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Enhancing the adsorption capacity of copper in aqueous solution by citric acid modified sugarcane bagasse

Nghiên cứu khả năng hấp phụ đồng trong nước của vật liệu bã mía biến tính bằng acid citric

Research article

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This study investigated the chemical modification method by citric acid and its enhancement effect on the adsorption capacity of sugarcane bagasse (SB) for copper removal from aqueous solution. Characterization studies were performed by using Fourier transform infra red (FTIR), which showed the introduction of carboxylic group in the structure the modified sugarcane bagasse (MSB). Batch study revealed the influence of pH, time, initial concentration of metal ion on adsorption capacity. The data showed an extremely good fit to Langmuir isotherm model from which the maximum adsorption capacity estimated reached 28.17 mg/g at optimum pH 5.5. Fixed bed column study using the adsorbent MSB confirmed that the breakthrough curves of the adsorption processes were dependent on bed height, initial concentration and flow rate. Linear regression analysis of the data demonstrated that Yoon-Nelson kinetic models were appropriate to explain the breakthrough curves.

Nghiên cứu đã thực hiện biến tính hóa học vật liệu bã mía bằng acid citric và đánh giá khả năng hấp phụ ion Cu(II) trong nước của bã mía (SB) trước và sau biến tính axit citric. Khảo sát cấu trúc vật liệu thông qua phổ hồng ngoại FTIR cho thấy các nhóm chức carboxylic có khả năng hấp phụ kim loại xuất hiện trong vật liệu biến tính. Thí nghiệm mẻ đánh giá sự ảnh hưởng của pH, thời gian và nồng độ của vật liệu tự nhiên và biến tính đến khả năng hấp phụ ion Cu(II). Kết quả của thí nghiệm mẻ phù hợp với mô hình Langmuir với khả năng hấp phụ cực đại đạt 28,17 mg/g tại nồng độ pH tối ưu là 5,5. Kết quả thí nghiệm trên mô hình cột cho thấy đường cong thoát của quá trình hấp phụ của vật liệu biến tính và chưa biến tính phụ thuộc và chiều cao lớp vật liệu, nồng độ ion Cu(II) ban đầu và vận tốc dòng chảy qua cột. Các dữ liệu thu nhận được từ thực nghiệm phù hợp với mô hình động học Yoon-Nelson.

Keywords: sugarcane bagasse, adsorption, heavy metals, modified material, fixed bed column

1. Introduction

In recent years, water pollution caused by heavy metals has become a matter of concern worldwide. Municipal and industrial waste water have been discharged directly to water sources and introduced considerable amounts of toxic metal into aquatic environments which can cause contamination and be dangerous to a variety of living species (Connell et al., 2008). Among all heavy metals, copper has gained much attention due to their highly toxic nature even at low concentrations and may cause gastrointestinal diseases and brain disorder; therefore, it needs to be removed from water sources (Gonte and Balasubramanian, 2013).

To deal with the copper pollution in water, there are various methods proposed to remove this toxic metal in water including precipitation, membrane technology, ion exchange, adsorption, etc (Connell et al., 2008). With the advantages of economical benefits and high efficiency at low concentration, adsorption method with the use of low-cost adsorbents prepared from cellulose in agricultural waste such as rice husk, saw dust, peanut shell, etc has received much attention (Demirbas, 2008). In Vietnam, sugarcane bagasse has become a potential material for heavy metal removal because it is low-cost, abundant and locally available. However, raw materials with unmodified cellulose

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show low adsorption capacity and physical stability (Hokkanen et al., 2016). Therefore, various direct chemical modification methods such as esterification, etherification, halogenation and oxidation have been used to try to enhance the efficiency of the material as well as to maintain structural stability. In esterification process, organic acid is introduced to react with the cellulosic hydroxyl groups in the material to form an ester linkage (Connell et al., 2008). The carboxylic content of material then is increased, leading to a corresponding increase in the sorption of divalent metal ions. The aim of this work was to study the adsorption capacity of sugarcane bagasse modified by the agent acid citric for the removal of copper from aqueous environment.

2. Materials and Methods

2.1 Materials

2.1.1 Pre-treatment

Bagasse was collected then washed thoroughly with distilled water to ensure the removal of dust then dried at 70^{o}C for 24 hours to remove all moisture. The material then was milled to get desired particle size of 1–2 mm for further treatments.

