

Study on the use of Roasted Barley Powder for Adsorption of Cu²⁺ Ions in Batch Experiments and in Fixed-bed Columns

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The potential to remove Cu²⁺ ions from aqueous solutions through biosorption using roasted barley powder and alkalized barley was investigated in batch experiments and in fixed-bed columns. The influences of initial concentrations (40 to 600 mg/L) of the metal ion, the amount of adsorbent (0.01 to 0.25 g), the contact time (2 to 240 min), and the pH (1.0 to 5.5) were all studied. An isotherm model was applied to describe the equilibrium. The percentage of adsorption increased with increasing pH-values up to 5.5 and with dosage of adsorbent up to 0.1 g. The equilibrium adsorption capacities of Cu²⁺ after 3 hours were 43.8 and 51.3 mg.g⁻¹ for barley and alkalized barley, respectively. These values are higher when compared with the adsorption capacity of various adsorbents reported in literature. The adsorption data fit well to the Langmuir isotherm model, and the experimental results indicate that chemisorption onto the surface of the barley and alkalized barley is the major adsorption mechanism for binding Cu²⁺ ions for both sorbents.

Keywords: Barley powder; Alkalized Barley; Adsorption; Isotherm; Copper ions

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INTRODUCTION

The effect of ingestion of toxic metal ions from water consumption is a major concern of health agencies. A large amount of toxic metal ions is discharged into rivers, lakes, and oceans, and this has led to the emergence of various diseases in populations that use these water resources. The International Agency for Research on Cancer (IARC) considers that some metals such as lead, mercury, nickel, cadmium, chromium, and copper are responsible for causing some types of cancer (Williams *et al.* 2000; Farajzadeh and Monji 2004; IARCA, 2006). Copper can cause problems such as gastrointestinal disturbances and Indian Childhood Cirrhosis, (Fewtrell *et al.* 1996). The absorption of excess copper can result in Wilson's Disease, in which excess copper is deposited in the brain, bone, pancreas, liver, and myocardium tissue, causing symptoms such as gastric ulcers, necrosis of the liver, and kidney problems (Volesky 1990). The electroplating industry applies chemical precipitation in alkaline medium to reduce the amount of metal ions in order to comply with the official regulations. This procedure does not completely solve the problem, since it generates a large amount of metal hydroxides that are dumped into the environment. Adsorption processes of metal ions are

widely applied for industrial wastewater treatments. Thus, systems using ion-exchange resins and activated carbon are available for water purification, but improvements should be investigated.

There has been a focus on processes that apply low-cost adsorbents (bioadsorbents from readily available natural sources), as evidenced by increasing numbers of literature reports in recent years (Annadurai *et al.* 2003; Vijayaraghavan *et al.* 2006; Febrianto *et al.* 2009; Mimura *et al.* 2010; Neto *et al.* 2011; Neto *et al.* 2012). The following materials have been used in recent studies: *Moringa oleifera* (Coelho *et al.* 2006 and Bhatti *et al.* 2007), sugarcane bagasse (Albertinil *et al.* 2007), banana peels (Boniole and Yamaura 2008), coffee powder (Oliveira *et al.* 2008), bottom ash (Nidheesh *et al.* 2011), watermelon shell (Koel *et al.* 2012), *Cyperus rotundus* (Ramesh *et al.* 2013), hydroxyapatite (Ramesh *et al.* 2012), and coffee husks (Oliveira *et al.* 2008). A natural material that still awaits exploration is roasted barley powder, which is used in the preparation of drinks and is usually discarded after the application. In this work roasted barley powder has been used for the first time (in its natural form and after alkaline treatment) as an alternative adsorbent for the removal of copper from aqueous solution. The study was aimed at investigating the adsorption capacity and kinetic equilibrium of Cu^{2+} ions using roasted barley powder in batch experiments and fixed-bed columns.

EXPERIMENTAL DATA

Materials

Roasted barley powder (100 g) obtained from the Superbom company (São Paulo, Brazil) was boiled in water (1 L) for 5 min. After cooling, the precipitated powder was collected and dried in an oven at 70 °C for 48 h, after which the fraction between 59 and 200 mesh was separated. The barley powder was treated with NaOH (0.1 M) and heated at 70 °C for 1 h with continuous stirring. The solid material was filtered, washed several times with distilled water, and dried at 70 °C for 48 h.

Methods

Biosorption experiments

For the batch-experiments, solutions of copper sulphate prepared in an acetate/acetic acid buffer at pH 5.5 were used. Concentrations were varied from 40 to 500 mg/L Cu^{2+} . The volume was 25 mL, and the adsorbent mass was about 5 mg. The flasks containing the solutions were shaken at a speed of 150 rpm for 4 h. The batch-experiments were performed in duplicate.

Fixed-bed experiments were conducted using a 50 mL burette as the column. A flow rate of 2.5 mL/min was controlled by a peristaltic pump with downward flow. The mass of adsorbent was 2.0 g. Aliquots were collected every 5 min for subsequent analysis.

Analytical procedure

Measurements of equilibrium concentrations were done using an atomic absorption spectrophotometer (VARIAN model AA240FS) with an air acetylene flame at a wave number of 232 nm. The adsorption capacity (Q) was calculated using equation (1),

$$Q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q is the metal uptake of Cu^{2+} g^{-1} biomass, C_0 is the initial concentration, C_e is the equilibrium concentration, V is the volume in L, and m is the mass of adsorbent in grams.

FTIR analysis

The alkalized roasted barley powder before and after adsorption of Cu^{2+} ions was analyzed by Fourier-transform infrared spectrophotometry in the ATR mode and in the wave number range of 500 cm^{-1} to 4000 cm^{-1} (BRUKER model Vertex 70).

Zero potential charge analysis

To investigate the surface charge of the roasted barley powder before and after alkaline treatment, a ZetaSizer Nano ZS instrument (Malvern) using a laser wave number of 633 nm and detected at an angle of 17° and particle size of 173 nm was used.

