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Branch Wastes of Grape Bushes as a Low-cost Adsorbent for Copper Ions Removal from Water Solutions

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ABSTRACT

. The branch wastes of grape bushes as adsorbent for copper (II) ions removal from water solutions was investigated. The equilibrium sorption data were fitted to Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherms. The coefficient of determination value of Langmuir equation was the highest (0.9994). The maximum monolayer sorption capacity is 3.47 mmol g⁻¹. The mean of free energy was determined to be 3.26 kJ mol⁻¹. The calculated value of heat of adsorption has been obtained 0.627 J mol⁻¹. The kinetic data are better described by the pseudo-second model. The calculated values of the maximum sorption capacity from the pseudo-second order equation (3.16 mmol g⁻¹) and from the D-R isotherm (3.145 mmol g⁻¹) are well agreements with its experimentally found value (3.264 mmol g⁻¹). The negative value of ΔH° (-0.15 kJ mol⁻¹K⁻¹) indicates a decreased disorder during adsorption process.

Key words: Adsorption, Branch wastes of grape bushes, Copper ions, Adsorption isotherms, Kinetics, Thermodynamic parameters.

1. INTRODUCTION

Pollution of the biosphere by heavy metals became one of the global problems caused by their receipt in environment with industrial sewage. These metals are capable to concentrate in plants, reservoirs, the soil, and then with food and drinking water to come to a human body. In this regard, the problem of development of sorbents is actual, effectively to take ions of heavy metals from water environments. The high cost of synthetic polymeric sorbents interferes with widespread introduction of sorption technologies on the extraction of heavy metals from water environments. Therefore, development of cheap and readily available sorbents based on the agricultural waste containing natural polymeric materials is economically expedient. The analysis of results of the published works shows that many wastes of agricultural products are effective sorbents for extraction of copper ions from water solutions. The potato peels, which are normally discarded as solid waste, have been used for removal toxic metal ions from water/industrial wastewater [1]. Kinetic and isotherm studies were carried out by studying the effects of various parameters such as temperature, pH, and solid liquid ratios. The equilibrium data at different temperatures were analyzed by Langmuir and Freundlich isotherms.

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In work [2], spent tea leaves were used as a nonconventional, cost-effective sorbent for removal of copper (II) ions from aqueous solutions in batch systems. The equilibrium sorption data were applied to various sorption isotherm models, and the order of fitness was Langmuir > Temkin > Freundlich. The maximum sorption capacity was found to be almost 90.9 and 68.4 mg g⁻¹, as evaluated using Langmuir isotherms at 27°C and 37°C, respectively. The observed decrease in sorption capacity with increase temperature indicated the exothermic nature of the uptake process. A pseudo-second-order kinetic model best interpreted the kinetic uptake data. The sorption mean free energy was found to be 9.91 kJ·mol⁻¹, indicating ion exchange/chemisorptions nature of uptake process. Papaya seeds and papaya wood are using for removal copper and of the heavy metals ions from water solutions [3,4]. Equilibrium data were analyzed using the Langmuir and Freundlich isotherms, whereas the pseudo-first-order and secondorder kinetic models evaluated the adsorption kinetics data. Adsorption isotherm analysis data fitted well to the Langmuir model with a maximum adsorption capacity of 212 mg g^{-1} . The kinetic experimental data correlated well with the pseudo-second-order kinetic model, which indicated that chemisorptions processes