2.1.2. Alkali treatment

The material was treated with NaOH 0.1 solution in order to extract noncellulosic binding materials like hemicelluloses/lignin complexes from sugarcane bagasse composition. After being stirred with NaOH in 2 hours, bagasse was washed with distilled water again and dried at 70^{o}C for 24 hours.

2.1.3 Modification by citric acid

In the modification step, sugarcane bagasse was mixed with citric acid following the weight ratio of 1gram sugarcane bagasse : 5 gram citric acid.

After being stirred with citric acid for 2 hours, the material was dried at 80°C. In the oven, sfter 6 hours, the temperature was raised to 120°C. After drying for 6 hours, the product was washed with distilled water to remove the excess citric acid. Lastly, the citric acid modified bagasse was dried at 70°C until constant weight and preserved in a desiccator for further use.

2.2 Methods

In this study, microstructure and surface morphology of the adsorbent samples were characterized by a 10 kV HITACHI S-4800 NIHE scanning electron microscope (SEM). To determine the functional groups of the adsorbent, Fourier transform infrared spectroscopy (FTIR) method was applied using FT-IR model 410 JASCO (Japan). Copper ion concentrations were determined by Atomic Absorption Spectrometry (AAS) method model AA-6800 Shimadzu.

3. Results and discussions

3.1 Characterisation studies

FTIR spectra for sugarcane bagasse in natural form and after modification are shown in Figure 1. There is a strong peak at 3408-3415 cm^{-1} representing the OH- stretching of phenol group of cellulose and lignin in the spectra of both materials. Besides, the peaks at 1162-1252cm^{-1} and 1048-1051cm^{-1} might be due to C–O stretching of phenolic group and ether group of cellulose, respectively (Rafatullah et al., 2009). Those functional groups are believed to enhance the metal biding ability on cellulosic adsorbents (Demirbas, 2008). After the chemical modification of sugarcane bagasse with citric acid (Figure 1b), the presence of carboxylic groups represented by stretching vibrations at 1735cm^{-1} was observed. This can be explained that the anhydride converted from citric acid reacted with the cellulosic hydroxyl groups in sugarcane bagasse to form an ester linkage, which increases adsorption ability (Connell et al., 2008). It can also be seen from the FTIR spectra that some peaks disappeared and new peaks were observed after sugarcane bagasse was pretreated with NaOH and then modified with citric acid. It is suggested that the alkaline pretreatment can cause degradation of cellular compounds, such as cell wall, proteins and complex organic components of biomass, and further acid oxidation can introduce some new functional groups to the biomass (Li et al., 2008). The appearance of carboxyl group from FTIR result indicates that modified sugarcane bagasse may have higher adsorption capacity of copper than the unmodified one.

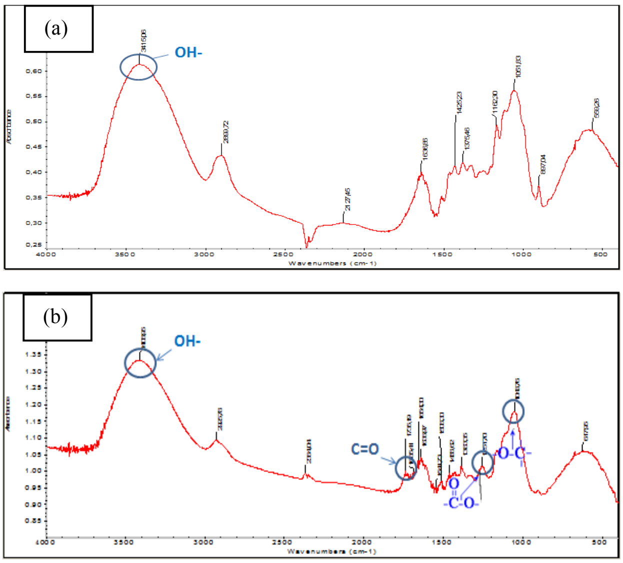


Figure 1. FTIR spectra of adsorbents: (a) unmodified sugarcane bagasse (USB) and (b) modified sugarcane bagasse (MSB)

3.2 Batch study

3.2.1 Effect of pH

pH of the solution is the most important parameter affecting metal ion adsorption because hydrogen ion competes with the positively charged metal ions on the active sites of the adsorbent (Rafatullah et al., 2009). The effect of pH on the equilibrium adsorption capacity of sugarcane bagasse was studied in the range of 1 – 7. As shown in Figure 2, the uptake of copper ions increased with the increase of pH and reached maximum efficiency at 5 – 5.5. It can be explained that at low pH, the high concentration of ion H^+ competes with metal ions for the same active adsorption site. When pH increases, the surface of adsorbent becomes less positive and the attraction force between metal ions and adsorbent's surface is likely to increase. A slightly decrease in adsorption at high pH is due to the formation of soluble hydroxyl complexes (Rafatullah et al., 2009). At higher pH, metal precipitation appears and the removal of heavy metal would not follow adsorption mechanism anymore.