RESULTS AND DISCUSSION

FTIR Spectroscopy Analysis

The ATR-IR spectra of the barley, alkalized barley, barley with adsorbed Cu^{2+} , and alkalized barley with adsorbed Cu^{2+} are shown in Fig. 1. In all four spectra a wide band was observed between 3600 cm^{-1} and 3200 cm^{-1} for the stretching of O-H groups present in the structures of both cellulose and lignin. It was also observed that there were two peaks at 2930 and 2853 cm^{-1} related to the C-H groups of the aliphatic chain. In the region between 1800 and 1200 cm^{-1} there were some characteristic peaks of the structures of cellulose and lignin. The peaks at 1738 cm^{-1} are characteristic of the C=O of aldehyde present in the lignin, and 1682 cm^{-1} is related to the C=O groups of the amides present in protein residue of barley. The region between 1300 and 700 cm^{-1} showed the characteristic peaks of aliphatic ethers at 1151 and 1055 cm^{-1} and aromatic ethers at 1021 cm^{-1} present in lignin.

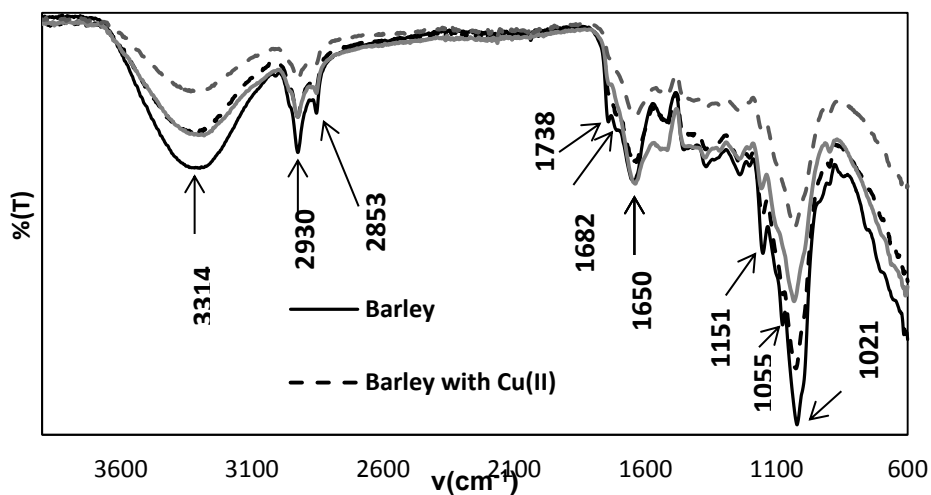


Fig. 1. ATR-IR spectra of barley, alkalized barley, barley with Cu^{2+} and alkalized barley with Cu^{2+}

When comparing each spectrum it was observed that there was no appearance of new bands when alkali treatment of barley powder was performed. This is to be expected because alkalization mainly provides for solubilization of the lignin, and the remaining material is essentially cellulose. When comparing barley with alkalized barley, a decrease in the intensity of the peaks was observed in the region between 3600 and 3100 cm^{-1} for the OH groups present in both the cellulose and lignin. A decrease in the intensity of

peaks at 1738, 1151, 1055, and 1021 cm^{-1} was observed. These peaks may be attributed to aldehyde groups, tertiary alcohol, primary alcohol, and ether, respectively (Montoneri 2005). By comparing the spectra of the two adsorbents (with and without copper), only a decrease in peak intensity in the same region 3600-3100 cm^{-1} was perceived. It is suggested that this decrease occurs by the emergence of the Cu-O bond in hydroxyl groups.

PZC Analysis

Point of zero charge (pH_{PZC}) is the pH below which the surface of the adsorbent is positively charged, whereas above this value the surface is negatively charged (Ayranci *et al.* 2005). The importance of this variable in the adsorption process of an adsorbent is based on the fact that the signs of charge of adsorbate and adsorbent ideally should be opposed so there is a greater electrostatic attraction between the two. If the charges are of the same sign, then the adsorption process will be affected due to electrostatic repulsion (Toledo *et al.* 2005). All experiments were performed in acetate buffer of pH 5.5. The result of PZC to barley and alkalized barley are shown in Fig. 2. An optimum effect was observed at pH 5.5, as already mentioned, because at this pH both materials have negative potential which allows the ion adsorption.

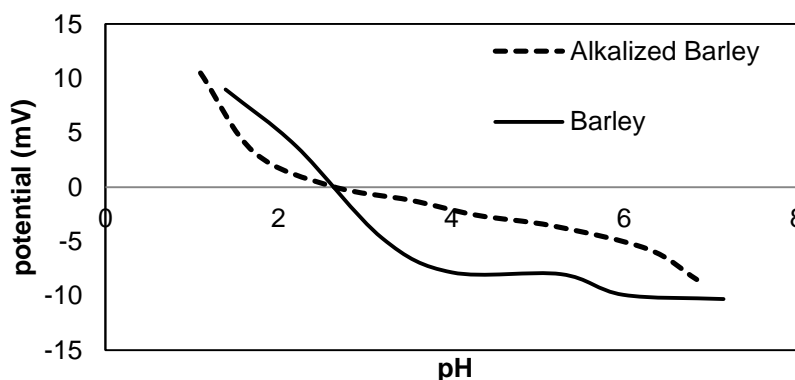


Fig. 2. PZC of barley and alkalized barley

Sorption Kinetics

The kinetic study establishes the times required to reach equilibrium under specific experimental conditions. Upon knowing these times, it becomes necessary to study adsorption and to perform a schedule of use of material as adsorbent so the process occurs in the fastest time possible and in an efficient manner, saving both time and costs. Moreover, the kinetics of adsorption is important for understanding the interaction of adsorbent / adsorbate by determining parameters such as reaction order, rate constant, activation energy, initial adsorption rate, and intraparticle diffusivity.

Several models were evaluated to determine the limiting step in the mechanism or process for each experimental case. The following kinetic and diffusion models were studied in this work: Pseudo-second order; Elovich equation; and intraparticle diffusion models (Ho and McKay, 1998; Roginsky and Zeldovich, 1934; Weber and Morris 1963; Boyd *et al.* 1947).

The pseudo-second order model developed by Ho and McKay (1998) was used when the rate of adsorption was assumed to follow a second-order mechanism; this is represented by Eq. (2),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where the constant k_2 is the second order of adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) and q and q_t are the amounts adsorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t (min), respectively.