could be the rate-limiting step in the adsorption process. Removal of copper (II) and lead (II) ions from aqueous solutions were studied using pomegranate peel [5]. The experimental equilibrium adsorption data are tested for the Langmuir, Freundlich, and Temkin equations. Adsorption kinetics data were modeled using the pseudo-first and pseudo-second order, Elovich equations, and intra-particle diffusion models. The results indicate that the second-order model best describes adsorption kinetic data. Newspaper pulp was found to be a potential adsorbent for removal of copper ions from aqueous medium [6]. The experimental data were analyzed using Freundlich, Langmuir, Dubinin-Radushkevich (D-R), and Redlich-Peterson isotherm models. It was found that Freundlich, Langmuir, and Redlich-Peterson models fitted well. Adsorption data were analyzed using Lagergren pseudo-first and pseudo-second order. It was observed that pseudosecond-order represented the best correlation. Sorption characteristics of the modified sugar beet pulp toward copper ions were studied with batch experiments [7]. Pseudo-first, pseudo-second-order, and intraparticle kinetic models were applied to the kinetic data and it was found that the sorption processes followed the pseudo-second-order rate kinetics with activation energy of $16.34 \text{ kJ mol}^{-1}$. The equilibration data fit best with the Langmuir isotherm the maximum copper sorption capacity of which is 119.43 mg g^{-1} . The mean free energy of copper sorption process calculated from D-R model and the Polanyi potential concept was found to be in the range of 10.91-11.95 kJ mol⁻¹. In works [8-11], data on the extraction of copper and other heavy metals ions from water solutions and industrial wastes with sawdust, maple wood sawdust, and cation exchanger sawdust are reported. The Langmuir and the Freundlich adsorptions models were applied to describe isotherms and isotherm constants considering the most important parameters. The grape stalks wastes generated in the wine production process has been investigated for the removal of copper and nickel ions from aqueous solutions [12]. The influence of pH, sodium chloride, and metal concentration on metal removal has been studied. Maximum uptake obtained was 1.59×10^{-4} mol of copper and 1.81×10^{-4} mol of nickel per gram of dry sorbent. Sorption of copper and nickel on grape stalks released an equivalent amount of alkaline and alkaline earth metals (K^+, Mg^{2+}, Ca^{2+}) and protons, indicating that ionic exchange is predominantly responsible for metal ion uptake. Equilibrium batch sorption studies were also performed using a two metal system containing (Cu (II) +Ni (II)). There is work on cleaning of wine and water from copper ions with grape bagasse [13].

This study aimed to investigate the efficiency of branch wastes of grape bushes (BGB) as adsorbent for the sorption of Cu^{2+} ions from water solution. Experiments were conducted to investigate the effects of pH, contact time, sorbent dosage and initial concentration copper

ions on the adsorption efficiency of copper ions by BGB. The Langmuir, Freundlich, D–R, and Temkin adsorption isotherms were applied to evaluate the adsorption properties and the pseudo-first-order and pseudo-second-order kinetic models were applied to examine kinetics of the sorption process. In addition, the thermodynamic parameters of the copper ions sorption have been determined. The novelty of this work is that BGBs are used by us first time as a sorbent for removal copper ions from water solutions.

2. EXPERIMENTAL

2.1. Materials

Copper (II) sulfate pentahydrate (Sigma-Aldrich, Germany) has been used for the preparation of stock standard solution of copper (II) ions. A stock standard solution was prepared by dissolving appropriate amount of $CuSO_4$ · SH_2O in deionized water to obtain a final concentration of Cu^{2+} ions of 0.005 M (320 mg L⁻¹). The stock solution was further diluted to obtain solutions with different concentrations of copper ions. A 0.001 mol L⁻¹ xylenol-orange (3,3¹-bis-di(carboxymethyl)aminomethyl-o-cresol sulfophtalein) solution was prepared by dissolving 0.076 g of the reagent in 100 ml of deionized water. Buffer solutions CH₃COOH/NH₄OH with pH 4-9 has been used for definition value pH, at which copper ions form a complex with xylenol orange.

2.2. Methods

Photocalorimeter (model KFK-3M, Russia) was used to determine concentration of copper (II) ions after sorption at 490 nm. The pH values were controlled using pH-meter (model pH-600-AO, Romania). Fourier transform infrared (FTIR) spectra of the sorbent were recorded using a Varian 3600 FTIR spectrometer. 40 ml of CuSO₄ solution of a certain concentration was placed in a 100 ml Erlenmeyer flask containing sample of sorbent and was agitated in a termocontrolled water bath to carry out sorption experiment. At the end of the experiment, a sorbent separated from solution and residual copper ions in solution was defined by a photometric method. For this purpose, 1 ml of the copper ion solution and 2 ml of the xylenol orange solution placed into the 25 ml graduated flask, were diluted with the buffer solution and the optical density has been defined. Residual amount of copper ions was determined using a calibration curve.

