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Kinetics and Equilibriums Adsorption of Cu (II) Ion by Chitosan and Cross-Linked Chitosan-Bentonite

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Abstract

The sorption of Cu(II) particle from aqueous solution onto chitosan and cross-linked chitosan-bentonite (CTS-BTN) as adsorbent were conducted in batch conditions. The effect of different test parameters: starting pH, sorption time was assessed. Equilibrium studies have been completed to decide the limit of chitosan and CTS-BTN for Cu(II) particle. The Langmuir and Freundlich isotherm models were used in the examination of the trial information as linearized conditions. It was discovered that the isotherm information was all around represented by the Langmuir isotherm. Chitosan and CTS-BTN showed an adsorption capacity of 125 mg/g and 142.86 mg/g, respectively. The constant of adsorption rate was investigation utilizing a pseudo first order and a pseudo second order model. The pseudo second order model brought about the best fit with test information (R^2= 0,991 for CTS and R^2= 0,995 for CTS-BTN), additionally giving a constant rate $k_{2,ads}$= 8.85 x 10^{-5} g/mg min for CTS and 3.72 x 10^{-4} g/mg min for CTS-BTN. Recommending that this model could be used in design and applications.

Keywords: *adsorption; Cu(II) ion; chitosan; cross-linked; isotherm; kinetics*

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INTRODUCTION

Wastewater carries heavy metals from industrial processes like mineral processing, electroplating, battery production, and so on, which are toxic to human wellbeing and nature (Ghorpade *et al.*, 2018). Heavy metals are lethal and not biodegradable, and they are known to impose serious health risks to living beings (Jamal *et al*.,2013).

Copper is one of the harmful heavy metals typically found in industrial wastewater. Copper, present as Cu(II) ions, is commonly used in electrical and electroplating industries. Once copper enters surface water, it attaches to natural tissues and minerals so it can be carried far away from its source. Copper does not break down and degrade in nature, so copper in contaminated water ends up accumulating in plant and animal cells. High level of copper is significantly dangerous to living organisms, with known toxicological effects targeting organs such as skin, liver and pancreas (Lakherwal, 2014). A range of treatment options can be utilized to separate and remove heavy metals from aqueous solutions, including ion exchange, precipitation of metal hydroxides, reverse osmosis, complexation, electrochemical treatment, and organic techniques. However, the conventional methods available to remove heavy metal ions within the industrial scale are quite ineffective and often costly, particularly in expelling heavy metal ions from extremely diluted solutions (Matouq *et al.*, 2015).

Various industrial effluents can also be treated using porous solid adsorbents to remove heavy metals from aqueous solutions. The adsorbent materials can be made of minerals, e.g. zeolites, silica, or alumina, and can also be comprised of organic origins such as activated carbon, wood scrap, sugar cane bagasse, chitin, or chitosan (Gupta *et al.*, 2012).

Chitosan is an excellent adsorbent material for metal ions, with advantages include its natural origin, low production cost, polymer chain structure being flexible, and high reactivity. The application of chitosan for adsorption is well-known, both in its powder and flaked form (Bailey *et al*., 1998). However, there are some limitations to these forms, such as poor acid resistance and low adsorption process rate (Kyzas *et al*., 2015). Due to these drawbacks, the synthesis of biocomposites has been under constant developments, recently focusing on chitosan composites such as chitosan-fly ash (Wen *et al*., 2011), chitosan-zeolite (Ngah*et al.*, 2012), and chitosan-montmorillonite (Nesic*et al.*, 2012; Pereira *et al.*, 2013).

Clay materials are made of hydrous aluminosilicates, which possess a high cation-exchange capacity and large specific surface areas. More importantly, clay minerals are abundant as well as chemically and mechanically stable, and their affordable production cost makes them a prospective option as immobilization material for chitosan (Nesic*et al*. 2012). Among the mineral clays, bentonite has been an attractive material for the preparation of chitosan composites because of its high cationic exchange capacity and the possibility of lamellar expansion (Anirudhan *et al*.,2010; Anirudhan and Rijith,2012).