The Elovich equation, represented by Eq.(3), is adequate for systems whose surfaces promote heterogeneous adsorption,

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (3)$$

where β is the constant of desorption ($\text{mg} \cdot \text{g}^{-1}$), α is the initial rate of adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), and q_t is the amount adsorbed ($\text{mg} \cdot \text{g}^{-1}$) at time t (min).

In order, the lowest values of the average percentage error (APE), and the determination coefficients R^2 were taken into account and used for the statistical evaluation of how well experimental fit to each kinetic model. The average percentage error (APE), is represented by Eq. 4,

$$APE(\%) = \frac{1}{N} \sum_i^N \left| \frac{(q_e - q_{ecal})}{q_{ecal}} \right| \quad (4)$$

where q_{ecal} is adsorption capacity theoretically obtained by calculation from the model, and q_e ($\text{mg} \cdot \text{g}^{-1}$) is the corresponding experimental value. In Eq. 4, N is the number of experimental points.

The models corresponding to the pseudo-second order and the Elovich equation of the barley gross/ Cu^{2+} system and the barley alkalized/ Cu^{2+} system are shown in Fig. 3. By analyzing the graphics, it is observed that the adsorption equilibrium time was rapid, occurring within the first 60 min for the Barley gross/ Cu^{2+} system and in the first 40 min for the barley alkalized/ Cu^{2+} system. After this period of time there was an increase in the percentage removal which tended to remain constant until the maximum study time (120 min). The same was observed in a study using coconut bagasse for the adsorption of toxic metals from wastewater (Neto *et al.* 2011).

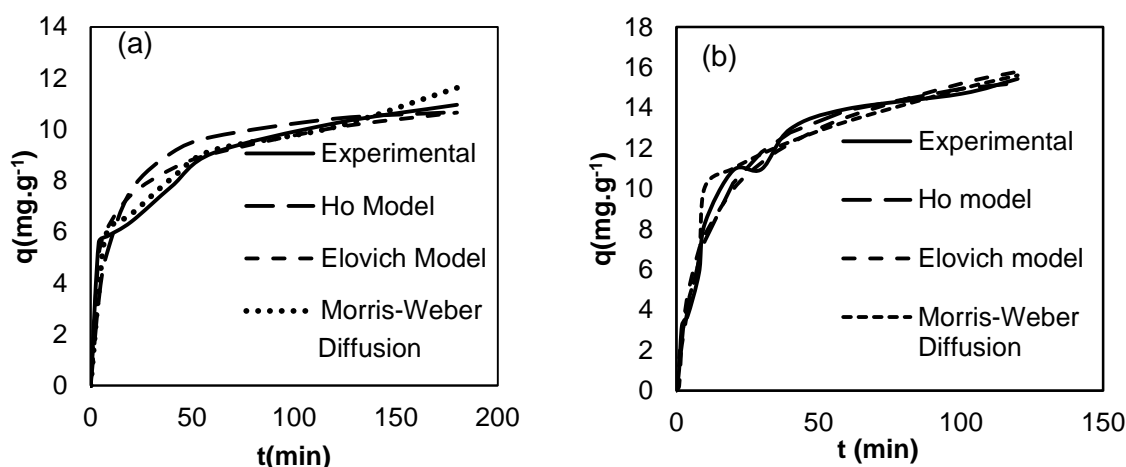


Fig. 3. Kinetic models of adsorption of Cu^{2+} using (a) barley, and (b) alkalized barley: Experimental condition: $\text{Cu}^{2+} = 100 \text{ mg} \cdot \text{L}^{-1}$, $\text{pH} = 5.5$ acetate buffer, adsorbent dose = $2 \text{ g} \cdot \text{L}^{-1}$

The short time required to reach equilibrium conditions, besides being beneficial to the process, is regarded as an indicator that the adsorption systems barley/Cu²⁺ and alkalized barley/Cu²⁺ are controlled by chemical interactions more than a diffusion process (Loukidou *et al.* 2004). Similar results were reported by Sousa *et al.* (2010) using the powder of green coconut shell treated for the adsorption of toxic metals from wastewater. This suggests that the adsorption is due to physic-chemical interactions between the adsorbent and the adsorbate in solution.

Table 1 shows the kinetic parameters for each model using the linear method. When analyzing the linear method, the pseudo-second order model (Ho 2000) presented a better approximation of the experimental value (R²), compared to the Elovich model. The results obtained using the second order equations with parameters k_2 , $Q_{e,cal}$, $Q_{e,exp}$, APE(%), and R² are shown in Table 1. The value of the sorption rate constant (k_2) for Cu²⁺ adsorption by barley and alkalized barley was determined from the plot of (t/q_t) against t . The values of the Elovich parameters α (mg.g⁻¹.min⁻¹) and β (mg.g⁻¹) were determined from the plot of (q) against $\ln(t)$ and are shown in Table 1. It is noted that the rate constant (K_2) of crude barley was greater than in alkalized barley, and this means that in the concentration studied (100 mg.g⁻¹), the adsorption rate was slightly higher when using barley without alkalization. The parameter (α) in the Elovich equation confirms that, under the conditions studied, the initial adsorption rate was higher before alkalization of the barley. However, the desorption rate is lower in the barley after alkalization.

Table 1. Parameters and Correlation Coefficients of Kinetic Models of Pseudo Second Order, Elovich Equation, and Intraparticle Diffusion Model for Systems Barley/Cu²⁺ and Alkalized Barley/Cu²⁺

Models		Barley/Cu ²⁺	Alkalized Barley/Cu ²⁺
Ho model	Q_e (mg.g ⁻¹)	11.35	15.43
	Q_{cal} (mg.g ⁻¹)	11.22	16.86
	K_2 (g.mg ⁻¹ .min ⁻¹)	9.47x10 ⁻³	4.62x10 ⁻³
	R ²	0.991	0.996
	APE(%)	2.32	1.99
Elovich Equation	α (mg.g ⁻¹ .min ⁻¹)	12.1	3.49
	β (mg.g ⁻¹)	0.686	0.307
	R ²	0,964	0.971

Diffusion Models

In order to gain insight into the mechanisms and rate-controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intra-particle diffusion (Weber and Morris 1963) and Boyd model (Boyd *et al.* 1947). The mathematical expression obtained for the Weber and Morris diffusion model is,

$$q_t = k_{id}t^{1/2} + C \quad (5)$$

where C is the intercept and k_{id} is the intra-particle diffusion rate constant (mg.g⁻¹.min^{1/2}), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. The values of C provide information about the thickness of the boundary layer; the larger the intercept, the greater is the boundary layer effect (Kavitha and Namasivayam 2007).