The sorption degree (%) and sorption capacity (mmol L^{-1}) of the sorbent were calculated by the equations (1) and (2), respectively.

Sorption degree (%) =
$$\frac{\left(C_0 - C_e\right)}{C_0} \times 100\%$$
 (1)

Sorption capacity (mmol g⁻¹) =
$$\frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}}$$
 (2)

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Where, C_0 and C_e (mmol L^{-1}) are initial and equilibrium concentrations of copper ions solutions, respectively, V_{sol} (L) is the volume of the copper ions solution submitted to sorption, and m_{sorb} (g) is the weight of sorbent.

2.3. Preparation of Sorbent

The cellulose containing sorbent-BGB was used in this work, which represents withdrawal of agro-technical processing of grape bushes. Branches with a diameter of 0.5-1.0 cm and 1.0-2.0 cm long were kept in hot water for 4-5 h to remove dust and other pollution. The clean branches then were processed with ethanol and dried in an oven at 40°C. The dried-up pieces of branches were ground in a blender and the obtained powdery sorbent was placed into the closed flask for further work.

3. RESULT AND DISCUSSION

3.1. Effect of pH

The effect of pH on the adsorption of Cu^{2+} ions by BGB was carried out over the pH range of 4-9, while keeping all other parameters constant. Results showed that copper ions sorption is almost negligible for a pH value below 4, although it increases significantly in the pH range from 4 to 6 and the maximum sorption degree reached at pH 6. This fact can be explained like that electrostatic forces in the adsorption process increase with the increase of negative charges on the adsorbent surface. It leads to increase number of negative groups necessary for fixing of metal ions, and as a result, competition between a proton and metal ions is eliminated. Results showed that BGB shows optimum sorption capacity toward Cu^{2+} ions at pH 6. The future increase in pH leads to decrease of the sorption degree. Whereas, $Cu(OH)_2$ will be the dominant species at pH more than pH 6 [14]. On the other hand, the dependence of copper uptake by the biomasses on pH is related to the association-dissociation of the functional groups, like the carboxylic groups, and to the competition between the H^+ and Cu^{2+} ions for the active sorption sites [15]. It is known that at low pH most of the carboxylic groups are not dissociated and cannot bind the metal in solution.

3.2. Effect of Adsorbent Dosage

Adsorbent dosage seemed to have a great effect on adsorption process. Dependence of the sorption degree from a sorbent weight has been studied in the range of a sorbent weight from 0.01 to 0.15 g at $C_0=4.0$ mmol L^{-1} , contact time 30 min, pH 6, $V_{so}=0.04$ L, 20°C. It has been established that with increase in weight of a sorbent from 0.01 to 0.05-0.06 g the sorption degree sharply increases, and then there is practically constant value. It is connected, probably, with gradual saturation of the active sites of a sorbent by copper ions at the fixed concentration of the metal ions. Therefore, in further experiments, 0.05 g of sorbent was used.

3.3. Effect of Contact Time

The adsorption of Cu^{2+} ions ions by BGB at different contact time is shown in Figure 1. The adsorption process increased with increasing contact time, and the adsorption occurred rapidly at the first 60 min, followed by a slower adsorption phase after this. The Cu^{2+} ions adsorption during the rapid phase was amounted to be around 80%. The adsorption of the remaining copper ions continued in the slower phase until the adsorption achieved almost 86.1% at 120 min. Therefore, the contact time equal to 60 min was considered to be sufficient for sorption of copper ions onto BGB and has been used for all experiments.