This study applied a combination of physical and chemical modifications in the preparation of cross-linked chitosan/bentonite (CTS/BTN) composite, where chitosan would intercalate in bentonite and be cross-linked with glutaraldehyde (GLA). $CuCl_2$ solution was used for the model in this study as it is water-soluble and widely used within the chemical, electrical and electroplating industries, despite its environmental hazards. Removal of Cu (II) from aqueous solutions was investigated by batch method. The factors affecting the adsorption of Cu (II) onto CTS/BTN composite included the ratio of chitosan to bentonite. initial pH value of $CuCl_2$ solution, and contact time were investigated.

The objective of this study were to evaluate the performance of commercial chitosan and chitosan modified by bentonite as an adsorbents for the removal of metal ions from dilute aqueous solutions. The effect of pH on adsorption capacity, kinetics and Langmuir and Freundlich adsorption isotherm was investigated in this study.

MATERIALS AND METHODS

Reagents

Low-molecular-weight chitosan powders with molecular weight of 170 kDa, a degree of deacetylation (DDA) of 90% and a particle size of 150 mesh were acquired from Biotech Surindo Indonesia and used for the experiment without any pre-treatment. Chitosan is soluble in weak acids like acetic acid and lactic acid. Extra-pure grade $CuCl_2$, 37% pure HCl, 98% H_2SO_4 and sodium acetate-nitric acid buffer were obtained from Merck (Sigma-Aldrich, Indonesia). All reagents in this experiment were of analytical grade and deionized water was used to prepare all solutions. Bentonite powder with a particle size of 15-20 micron was purchased from Sigma-Aldrich, Indonesia. Commercial glutaraldehyde (GLA) in the form of 25 and 50% aqueous solutions (Merck, Germany) were used for the experiment.

Adsorption Kinetics

Two grams of chitosan powder was dissolved in 100 mL of 2% (wt/v) acetic acid solution. 2 g of bentonite was then mixed into the solution at 20°C for 2 h. Next, GLA solution (25 wt%) was added into the mixed solution, with the ratio of 5 mL GLA per g of chitosan. Cross-linking reaction occurred at 60°C for 23 h, and then distilled water was used to wash the CTS-BTN composite in order to remove any free GLA present. The composite was subsequently dried in an oven at 60°C for 24 h. After drying, the composite was ground and sieved. The composite with 200 mesh particle size was collected and used for the batch experiments.

Batch experiments were conducted by reacting Cu(II) solutions in conical flasks. The initial concentrations of Cu(II) solutions were 10-200 mg/L. A 10 mL volume of each solution was transferred separately into flasks containing 0.1 g CTS-BTN in ratio of 1:1; 1:1,5; 1:2; 1:2,5; 1:3; and 1:3,5. The flasks were continuously stirred at 200 rpm throughout the required time to achieve adsorption equilibrium at pH 6. Adjustments to pH were made using sodium acetate-nitric acid buffer. The metal ion concentrations in the liquid phase for each sample were determined by atomic absorption spectroscopy (Shimadzu AA-670 spectrophotometer at 540 nm). Experiments were performed at 30 ºC for 150 min at pH 6 and in duplicates.

Metal Ion Adsorption by chitosan

The adsorption capacity of chitosan and efficiency of Cu(II) removal were determined using the following equations (Kowanga *et al*., 2016):

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

Where q_e is the measure of Cu(II) particle adsorbed by the chitosan or chitosan-bentonite as adsorbents (mg of copper per gram of adsorbent), Co and Ce are the underlying and balance of Cu(II) particle fixations (mg/L), individually, V is the volume of Cu(II) particle arrangement (L); and m is the mass of adsorbents utilized (g).

Adsorption isotherm

The Langmuir and Freundlich isotherms are the two most widely used adsorption isotherms, and the experimental data in this study were analyzed in term of these isotherms. The Langmuir adsorption isotherm equation is expressed as follows (Laus *et al*, 2010):

$$q_{\mathrm{e}} = \frac{K_{LC_e}q_{max}}{1+K_LC_e} \qquad (2)$$

Where q_e and C_e are the adsorbed mass fraction (mg/g) and the adsorbed concentration in solution (mg/L), respectively and both at equilibrium, K_L is the Langmuir constant (L/g), and qmaxis maximum adsorption capacity (mg/g). The Langmuir model is based on the assumptionsof homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between the adsorbed species (Arica *et al.*, 2004; Wan *et al.*, 2010). The linear form of the Langmuir isotherm represented by Eq.(3), is used to determine the q_{max} and K_L values from the angular and linear coefficients obtained by plotting C_e/q_e as a function of C_e (Harmoud *et al*, 2014).

$$\frac{C_e}{q_e} = \frac{1}{K_Lq_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

Another important parameter, $R_{L,}$ or called the separation factor was calculated to determine whether an adsorption process is favorable or unfavorable:

$$R_L = \frac{1}{1+K_LC_0} \qquad (4)$$

Where $R_L$value between 0 and 1 means the adsorption process is favorable (Futalan *et al.*, 2011).