If intra-particle diffusion occurs, then q_t versus $t^{1/2}$ will be linear, and if the plot passes through the origin, then the rate limiting process is only due to the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved. In Eq. (6), k_{id} ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$) is defined as the intraparticle diffusion rate constant and is related to the intraparticle diffusivity in the following way,

$$k_{id} = \left(\frac{3q_e}{d_p} \right) \sqrt{\frac{D}{\pi}} \quad (6)$$

where d_p (cm) is the particle diameter and q_e ($\text{mg}\cdot\text{g}^{-1}$) is the solid phase concentration at equilibrium.

The Cu^{2+} adsorption data were plotted according to Eq. (5) as shown in Fig. 4 (a) and (b). As seen in Fig. 4, the points were not linear over the whole time range, implying that more than one process affected the adsorption. This deviation might be due to the difference in the mass transfer rate in the initial and final stage of adsorption, indicating that diffusion process into pores was not the only rate-limiting mechanism in the adsorption process. The results obtained using the Weber-Morris model to parameters k_{id} , D_i , C , and R^2 are presented in Table 2.

The break point time determines whether the process occurs by external diffusion mechanism or intra-particle diffusion. This is seen by the interception of the two lines. We can observe from the graphs that initially the adsorption occurred in barley by an external diffusion mechanism, and after the break point it occurred by intra-particle diffusion. When alkalized barley was used, the opposite effect was observed with intra-particle diffusion primarily occurring. This may indicate that the alkalization process enables the active sites of the cellulose to become more accessible.

By the Webber-Morris model, the break points in Fig. 4 were 14.7 min for barley and 42 min for alkalized barley.

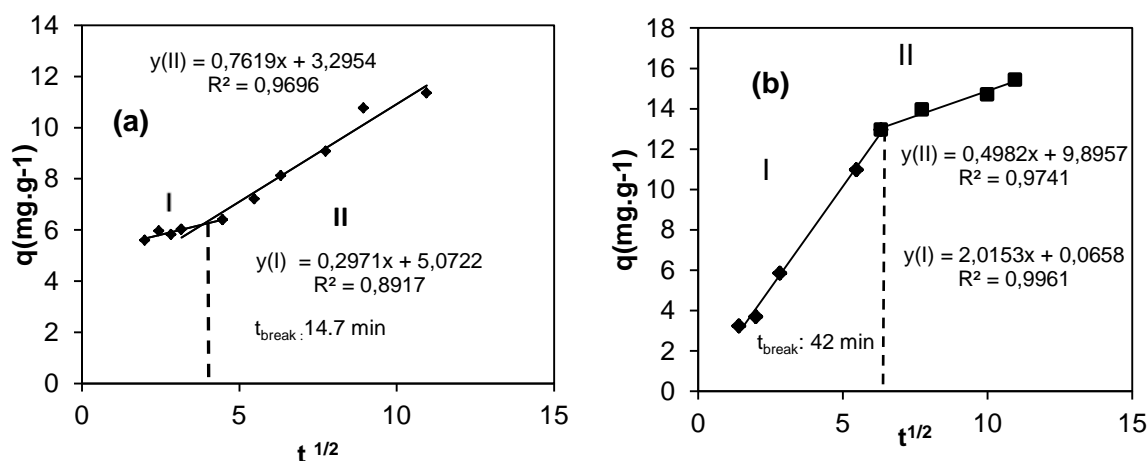


Fig. 4. Weber-Morris Intraparticle diffusion models plots for Cu^{2+} adsorption on (a) Barley, and (b) Alkalized Barley. Experimental condition: $\text{Cu}^{2+} = 100 \text{ mg}\cdot\text{L}^{-1}$, pH = 5.5 acetate buffer, adsorbent dose = $2 \text{ g}\cdot\text{L}^{-1}$.

Table 2. Results for the Sorption of Cu²⁺ ion onto Barley and Barley Alkalized by the Weber's Pore-Diffusion Model using the Linear Method

Barley							
I				II			
K _{id(II)} (mg.g ⁻¹ .min ^{1/2})	C ₁ (mg.g ⁻¹)	D _i (cm.min ⁻¹)	R ²	K _{id(II)} (mg.g ⁻¹ .min ^{1/2})	C ₁ (mg.g ⁻¹)	D _i (cm.min ⁻¹)	R ²
0.297	5.07	4.48x10 ⁻⁸	0.892	0.762	3.30	2.95x10 ⁻⁷	0.969
Alkalized Barley							
I				II			
K _{id(II)} (mg.g ⁻¹ .min ^{1/2})	C ₁ (mg.g ⁻¹)	D _i (cm.min ⁻¹)	R ²	K _{id(II)} (mg.g ⁻¹ .min ^{1/2})	C ₁ (mg.g ⁻¹)	D _i (cm.min ⁻¹)	R ²
2.02	0.066	1.12x10 ⁻⁶	0.996	0.498	9.90	6.83x10 ⁻⁸	0.974

To determine whether the adsorption process occurs by external diffusion or intraparticle mechanism, the kinetic data were investigated by the model of Boyd *et al.* (1947). If diffusion inside the pores is the rate limiting step, then the results can be expressed as:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-\pi^2 Bt) \quad (7)$$

where B is a constant and F is the fractional attainment of equilibrium at different times t given by Eq. (7):

$$F = q_t / q_e \quad (8)$$

In this expression, q_t and q_e are the Cu²⁺ uptakes (mg/g) in equilibrium at a time t . The term Bt is calculated by the following equations of Reichenberg (1953):

$$\text{For } F \text{ values } > 0.85 \quad Bt = -0.4977 - \ln(1-F) \quad (9)$$

$$\text{and for } F \text{ values } < 0.85 \quad Bt = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3}\right)}\right)^2 \quad (10)$$

In order to apply this model, the product term Bt is calculated for each value of F , and then the resulting Bt values are plotted against t (Boyd plot), as given in Fig. 5. If the plot is linear, then the slope is equal to B , and it can be concluded that pore-diffusion is the rate controlling step. The effective diffusion coefficient, D_i , (cm².s⁻¹) can be calculated from Eq. (11).

$$B = (\pi^2 D_i) / r^2 \quad (11)$$

Linear segments can also be encountered in Boyd plots, and in such cases every segment is analyzed separately to obtain the corresponding diffusion coefficient.