3.4. Effect of Copper Ions Initial Concentration

The solutions containing different initial concentrations of copper ions (2.0-8.0 mmol L^{-1}) were prepared and employed for the adsorption studies to check the applicability of the Langmuir, Freundlich, D–R, and Temkin adsorption isotherms under optimum



Figure 1: The effect of contact time on adsorption (C_0 =4.0 mmol L⁻¹, m_{sorb}=0.05 g, V_{sol}=0.04 L).



Figure 2: Plot of C_e versus q_e (C_o =2.0-8.0 mmol L⁻¹, V_{sol} =0.04 L, m_{sorb} =0.05 g, 60 min).

conditions obtained previously. The results showed that with increasing of initial concentration, sorption degree is decreasing. It is explained that with increasing metal ion concentration; the specific sites of a sorbent were saturated and active sites were filled. According to the dependence of sorption degree from initial concentration of copper ions, the dependence graph of sorption capacities from equilibrium copper ions concentration has been constructed (Figure 2). It is seen that the equilibrium copper ions uptake capacities increase with increasing of the equilibrium concentrations of copper ions solutions. When the copper ion concentration reached a certain extent, the increasing of adsorption capacity became slower and approaching a constant value. It can be concluded that the experimentally maximum sorption capacity (qexp) of the BGB at the equilibrium conditions is equal to 3.264 mmol L^{-1} .

3.5. Adsorption Isotherms

The adsorption isotherms are generally used to establish the relationship between the amount of metal ion adsorbed and its equilibrium concentration in solution. The Langmuir, Freundlich, D–R, and Temkins isotherms were applied in this study.

The Langmuir isotherm is used for monolayer adsorption onto a surface containing a finite number of identical binding sites. The linearized form of the Langmuir isotherm can be described by the equation (3):

$$C_e/q_e = 1/(q_m K_L) + C_e/q_m$$
(3)

Where, C_e is the equilibrium concentration of copper ions (mmol L⁻¹), q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mmol g⁻¹), q_m is the maximum monolayer adsorption capacity (mmol g⁻¹), and K_L is the Langmuir isotherm constant (L mmol⁻¹) related to the energy of adsorption. The essential characteristics of the Langmuir isotherm can be



Figure 3: Langmuir adsorption isotherm

expressed in terms of a dimensionless constant separation factor R_L , which is given by the equation (4) [16]:

$$R_{L} = 1/(1 + K_{L} C_{0}) \tag{4}$$

Where, C_0 is the initial concentrations of Cu^{2+} ions solutions (mmol L^{-1}). $0 < R_L < 1$ indicates a favorable adsorption process, $R_L=1$ indicates a linear adsorption, $R_L=0$ indicates irreversible adsorption, while $R_L>1$ signifies an unfavorable adsorption process [17]. The linear curve of the Langmuir equation of specific sorption (C_e/q_e) versus equilibrium concentration of the copper ions (C_e) given in Figure 3.

The Freundlich adsorption isotherm is an empirical model and can be used in the case of a heterogeneous surface energy system [18]. Linearizing equation (5) of the Freundlich isotherm can be written as:

$$\log q_e = \log K_F + (1/n) \log C_e$$
(5)

Where, Ce - The equilibrium concentration of copper ions (mmol L^{-1}), q_e - The amount of metal adsorbed per gram of the adsorbent at equilibrium (mmol g^{-1}). The Freundlich constant K_F is an approximate indicator of adsorption capacity related to bond strength, while 1/n is the heterogeneity factor and a function of the strength of adsorption in the adsorption process [19]. If 0 < (1/n) < 1 for the adsorbents, which indicate a normal adsorption and a favorable sorption process. Freundlich constant K_F and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of isotherm models. The Freundlich adsorption isotherm is shown in Figure 4. From the data in Table 1, $K_F=2.37$, 1/ n=0.2761 and n=3.62 indicating that the sorption of Cu²⁺ onto BGB is favorable.