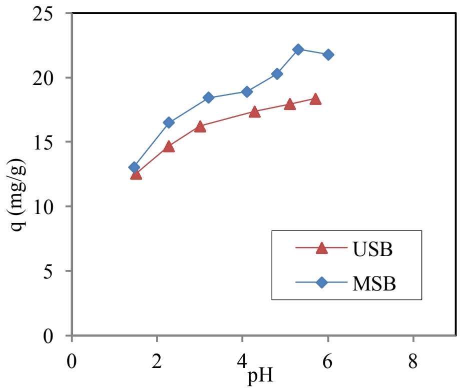


Figure 2. Effect of pH on the adsorption of copper on sugarcane bagasse; USB - Unmodified sugarcane bagasse, MSB: modified sugarcane bagasse

3.2.2 Effect of initial concentration

The adsorption of Cu(II) by sugarcane bagasse was conducted in different initial concentrations ranging from 1 mg/L to 400 mg/L. Figure 3 shows the relationship between the initial concentration of Cu(II) and the removal efficiency of adsorbents. From Figure 3, it can be seen that the removal percentage of copper adsorbed by sugarcane bagasse decreased with the increase of initial metal concentration.

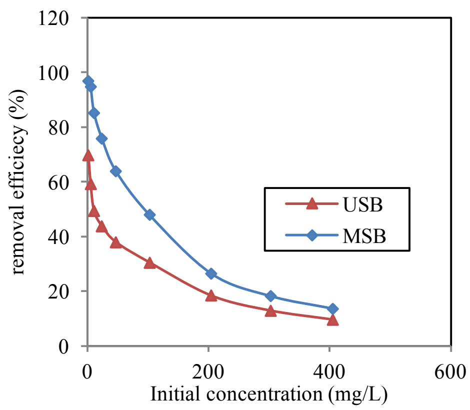


Figure 3. Effect of initial concentration on the adsorption of copper on sugarcane bagasse; USB - Unmodified sugarcane bagasse, MSB- modified sugarcane bagasse

When the concentration of Cu(II) increased from 1 to 400 mg/L, the adsorption efficiency of Cu(II) adsorbed onto USB and MSB decreased from 97% to 14% and from 70% to 9.5%, respectively. This can be explained that for the low concentration, the competition for active sites on the surface of sugarcane bagasse is relatively low, leading to the high efficiency of copper removal. Increase of initial concentration can be attributed to decreased surface area and availability of adsorption sites, therefore, the percentage of Cu(II) adsorbed decreases (Rafatullah et al., 2009).

3.2.3 Isotherm models

In this research, Langmuir and Freundlich isotherm models were applied to predict the ability of adsorbents for copper ion removal in solution.
The linear form of Langmuir model is defined by (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \qquad (1)$$

Where C_e (mg/L) is the equilibrium concentration of Cu(II) in solution; q_e (mg/g) is the amount of copper adsorbed at equilibrium; K_a(L/mg) and q_m(mg/g) are the isotherm constants. The constant q_m represents the amount of adsorbate require to form a monolayer (Rafatullah et al., 2009).

Equation (2) shows the linear expression of Freundlich equation:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \qquad (2)$$

Where K_F ((mg/g)(L/mg)1/n) and n are Freundlich constants. They are related to adsorption capacity and energy of adsorption, respectively (Connell et al., 2008). When lnqe is plotted versus lnCe and the data are analyzed by linear regression, the constants 1/n and K_F can be calculated from the slope and intercept (Pham et al., 2012).

Langmuir isotherm's linear form was given by Figure 4 by the plots of C_e/q_e against C_e. From the slope and the intercept of this equation, q_m, K_a constants and R^2 values were calculated and reported in Table 1. According to Langmuir isotherm, the estimated maximum adsorption capacity of MSB was found to reach 28.17 mg/g, which was higher than USB with the capacity of 21.27 mg/g. High values of correlation coefficient (R^2=0.99) indicates that Langmuir model showed a better fit with the experimental isotherm data than the Freundlich model (R^2=0.96). This result demonstrates the formation of monolayer coverage of copper ion at the outer surface of sugarcane bagasse (Rafatullah et al., 2009).