Applying Boyd's model in step (I), the values of $B_{(I)}$, $D_{i(I)}$, and R^2 obtained for the plots were 0.0065, 3.09x 10⁻⁸ cm².s⁻¹, and 0.892, respectively, for barley and 0.033, 1.55x10⁻⁷cm².s⁻¹, 0.975, respectively for alkalized barley. In step (II), $B_{(II)}$, $D_{i(II)}$, and R^2 were 0.018, 8.57x10⁻⁸ cm².s⁻¹, and 0.996, respectively for barley and 0.024, 1.14x10⁻⁷,

and 0.999, for alkalized barley. The break points in Fig. 5 are 20.7 min for barley and 55.8 min for alkalized barley.

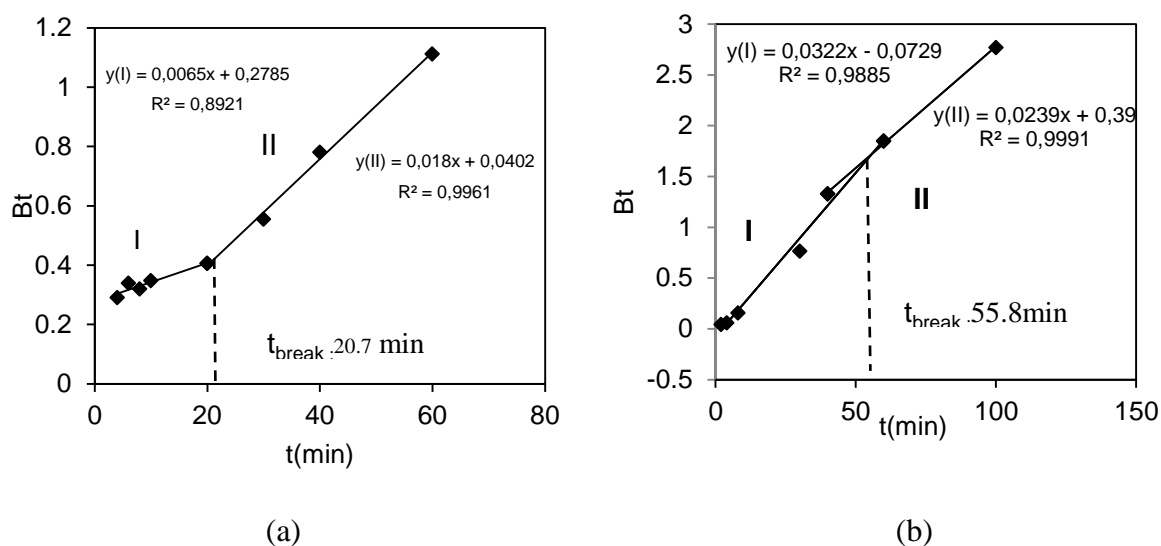


Fig. 5. Boyd plot for adsorption of Cu^{2+} onto (a) Barley, and (b) Alkalized Barley Experimental condition: $\text{Cu}^{2+} = 100 \text{ mg.L}^{-1}$, $\text{pH} = 5.5$ acetate buffer, adsorbent dose = 2 g.L^{-1} . In step I, $F < 0.85$ Eq. (8) was applied, in step II, $F > 0.85$, Eq.(9) was applied.

Table 3. Results for the Sorption of Cu^{2+} Ion onto Barley and Barley Alkalized by the Boyd's Diffusion Model Using the Linear Method

Barley					
I			II		
B	D_i	R^2	B	D_i	R^2
0.0065	3.09×10^{-8}	0.892	0.018	8.57×10^{-8}	0.996
Alkalized Barley					
I			II		
B	D_i	R^2	B	D_i	R^2
0.033	1.55×10^{-7}	0.975	0.024	1.14×10^{-7}	0.999

Effect of pH

The pH is one of the parameters investigated in the adsorption study. The same is required to be investigated for the behavior of the adsorbed species in the face of situations in different pH, since it is a determining factor in the formation of several species. Furthermore, the adsorbent is also influenced by pH because it will determine the type of surface charge. This test used a synthetic solution of $\text{Cu}^{2+} 105 \text{ mg.g}^{-1}$. Figure 6 shows the behavior of the adsorption of Cu^{2+} in raw barley for a pH range from 3.1 to 5.5. As the pH was decreased, the adsorption capacity decreased. This is because there was a competition with the H^+ ion by ion Cu^{2+} adsorption sites. At pH value below the PZC of the adsorbent has a positive surface charge and thus hinders the adsorption of the metal ion. At a pH above 6.0, copper undergoes hydrolysis and precipitate formation occurs. Some studies have demonstrated the effect of acetate in removing metal ions by adsorption (Khattak and Khan 1995). However, in our work did not do a control study,

but experimental data showed no evidence of precipitation of copper ion in the acetate form, and there was a clear solution at pH 5.5.

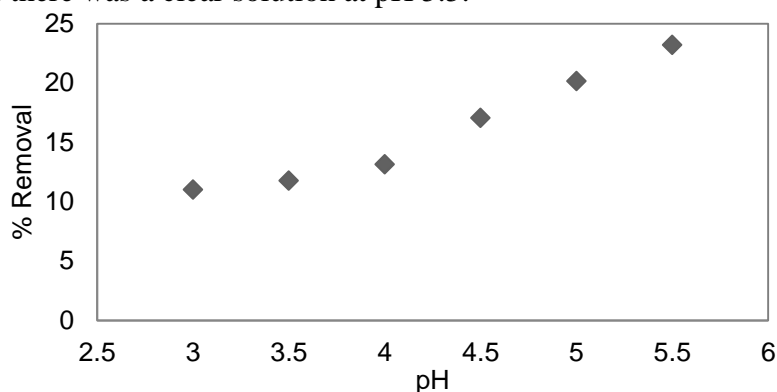


Fig. 6. Effect of pH on the adsorption of Cu²⁺ in Barley

Effect of Amount of Adsorbent

Adsorption is a process of chemical equilibrium; therefore the quantity of one component will influence this balance. One of the studies that have been conducted was the test dosage. This test shows that above a certain mass of sorbent used, there were no significant changes in adsorption capacity. For barley, it was noticed from Fig. 7 that above a mass of 0.3 g to 25 mL of solution (12 g.L⁻¹) there was no more of an increase in removal capacity for Cu²⁺ at a concentration of 100 mg.L⁻¹.