Figure 4: Freundlich adsorption isotherm

The D–R isotherm equation, which is more generally used to distinguish physical and chemical adsorption, is given by the linearizing equation (6):

$$\ln q_e = \ln B_{DR} - K_D \varepsilon^2 \tag{6}$$

Where, q_e is the amount of metal ions adsorbed per gram of the adsorbent at equilibrium (mmol g⁻¹), B_{DR} is the maximum adsorption capacity of metal ions (mmol g⁻¹), K_D is the D–R equation constant (kJ² mmol⁻²), and ε is Polanyi potential (mmol kJ⁻¹), which is defined by the equality (7):

$$\varepsilon = RT \ln \left(1 + 1/C_e \right) \tag{7}$$

Where, R is the gas constant (8.314 J $K^{-1}mol^{-1}$), T is the temperature (K), and C_e is the equilibrium concentration of metal ions (mmol L⁻¹). A plot of ln q_e against ϵ^2 gives a straight line with a slope of K_D and an intercept of B_{DR}. The parameter B_{DR} of the D–R isotherm can give the valuable information regarding the mean of free energy (E_D) of adsorption by the equality (8):

$$E_{\rm D} = 1/(2 \ {\rm K}_{\rm D})^{\frac{1}{2}}$$
 (8)

Where, E_D is the mean of free energy (kJ mol⁻¹). The E_D value is used to ascertain the type of adsorption



Figure 5: Dubinin-Radushkevich adsorption isotherm

process under consideration. If $8>E_D>16 \text{ kJ mol}^{-1}$, the adsorption process can be assumed to involve chemical sorption. On the other hand, $E_D<8 \text{ kJ mol}^{-1}$ indicate that the adsorption process is of a physical nature [20]. The coefficient determination value (0.980) for D–R model showed that this isotherm also gave a good description of the copper ions sorption process onto BGB (Figure 5). The D–R isotherm constants are shown in Table 1.

The high value of the constant B_{DR} (3.145 mmol g⁻¹) shows high sorption capacity of the BGB toward copper ions and well as well agreement with its experimentally found value (3.264 mmol g⁻¹) and value from Langmuir model (3.47 mmol g⁻¹). For mean free energy value, 3.26 kJ mol⁻¹ has been obtained. Therefore, $E_D < 8$ kJ mol⁻¹ indicate that the copper ions adsorption onto BGB is of a physical nature. However, it does not exclude at least weak chemical interaction between functional groups of the BGB and copper (II) ions.

The Temkin adsorption isotherm contains a factor that is explicitly taking into the account of adsorbentadsorbate interactions. The model is given by the linearizing equation (9):

$$q_e = B \ln A_T + B \ln C_e \tag{9}$$



Figure 6: Temkin adsorption isotherm.

Table 1: Parameters of the Langmuir, Freundlich, D-R and Temkin equetions.

Langmuir equation				Freundlich equation			
q_m , mmol g^{-1}	K_L , L mmol ⁻¹	R _L	R ²	K _F	1/n	n	R ²
3.47	2.985	0.072	0.9994	2.37	0.2761	3.62	0.9328
D – R equation				Temkin equation			
K_D , mol ² kJ ⁻²	B_{DR} , mmol g ⁻¹	E _D , kJ mol ⁻¹	R ²	A_T , L mmol ⁻¹	B, J mol ⁻¹	bT, J mol ⁻¹	R ²
0.047	3.145	3.26	0.980	51.4	0.627	3885.2	0.952

D-R=Dubinin-Radushkevich

B=RT/b_T

 A_T - Temkin isotherm equilibrium binding constant (L g⁻¹), b_T - Temkin isotherm constant, R - Universal gas constant (8.314 J mol⁻¹ K⁻¹), T - Temperature (K), B - Constant related to heat of sorption (J mol⁻¹).