The Langmuir isotherm can also be given by the separation factor (R_L). The dimensionless equilibrium parameter R_L can express the essential characteristics of Langmuir isotherm. The value of R_L indicates the type of isotherm to be either unfavorable (R_L>1), linear (R_L<1), favorable (0<R_L<1), or irreversible (R_L=0). R_L was calculated and reported in Table 1. In this study, R_L was found to be in the range from 0 to 1 (R_L=0.401 for USB and R_L=0.1455 for MSB), suggesting that the adsorption of Cu(II) was favourable (Pham et al., 2012). Besides, the R_L value of MSB is closer to 0 in comparison with USB, indicating that MSB has higher adsorption ability (Pham et al., 2012).

Table 1. Adsorption isotherm model constants and correlation coefficients for the adsorption of copper on unmodified and modified sugarcane bagasse; USB- Unmodified sugarcane bagasse, MSB-modified sugarcane bagasse

Adsorption isotherm	Parameter	Adsorbent	
		USB	MSB
Langmuir	K_a(L/mg)	0.032	0.13
	q_m(mg/g)	21.27	28.17
	R^2	0.996	0.99
	R_L	0.401	0.14
Freundlich	K_F((mg/g)(L/mg)1/n)	0.94	1.53
	1/n	0.5789	0.43
	R^2	0.9674	0.96

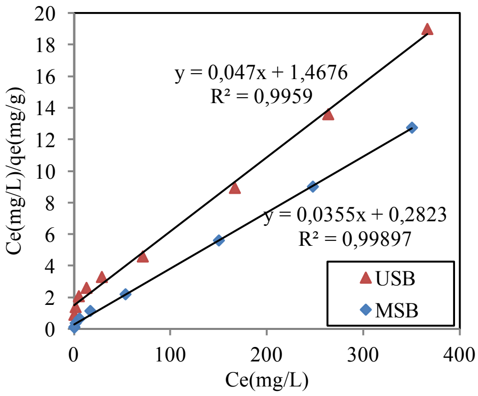


Figure 4. Langmuir adsorption isotherm plots for the adsorption of copper on unmodified and modified sugarcane bagasse; USB- Unmodified sugarcane bagasse, MSB- modified sugarcane bagasse

3.3 Fixed bed column study

3.3.1 Effect of bed height

Breakthrough curves for the adsorption of Cu(II) onto sugarcane bagasse at two different bed heights 6cm and 3cm (2g and 1g of adsorbent respectively) were illustrated in Figure 5. For this case, inlet concentration of 90 mg/l and flow rate of 2ml/min were kept constant. The breakthrough curves showed comparatively less steep tendencies for higher bed height, reflecting an extended breakthrough time. As seen from the plots, the exhaustion time for was found to be longer with the increase of bed height. While the adsorbent reached saturation after only 260 minutes with the bed height of 3cm, the exhaustion time for 6cm bed height was 520 minutes. It can be explained that for a higher bed height, more adsorbent were used for column packing, thus, there were more active sites for capturing Cu(II) ion, resulting in a greater uptake capacity (Karunarathne and Amarasinghe, 2013). Therefore, higher bed was shown to have higher efficiency in Cu(II) removal.

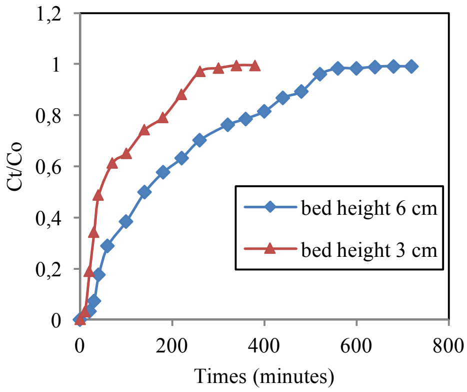


Figure 5. Breakthrough curves for the adsorption of copper on sugarcane bagasse for two different bed heights 6cm and 3cm