The Freundlich model, on the other hand, describes reversible heterogeneous adsorption since it does not assume monolayer adsorption (Arica *et al.*, 2004). The Freundlich isotherm is an empirical equation and is one of the most widely used isotherms for the description of multi-site adsorption. It is expressed mathematically as follows:

$$q_e = K_F{C_e}^{1/n} \qquad (5)$$

Equation 5 can also be shown in the linearized logarithmic form as (Li *et al*, 2012):

$$\mathrm{loq}\, q_e = \log K_F + \frac{1}{n}\log C_e \qquad (6)$$

Where K_F and n are the Freundlich isotherm constants indicating the adsorption capacity and adsorption force, separately (Febrianto *et al.*, 2009). The Freundlich model is not restricted to a monolayer covering of adsorbate; it describes the equilibrium on the heterogeneous surfaces.

In order to explore the adsorption mechanism and potential rate-controlling step, adsorption kinetics models such as pseudo-first-order and pseudo-second-order are necessary to fit the experimental data. Generally, the linear form of pseudo-first-order kinetic model is expressed by (Justi *et al.*, 2005):

$$\log(q_e - q_t) = logq_e - \frac{k_{1,ads}}{2.303}t \qquad (7)$$

Where q_t is the adsorption capacity at time t and q_e is adsorption capacity at equilibrium, mg/g; $k_{1,\ ads}$ is the rate constant of the pseudo first-order kinetic model, 1/h; t is the contact time, h. The constants of the equation are determined by the slope and intercept of the linear plot of $1/q_t$ versus 1/t. The pseudo second-order model can be presented as follow (Repo *et al.*, 2013):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{2,ads}\,{q_e}^2} \qquad (8)$$

Where $k_{2,ads}$ is the rate constant of the pseudo second-order adsorption model, g/mg.h. The values of $k_{2,ads}$ and q_e are calculated from the intercept and slope of the linear plot of t/q_t versus t, respectively.

RESULTS AND DISCUSSIONS

Effect of pH

The pH of the aqueous solution represents the most important parameter controlling the adsorption capacity processes. In this experiment, the effect of pH on the adsorption of Cu(II) ion onto chitosan was observed within the pH range of 4 to 8 at an initial concentration of 50 mg/L as demonstrated in Figure 1. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface-active sites.

Figure 1 demonstrates the effect of pH on the adsorption capacity of Cu(II) ion onto chitosan. It is shown that the amount of Cu(II) ion adsorbed increases with solution pH up to almost pH 6 and then decreases with increasing pH.

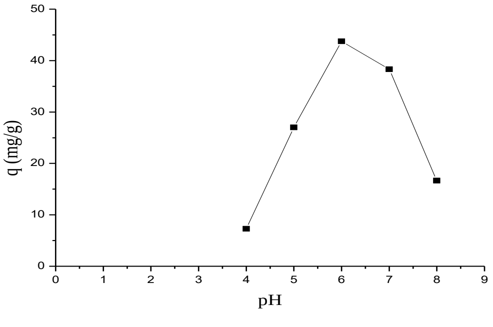

Figure 1. Relation of pH vs q by chitosan. Volume = 50.0 mL; mass of chitosan = 50.0 mg; temperature = 30ºC and stirring = 200 rpm.

