent dosage, and 60 min contact time. Equilibrium adsorption data were well represented by Langmuir isotherm, showing maximum adsorption capacity of 21.50 mg/g at 25℃. The adsorption kinetic data were well described by the pseudo-second-order model. The calculated thermodynamic parameters showed that the adsorption of Cd(II) on grape stalk was spontaneous and exothermic. Grape stalk is freely, abundantly, and locally available; the resulting adsorbent is expected to be economically viable for removal of Cd(II) from aqueous solution.

## References

[1] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater. 135 (2006) 264–273.
[2] D. Park, J.H. Yun, Y. Jo, J.M. Park, Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-scale feasibility test, Ind. Eng. Chem. Res. 45 (2006) 5059–5065.
[3] T.A. Kurniawan, Y.S.G. Chan, W.H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366 (2006) 409–426.
[4] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.
[5] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: A review, J. Hazard. Mater. 157 (2008) 220–229.
[6] O.E.A. Salam, N.A. Reiad, M.M. ElShafei, A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents, J. Adv. Res. 2 (2011) 297–303.
[7] M. Ahmaruzzaman, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, Adv. Colloid Interfac. 166 (2011) 36–59.
[8] G. Cimino, A. Passerini, G. Toscano, Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell, Water Res. 34 (2000) 2955–2962.
[9] A. Hashem, E.S. Abdel-Halim, Kh.F. El-Tahlawy, A. Hebeish, Enhancement of the adsorption of Co(II) and Ni(II) ions onto peanut hulls through esterification using citric acid, Adsorp. Sci. Technol. 23 (2005) 367–380.
[10] Y. Bulut, Z. Tez, Removal of heavy metals from aqueous solution by sawdust adsorption, J. Environ. Sci. 19 (2007) 160–166.
[11] G. Vázquez, J. González-Álvarez, S. Freire, M.L. López-Lorenzo, G. Antorrena, Removal of cadmium and mercury ions from aqueous solution by sorption on treated Pinus pinaster bark: Kinetics and isotherms, Bioresour. Technol. 82 (2002) 247–251.

[12] N.A.A. Babarinde, Adsorption of zinc (II) and cadmium (II) by coconut husk and goat hair, J. Pure Appl. Sci. 5 (2002) 81–85.

[13] K.S. Low, C.K. Lee, A.Y. Ng, Column study on the sorption of Cr(VI) using quaternized rice hulls, Bioresour. Technol. 68 (1999) 205–208.

[14] Z. Wang, P. Yin, R. Qu, H. Chen, C. Wang, S. Ren, Adsorption kinetics, thermodynamics and isotherm of Hg(II) from aqueous solutions using buckwheat hulls from Jiaodong of China, Food Chem. 136 (2013) 1508–1514.

[15] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res. 36 (2002) 2304–2318.

[16] E. Marañón, H. Sastre, Heavy metal removal in packed beds using apple wastes, Bioresour. Technol. 38 (1991) 39–43.

[17] F.A.A. Al-Rub, Biosorption of zinc on palm tree leaves: Equilibrium, kinetics, and thermodynamics studies, Sep. Sci. Technol. 41 (2006) 3499–3515.

[18] G. Annadurai, R.S. Juang, D.L. Lee, Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol. 47 (2002) 185–190.

[19] M.A. Ashraf, M.A. Rehman, Y. Alias, I. Yusoff, Removal of Cd(II) onto *Raphanus sativus* peels biomass: Equilibrium, kinetics, and thermodynamics, Desalin. Water Treat. 5 (2013) 22–44.

[20] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of heavy metals, Res. J. Chem. Environ. 7 (2003) 71–79.

[21] M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste, J. Hazard. Mater. 133 (2006) 203–211.

[22] N. Fiol, C. Escudero, I. Villaescusa, Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark, Bioresour. Technol. 99 (2008) 5030–5036.

[23] C. Escudero, N. Fiol, J. Poch, I. Villaescusa, Modeling of kinetics of Cr(VI) sorption onto grape stalk waste in a stirred batch reactor, J. Hazard. Mater. 170 (2009) 286–291.

[24] C. Valderrama, J.A. Arévalo, I. Casas, M. Martínez, N. Miralles, A. Florido, Modelling of the Ni(II) removal from aqueous solutions onto grape stalk wastes in fixed-bed column, J. Hazard. Mater. 174 (2010) 144–150.

[25] P.C.E. Lopez, H. Herrera, Pyrolysis of lignin and IR analysis of residues, Thermochim. Acta 293 (1997) 39–46.

[26] A.I. Vogel, Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis, Longman, New York, NY, 1979.

[27] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: Kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[28] M.R. Panuccio, A. Sorgonà, M. Rizzo, G. Cacco, Cadmium adsorption on vermiculite, zeolite and pumice: Batch experimental studies, J. Environ. Manage. 90 (2009) 364–374.

[29] M.I. Kandah, Zinc and cadmium adsorption on low-grade phosphate, Sep. Purif. Technol. 35 (2004) 61–70.

[30] M. Erdem, A. Ozverdi, Kinetics and thermodynamics of Cd(II) adsorption onto pyrite and synthetic iron sulphide, Sep. Purif. Technol. 51 (2006) 240–246.

[31] N. Gupta, S.S. Amritphale, N. Chandra, Removal of lead from aqueous solution by hybrid precursor prepared by rice hull, J. Hazard. Mater. 163 (2008) 1194–1198.

[32] H. Qiu, L. Lv, B. Pan, Q.J. Zhang, W.M. Zhang, Q.X. Zhang, Critical review in adsorption kinetic models, J. Zhejiang Univ. Sc A 10 (2009) 716–724.

[33] J.M. Smith, Chemical Engineering Kinetics, McGraw-Hill, New York, NY, 1981.

[34] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process Biochem. 36 (2000) 59–64.

[35] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (2006) 104–109.

[36] R. Zacaria, C. Gerente, Y. Andres, P.L. Cloirec, Adsorption of several metal ions onto low-cost biosorbent: Kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[37] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 19–29.