As implied in the equation, its derivation is characterized by a uniform distribution of binding energies was carried out by plotting the sorption capacity q_e against ln C_e, and the constants were determined from the slope and intercept (Figure 6). The Temkin models constants are shown in Table 1. For the Temkin constant B, which related to heat of sorption, was estimated at 0.627 J mol^{-1} . The values of Temkin isotherm constant b_T (3885 J mol⁻¹) and Temkin isotherm equilibrium binding constant A_T $(51.4 \text{ L} \text{ mmol}^{-1} \text{ or } 3.29 \text{ L} \text{ g}^{-1})$ were in good agreement with values presented by Hameed [21] on the evaluation of papaya seed as an adsorbent for removal of methylene blue. The energy parameters of the D-R and Temkin models were used to present sorption energy value (K_D), mean free energy (E_D), and heat of sorption (B). They were estimated as $0.047 \text{ mol}^2 \text{ kJ}^{-2}$ 3.26 kJ mol⁻¹, and 0.627 J mol⁻¹, respectively.

4. ADSORPTION KINETICS

Kinetic studies were carried out under the optimized conditions from 10 to 120 min. The kinetic data obtained were fitted to linear form of Lagergren pseudo-first-order and pseudo-second-order kinetic models [22]. The pseudo-first-order kinetic model known as equation (10):

$$\log \left(q_e - q_\tau\right) = \log q_e - 0.434 K_1 \tau \tag{10}$$

Where, q_t and q_e are the amounts of ion adsorbed at time τ (min) and equilibrium (mmol g⁻¹), respectively, and K_1 is the rate constant of pseudo-first-order adsorption process (min⁻¹). The pseudo-second-order kinetic model is expressed by the equation (11):



Figure 7: Pseudo-first-order plots (C_0 =4.0 mmol L⁻¹, m_{sorb} =0.05 g, V_{sol} =0.04 L, 20°C).

$$\tau/q_{\tau} = 1/(K_2 q_e^2) + \tau/q_e$$
 (11)

Where, q_{τ} and q_e are the amounts of copper ions sorbed at time τ and at equilibrium (mmol g⁻¹), respectively, K₂ is the pseudo-second-order equilibrium rate constant (mmol g⁻¹ min⁻¹).

The slope and intercept of plots of log (q_e-q_t) versus τ were used to determine the first-order rate constant K_1 and equilibrium adsorption capacity q_e (Figure 7). The plot of τ/q_{τ} versus τ gives a linear relationship, and K_2 and q_e can be calculated from the slope and intercept of the line (Figure 8).

In Table 2, the kinetic rate constants K_1 and K_2 , value of experimental q_e and calculated q_e for sorbent were illustrated. According to these results, the kinetic data are well described on pseudo-second-order kinetic equation.

From the obtained results, it can be concluded that the pseudo-second-order equation provides the best coefficient of determination ($R^2=0.9992$) and conformity between calculated (3.16 mmol g⁻¹) and experimental (3.264 mmol g⁻¹) values q_e for copper ions adsorption process on the BGB.

5. THERMODYNAMIC PARAMETERS OF ADSORPTION

Thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) were determined to explain the effect of temperature on the adsorption of Cu²⁺ ions on the BGB. These parameters can be calculated from the following equations (12) and (13):

$$\Delta G^{\circ} = -2.3 \text{ RT} \log K_d \tag{12}$$

$$K_d = q_e/C_e$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{13}$$



Figure 8: Pseudo-second-order plots (C_o =4.0 mmol L⁻¹, m_{sorb}=0.05 g, V_{sol}=0.04 L, 20°C).

Kinetic model	q _e , mmol g ⁻¹	K_1 , min ⁻¹	K_2 , L mmol ⁻¹ min ⁻¹	
Pseude-first-order	2.13	3.92×10^{-2}	-	
Pseude-second-order	3.16	-	1.97×10^{-2}	
q _{eks}	3.264	-	-	

Table 2: Regression parameters for the kinetics models.

Table 3: Thermodynamic parameters of the copper (II) ions adsorption.

Temperature, K	ΔG^{o} , kJ mol ⁻¹	ΔH^{0} , kJ mol ⁻¹	ΔS^{o} , kJ mol ⁻¹ K ⁻¹
293	-2.72	-46.767	-0.15
300	-1.70		
308	-0.467		

Where, R is the gas constant, 8.314×10^{-3} kJ mol⁻¹ K⁻¹, T is absolute temperature, K_d is equilibrium constant at the temperature T. The values of Δ H° and Δ S° were obtained from the slope and intercept of the plots of Δ G° versus T (Figure 9).