3.3.2 Effect of initial concentration

The effect of initial concentration on the adsorption of Cu(II) onto modified sugarcane bagasse was investigated at the concentrations of 90mg/L and 170mg/L. In this case, the flow rate of 2mL/min and bed height of 6cm were kept constant. The breakthrough curves obtained for various concentration ranges are shown in Figure 6. It is observed that as the initial ion concentration increased from 90 to 170mg/l, the exhaustion time decreased and the curve changed from a flatter shape to a steeper concave shape. For the concentration of 90mg/L, the exhaustion time was 600 minutes. For the concentration of 170mg/L, the adsorbent was saturated in 400 minutes. After 200 minutes, the removal efficiency of copper at the concentration of 90mg/L was found to be 1.3 times higher than at 170mg/L. It is suggested that for the higher concentration, the active sites were occupied more rapidly, and the column bed was saturated within a short period of time (Chowdhurry, 2015). When the concentration decreases, relatively longer contact time was required for the fixed bed to be exhausted due to a slower transportation of cations. Therefore, it is concluded that at lower concentration, the adsorption capacity and breakthrough time will be higher.

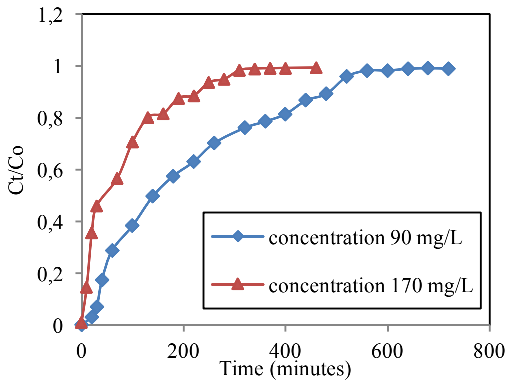


Figure 6. Breakthrough curves for the adsorption of copper on modified sugarcane bagasse for different initial concentration 90mg/L and 170mg/L.

3.3.3 Effect of flow rate

The effect of flow rate on the adsorption of Cu(II) onto sugarcane bagasse using fixed bed column was studied by varying the flow rates of 2 and 0.5 ml/min while keeping the inlet ion concentration of 90mg/l and bed height of 6cm constant. The breakthrough curves were shown in Figure 7. It can be observed that at a higher flow rate, the column was exhausted earlier and the breakthrough curve was steeper. When the flow rate increased from 0.5mL/min to 2mL/min, the exhaustion time decreased from 1150 minutes to 520 minutes. The removal efficiency was higher with lower flow rate. After 500 minutes, the copper removal efficiency for the flow rate of 0.5mL/min was 2 times higher than for 2mL/min. The phenomenon can be explained that for a higher flow rate, the front of the mass transfer zone reached the end of the fixed bed more quickly, and the adsorbent was saturated at a higher rate. In the lower rate, longer contact time was required for the exhaustion of the column (Chowdhurry, 2015). It is then indicated that with the decrease of flow rate, adsorption capacity and breakthrough time will increase. The speed of the influent was proved to be remarkably affected the contact between the adsorbate and adsorbent.

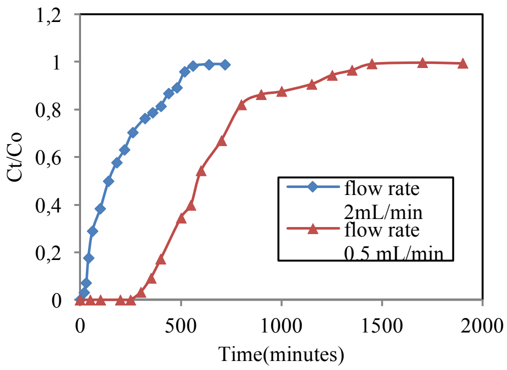
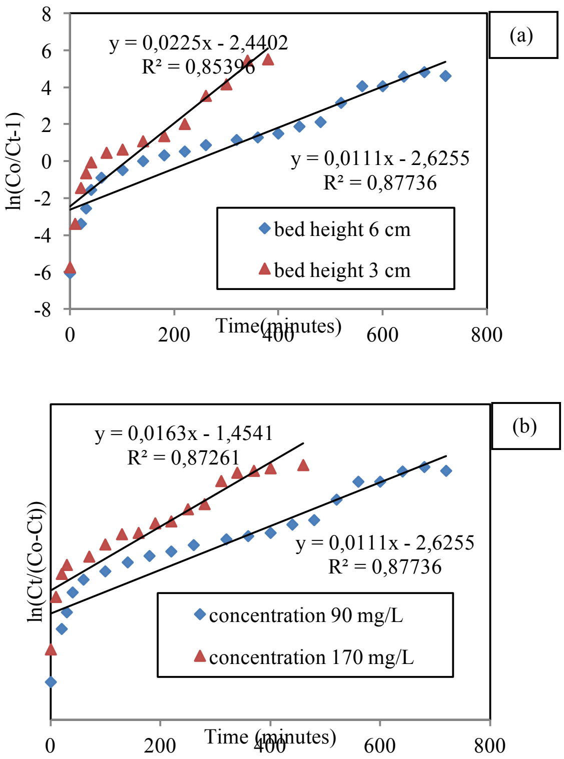