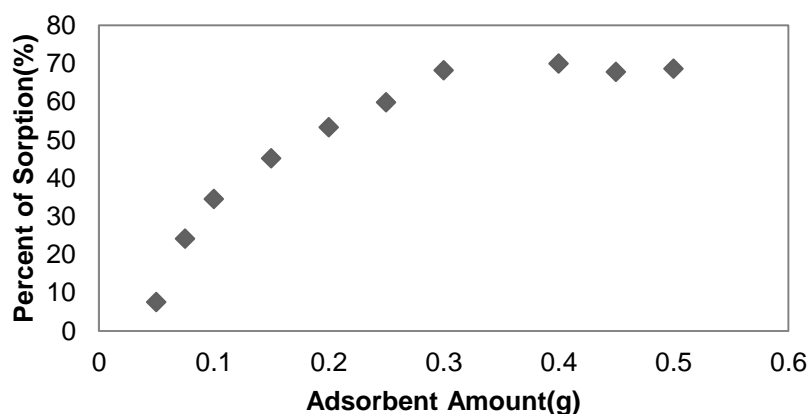


Fig. 7. Effect of the amount of Barley in adsorption of Cu²⁺. Volume to 25 mL of solution.

Adsorption Isotherm Models

The Langmuir model (Langmuir 1918) is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface with no lateral interaction between the adsorbed metal ions. The Langmuir adsorption model has been successfully used to explain the metal ions adsorption from aqueous solutions. The expression of the Langmuir model is given by Eq. (12),

$$q_e = \frac{Q_o K_L C_e}{(1 + K_L C_e)} \quad (12)$$

The Langmuir isotherm has been generally applied in the following linear form,

$$\frac{C_e}{q_e} = \frac{1}{Q_o} C_e + \frac{1}{Q_o K_L} \quad (13)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the amount adsorbed per unit mass of sorbent and the metal concentration in solution at equilibrium, respectively. Q_o is the maximum amount of the metal per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e , and K_L is a constant related to the affinity of the binding sites (L/mg).

The Langmuir constants (Q_o and K_L) were determined from adsorption isotherm by linear method and are presented in Table 4. The K_L values were found to be $9.89 \times 10^{-3} \text{ L}\cdot\text{mg}^{-1}$ and 3.67×10^{-2} for barley and alkalized barley, respectively. The highest adsorption capacities were found to be 43.8 and 51.3 mg g^{-1} for barley and alkalized barley, respectively. Table 5 shows adsorption capacity values for Cu^{2+} uptake for various adsorbents.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems (Freundlich 1906). The Freundlich equation can be expressed as

$$q_e = K_F C_e^{1/n} \quad (14)$$

The Freundlich isotherm has been generally applied in the following linear form,

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log C_e \quad (15)$$

where q_e is the equilibrium amount adsorbed ($\text{mg}\cdot\text{g}^{-1}$) and C_e is the equilibrium concentration of the adsorbate ($\text{mg}\cdot\text{L}^{-1}$). K_F and n are the Freundlich constants related to adsorption capacity and intensity of adsorption, respectively.

The estimated parameters of these models were evaluated by regression analysis and the results are shown in Table 4. Figures 8(a) and (b) show the Freundlich isotherms obtained for the Cu^{+2} adsorption onto barley and alkalized barley adsorbents. The K_F values were found to be 1.00 and 9.32 for barley and alkalized barley, respectively. The n values obtained were 1.62 and 3.45 for barley and alkalized barley, respectively which represents a favorable adsorption to both adsorbents. However, the Freundlich model to Barley did not fit the experimental data well, since the R^2 values were relatively low (0.915).

Temkin and Pyzhev (1940) considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage.

The Temkin isotherm has been generally applied in the following form:

$$q_e = \left(\frac{RT}{b} \right) \ln(AC_e) \quad (16)$$

which can be linearized as

$$q_e = B \ln(A) + B \ln(C_e) \quad (17)$$

where $B = RT/b$. b is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L.mg⁻¹), R the gas constant (8.314 J mol⁻¹K⁻¹), and T is the absolute temperature (K). Therefore, the plotting of q_e versus $\ln C_e$ enables one to determine the constants A and b , which are listed in Table 4.

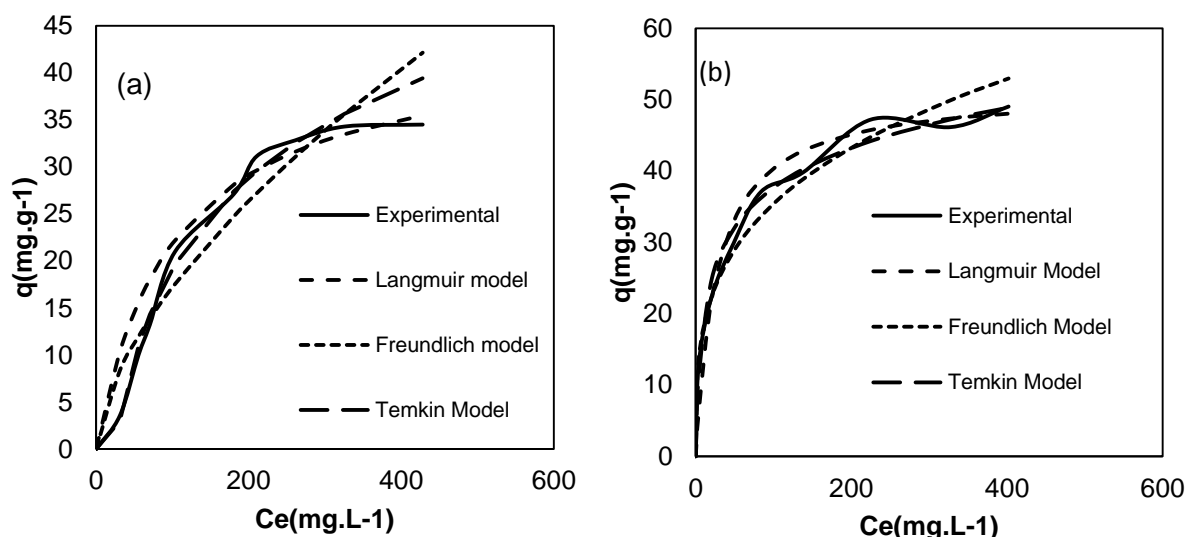


Fig. 8. Theoretical isotherms and experimental data for adsorption of Cu²⁺ onto (a) Barley and (b) Alkalized Barley