Obtained thermodynamic parameters values were listed in Table 3. The negative value found for enthalpy change indicates exothermic nature of adsorption process. The negative values found for free energy change indicate that the sorption process is spontaneous in nature. The negative values of entropy change indicate a decreased disorder at the solid/liquid interface during Cu^{2+} ions adsorption.

6. FTIR SPECTRA ANALYSIS

The mechanism of adsorption and biosorption process of the metal ions on agricultural waste biomass includes chemisorptions, a complex formation, an ionic exchange and physcosorption on the surfaces and pores of the adsorbent. The chemical composition of macromolecular components of grape stalks have been evaluated, and these are composed mainly of cellulose (30.3%), hemicelluloses (21.0%), lignin (17.4%), tannins (15.9%), and proteins (6.1%) [23]. The functional groups that present in macromolecules of the BGB components were identified using FTIRspectra before and after sorption process. In the FTIR spectrum of the BGB, from Figure 10a, the broad peak at 3446 cm⁻¹ was attributed to the stretching of O-H group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols as in pectin, hemicelluloses, cellulose, and lignin.

The peaks around 1653 cm⁻¹ corresponded to the C=C stretching which might be attributed to the presence of lignin and tannin aromatic bond [24]. The peak at 1068 and 1252 cm⁻¹ corresponded to the C–O stretching of alcohols, carboxylic acids, ethers and esters groups. The absorption band at 1740 cm⁻¹ is attributed to the vibrations by carbonyl groups of ester and carboxylic



Figure 9: Plot of ΔG° versus T.

acid groups. Regarding the FTIR spectra for BGB after Cu^{2+} ions uptake (Figure 10b), it was found that oxygen-containing functional groups such as cellulosic, hemicellulosic, phenolic –OH, carboxyl – COOH, and methoxy –OCH₃ groups are affected after uptake process. That was confirmed with shifts in their band intensity and in position from 3446 to 3432 cm⁻¹, 1068, 1252 to 1026, 1244 cm⁻¹ and from 1740 to 1717 cm⁻¹ [24-26]. Essential changes of specific peaks to low wavenumber after Cu²⁺ ions adsorption showed that interactions between metal ions and the functional groups occur on the BGB surface.

7. CONCLUSIONS

The ability of BGBs to be used as the adsorbent for the removal of copper ions from water solution was investigated. The effect of pH, adsorbent dosage, contact time and initial copper ions concentration on the metal removal efficiency and uptake capacity were investigated. Experimentally found value of the maximum experimental sorption capacity of the sorbent is 3.264 mmol g^{-1} . The equilibrium sorption data were fitted to Langmuir, Freundlich, D–R, and Temkin isotherm models. The maximum



Figure 10: Fourier transform infrared-spectra of the branch wastes of grape bushes (a) before and (b) after adsorption

monolayer adsorption capacity of the BGB for Cu^{2+} ions was found as 3.47 mmol g⁻¹. The value of the maximum sorption capacity from the D-R isotherm (3.145 mmol g^{-1}) well as well agreement with its experimentally found value and value from Langmuir model. The kinetic data are best described by pseudo-second-order model. The calculated value of the maximum sorption capacity on the pseudosecond-order equation is 3.16 mmol g^{-1} . For the values of the sorption energy, mean free energy and heat of sorption have been determined as 0.047 mol^2 kJ^{-2} , 3.26 kJ mol⁻¹, and 0.627 J mol⁻¹, respectively. Standard enthalpy (ΔH°) and standard entropy (ΔS°) have values $-46.767 \text{ kJ mol}^{-1}$ and $-0.15 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of ΔH° indicates exothermic nature of the adsorption process. The negative value of ΔS° indicates a decreased disorder during copper (II) ions adsorption.

8. ACKNOWLEDGMENT

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