Figure 7. Breakthrough curves for the adsorption of copper on modified sugarcane bagasse for different flow rate 2mL/min and 0.5mL/min



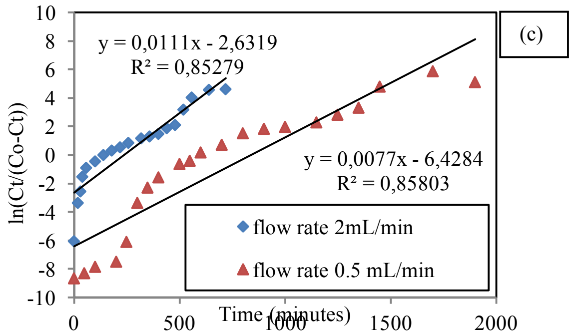


Figure 8. Yoon-Nelson kinetic plot for the adsorption of copper on modified sugarcane bagasse at (a) different bed heights; (b) different initial concentration; (c) different flow rate

3.3.4 Yoon-Nelson models

Yoon-Nelson kinetic plot for the adsorption of copper on modified sugarcane bagasse at different conditions was shown in Figure 8. The linear form of Yoon-Nelson model was expressed by (3).

$$\ln\left[\frac{C_t}{C_o - C_t}\right] = K_{YN}t - \tau K_{YN} \qquad (3)$$

where k is the rate constant (l/min), τ is the time required for 50% adsorbate breakthrough (min) and t is the breakthrough time (minutes) (Chowdhurry, 2015).

The plot of ln $C_t/(C_o-C_t)$ versus t gives a straight line with slope of K_{YN}, and intercept of $-\tau.K_{YN}$. The values of Yoon-Nelson constants and parameter were given in Table 2. The results show that the rate constant, K_{YN} increased with increased inlet ion concentration, flow rate and decreased with the increase of bed height. The constant τ is the time required for 50% to breakthrough. From Table 2, it can be seen that the time required for 50% exhaustion of column increase with the increase of bed height and decrease when the flow rate and initial concentration increase. 90 minutes was the time required for 50% exhaustion of 3cm bed height column with the flow rate 2mL/min and concentration 170mg/L while the adsorbent in the column with bed height of 6cm, initial concentration of 90mg/L and flow rate of 0.5mL/min did not achieve 50% saturated before 835 minutes. High values of regression coefficients (R^2>0.85) were determined indicating that the kinetic data fit well with Yoon-Nelson model. It then can be concluded that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of Cu(II) adsorption and the probability of adsorbate breakthrough on the adsorption (Chowdhurry, 2015).

4. Conclusion

The study investigated the adsorptive removal of copper from aqueous solution by citric acid modified sugarcane bagasse using batch experiment and fixed bed column system. From batch experiment, the adsorption capacity of sugarcane bagasse was found to increase with the increase of initial concentration and reached optimum at pH 5.5. The adsorption process followed the Langmuir isotherm model follow which modified sugarcane bagasse's maximum capacity was estimated to be 28.17 mg/g, higher than unmodified material with 21.27 mg/g.

The results of fixed bed column experiment showed that the shape of the removal efficiency of Cu(II) and exhaustion time was dependent on bed height, flow rate and initial concentration. The experimental data obtained from fixed bed column study were fitted well with Yoon-Nelson kinetic models.

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Table 3. Yoon-Nelson kinetic parameters for the adsorption of Cu(II) on sugarcane bagasse

Bed height (cm)	Initial concentration (mg/L)	Flow rate (mL/min)	K_{Th} (ml/min /mg)	q_o (mg/g)	R_{Tm}^2	K_{YN} (l/min)	τ (min)
6	90	0.5	0.086	18.87	0.863	0.008	835
6	90	2	0.123	21.29	0.877	0.011	237
3	90	2	0.250	19.52	0.854	0.023	108

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