Table 4. Langmuir, Freundlich, and Temkin Isotherm Model Constants and Coefficients of Determination for Adsorption of Cu²⁺ onto Barley and Alkalized Barley

Isotherm Parameters		Barley	Alkalized Barley
Langmuir	$Q_o(\text{mg.g}^{-1})$	$43.8 \pm 0,92$	$51.3 \pm 1,0$
	$K_L(\text{L.mg}^{-1})$	9.89×10^{-3}	3.67×10^{-2}
	R^2	0.985	0.995
Freundlich	n	1.62	3.45
	$K_F(\text{mg.g}^{-1})(\text{L.mg}^{-1})^{1/n}$	1.00	9.32
	R^2	0.915	0.980
Temkim	$A (\text{L.mg}^{-1})$	3.98×10^{-2}	1.06
	B	13.9	8.07
	R^2	0,990	0.979
	$b (\text{J.Mol}^{-1})$	180	310

Table 5. Comparison of Parameters of Langmuir for Adsorption of Cu²⁺ onto Materials Studied and Literature

Adsorbents	q_{max} (mg/g)	pH	K_L (L/mg)	References
Roasted barley powder	54.64	5.5	7.6×10^{-3}	present study
Alkalized roasted barley powder	50.21	5.5	38.0×10^{-3}	present study
Sunflower Leaves	89.37	5-6	4.2×10^{-2}	(Benaissa <i>et al.</i> 2007)
<i>Tectona grandis</i>	95.40	5.5	0.1346	(King <i>et al.</i> 2006)
Sour orange residue	23.47	4.5	54.0×10^{-3}	(Khormaei <i>et al.</i> 2007)
Sour orange residue (NaOH treated)	52.08	4.5	66.0×10^{-3}	(Khormaei <i>et al.</i> 2007)
<i>Rhizopusoryzae</i> (viable)	19.40	4 - 6	0.1290	(Bhainsa <i>et al.</i> 2008)
<i>Rhizopusoryzae</i> (NaOH-treated)	43.70	4-6	0.0280	(Bhainsa <i>et al.</i> 2008)
Saw-dusts (RSD)	8.11	6.0	0,1592	(Kalavathy <i>et al.</i> 2010)
Saw-dusts(SMSD3)	12.48	6.0	0.1012	(Kalavathy <i>et al.</i> 2010)

Study in Fixed Bed

Thomas Model

When comparing the performance of barley to alkalized barley, it is perceived that the volume of rupture at 50% (C_e/C_0) in 63 mL varies. The volume of rupture (V_b) at 50% (C_e/C_0) for samples of barley and alkalized barley were 212 and 275 mL, respectively (Table 6). The alkali treatment causes a displacement curve of rupture at 50% (C_e/C_0) to the right, indicating that there was an improvement in performance in metal ion removal when compared to unmodified adsorbent. The exhaust volume (V_x) at 90% (C_e/C_0) for samples of barley and alkalized barley were 287 and 325 mL, respectively. The capacity (mg / g) also increased as shown in Table 7.

The Thomas model was used (Equation 18) to calculate the maximum capacity of the column,

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{k_{TH}q_0m}{F} - k_{TH}C_0t \quad (18)$$

where C_e is the concentration of metal in the outlet of the column, C_0 is the initial concentration of the solution, K_{TH} is the Thomas constant, q_0 is the maximum concentration of solute in the solid phase, m is the mass of adsorbent in grams (g), F is the volumetric flow (L / min), V is the volume of column effluent (mL), and t is time in minutes.

Table 6. Experimental Data of Fixed Bed Column

Column Data	Adsorbents	
	Barley	Alkalized Barley
Flow (mL.min ⁻¹)	2.50	2.50
$V_x(mL) C_e/C_0 - 0.90$	287	325
$V_bC_e/C_0 - 0.50$	212	275
$V_bC_e/C_0 - 0.05$	137	212

The values of capacities of adsorption columns using barley and alkalized barley were calculated by applying the linear Thomas model. Adsorption capacity values were

23.2 and 29.6(mg.g⁻¹), respectively. Figure 9 shows the comparison between the experimental data and theoretical adsorption column. Table 7 shows the parameters obtained using the linear model of Thomas. The alkali treatment causes a displacement curve of rupture at 50% (C_e / C_o) to the right indicating that there was an improvement in performance of metal ion removal when compared to unmodified adsorbent.

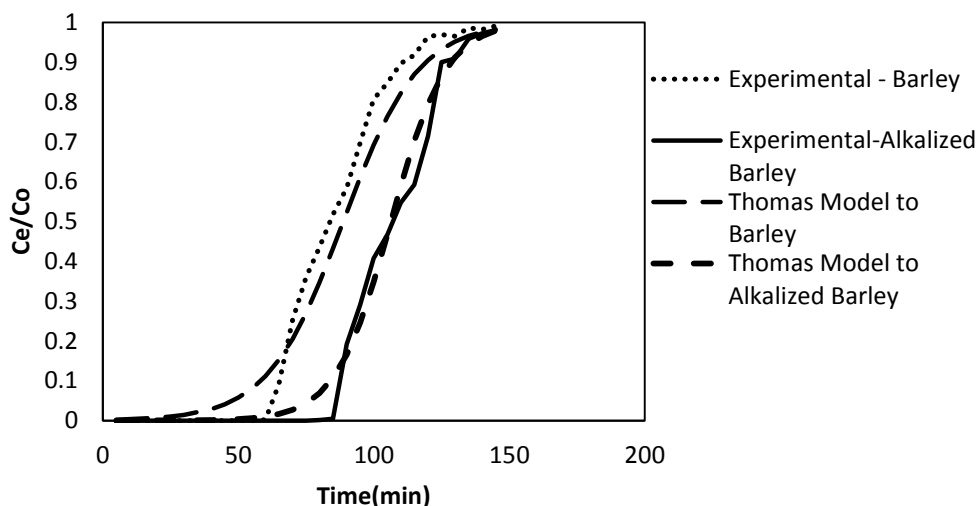


Fig. 9. Breakthrough curves for the study in fixed bed column adsorption of ion Cu^{2+} in barley and alkalyzed barley. Experimental results vs. Thomas model

Table 7. Parameters of Thomas Model

	Barley	Alkalyzed Barley
$Q(\text{mg.g}^{-1})$	23.2	29.6
K_{Th}	3×10^{-4}	4×10^{-4}
R^2	0.982	0.973

Bed Depth Service Time (BDST) Model

The BDST (Bed Depth Service Time) is a model used to predict the relationship between the bed depth, Z , and length of service (Vijayaraghavan 2006). This model is used only to describe the initial part of the curve to break the breakpoint in the range 10-50% of saturation points (Sarin *et al.* 2006). The model was developed to estimate the parameters in maximum adsorption capacity (mg.dm^{-3}) and kinetic constant K_a . The BDST model was originally developed by Adams and Bohart and can be expressed by Eq. 19 (Singhand Pant 2006):

$$t = \frac{N_o}{C_o v} - \frac{1}{K_a C_o} \ln \left(\frac{C}{C_o} - 1 \right) \quad (19)$$

where C is the breakthrough dye concentration (mg.L^{-1}), C_o is initial concentration, N_o is the sorption capacity of bed (mg.L^{-1}), v is the linear velocity (cm.min^{-1}), and K_a is the rate constant ($\text{L.mg}^{-1} \text{min}^{-1}$).

The quantity of adsorbed metal when the exit concentration is 10% of the initial concentration (qv in mg.g^{-1}) can be obtained from the following relation (20):

$$q_v = \frac{q_v t_{10\%} C_0}{m} \quad (20)$$

where $t_{10\%}$ is the service time (min) obtained when the outlet concentration is 10% of C_0 , q_v the effluent volumetric flow rate ($L \cdot \text{min}^{-1}$), and m the amount of adsorbent (g).

BDST model parameters for the sorption of Cu^{2+} using barley and alkalized barley are shown in Table 8. We observed that the ability of hydrodynamics in the bed increases $7.03 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$, when alkaline barley was used. We also observed that the amount of adsorbed metal output when the concentration is equal to 10% of the initial concentration horsepower increases from 18.15 to $22.9 \text{ mg} \cdot \text{g}^{-1}$ when comparing two materials. These values agree with the ones found by the Thomas model presented earlier. Besides that, the correlation coefficient value (R^2) shows this model is applicable as all the values are above (0.96). The constants obtained from this model could be utilized for ascaling up process of this fixed bed column.

Table 8. Bed Depth Service Time (BDST) Constants for the Column at Barley and Alkalized Barley

Constants	Barley	Alkalized Barley
$N_0(\text{mg} \cdot \text{L}^{-1})$	3.16×10^4	7.03×10^4
$K_a(\text{Lmg}^{-1} \cdot \text{min}^{-1})$	0.0583	0.0452
$V(\text{cm} \cdot \text{min}^{-1})$	3.185	3.185
R^2	0.984	0.969
$Q_{10\%}(\text{mg} \cdot \text{g}^{-1})$	18.15	22.9

Figure 10 shows the application of the BDST model for the two materials. This model is well accepted when the C / C_0 does not exceed a value of 50%.

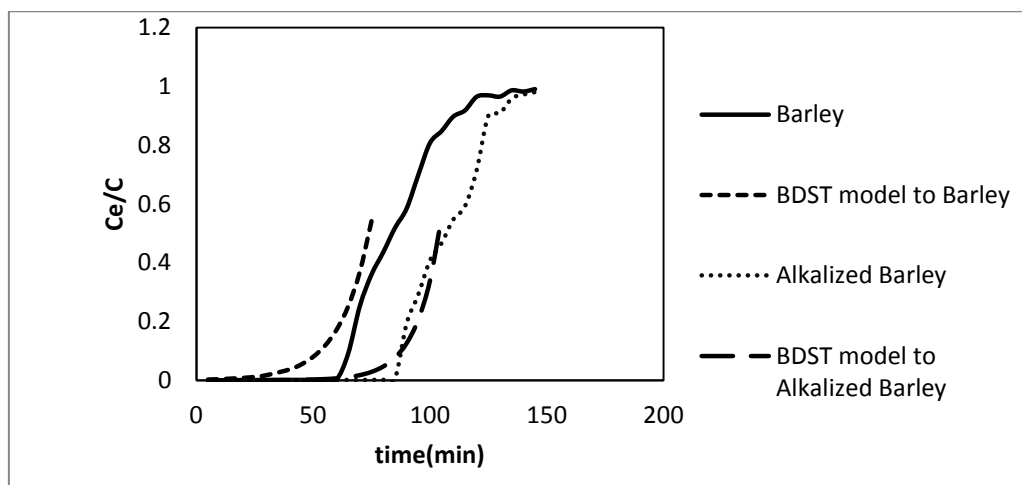


Fig.10. Breakthrough curves for sorption of Cu^{2+} onto Barley and Alkalized Barley – BDST model

CONCLUSIONS

1. It was observed that the best pH for adsorption is about 5.5, since below this value, the adsorption capacity is low and above this value, precipitation may occur from Cu^{2+} .
2. The adsorption capacities of the Cu^{2+} in a batch system were 43.8 mg.g^{-1} for barley and 51.3 mg.g^{-1} for alkalized barley. This suggests that after treatment, the availability of active sites increased, generating the expected result. However, in the fixed bed, system capacity values were 9.27 mg.g^{-1} for barley and 11.9 mg.g^{-1} for alkalized barley.
3. The equilibrium adsorption time for barley as compared to alkalized barley is about 20 min. Intra-particle diffusion was not the only rate-controlling step.
4. The adsorption process occurs by the hydroxyl groups present in the crude and modified materials.
5. The study of the column shows that the alkalized barley has a larger volume breakdown when compared to barley.
6. Barley powder can be another cheap alternative in Cu^{2+} ion adsorption.

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