The maximum equilibrium uptake value of 43.75 mg/g was obtained at pH 6. A similar experiment was proposed by an earlier work by Laus *et al.* (2010) for metal adsorption using chitosan crosslink. At low pH, the adsorbent surface will be completely covered with hydronium ions which compete strongly with metal ions for adsorption sites. The concentration of H_3O^+ ions decreases as the pH increases, facilitating the adsorption of metal ions by the adsorbent (Gupta and Bhattacharyya, 2006)

Effect of Ratio Chitosan and Bentonite

The adsorption capacity for Cu(II) ion particle adsorption by various ratio of CTS-BTN is shown in Figure 2. In this study, CTS-BTN at 1:1 ratio gave an adsorption capacity of 65.82 mg/g and the addition of bentonite was found to increase the adsorption capacity. A maximum adsorption capacity of 87.14 mg/g was achieved on CTS-BTN at 1:2.5 ratio, and the adsorption capacity decreased on CTS-BTN at above 1:2.5 ratio, with the ratio of 1:3.5 CTS-BTN resulted to an adsorption capacity of 75.76 mg/g. The high adsorption capacity may be due to the large interlayer spacing resulting from the insertion of chitosan in bentonite and the strong interaction between the composite and dye molecules. However, the adsorption capacity reduced with the increase above the optimal maximum ratio, suggesting that increasing content of bentonite in CTS-BTN composite was adverse to the adsorption of Cu(II) onto CTS-BTN composite (Huang *et al.*, 2015). According to Huang *et al.* (2015), a maximum efficiency of 90% was attained at ratio of 2:2 chitosan to bentonite.

Figure 3 represents the adsorption kinetics for Cu(II) ion adsorption by chitosan and ratio of CTS-BTN. The adsorption capacity curve demonstrated that the adsorption equilibrium was reached within 90 mins, and then remained constant until the end of the experiment at t=150 min. It was observed that 54.65 mg Cu(II)/g chitosan and 93.88 mg Cu(II)/g ratio of CTS-BTN was adsorbed at equilibrium at 30ºC.

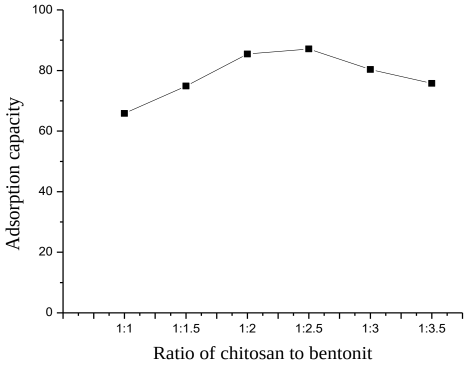

Figure 2. Relation of ratio CTS-BTNvs adsorption capacity; [Cu^{2+}] = 100 mg/L; pH 6.0; Volume = 50 mL; adsorbent mass = 50.0 mg; temperature = 30ºC; stirring = 200 rpm

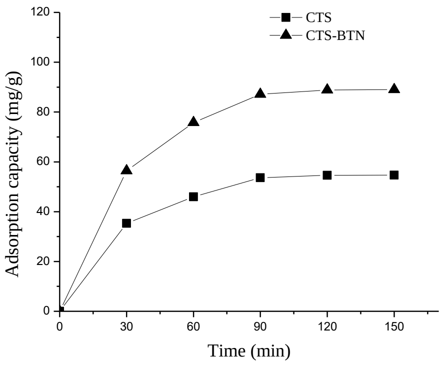

Figure 3. Relation of time vs adsorption capacity by CTS and CTS-BTN.Volume = 50.0 mL; [Cu^{2+}] = 100 mg/L; pH 6.0; mass of adsorbent = 50.0 mg; temperature = 30ºC; stirring = 200 rpm.

Ngah *et al.* (2002) used chitosan microspheres and reported 80.7 mg/g, whereas Laus *et al.* (2010) reported an adsorption kinetic of Cu(II) ion by chitosan modified (CTS-ECH-TPP) at 72.50 mg/g. On the other hand, Popuri *et al.* (2013) obtained an adsorption kinetic of chitosan of 51.00 mg/g. It is important to highlight that several studies on adsoprtion from different experiments have shown that each chitosan sample and derivatives have their own adsorption features, which are related to deacetylation degree, type of particles, porosity, as well as crosslinking degree (Vasconcelos *et al.*, 2007).

Adsorption equilibrium isotherm

The equilibrium studies were conducted with the necessary contact time of 90 mins at pH of 6 as the optimum condition for adsorption. Figure 4 demonstrates the adsorption equilibrium isotherm obtained for Cu(II) ions, showing the relationship between the amount of metal ion adsorbed on the adsorbent surface and the remaining metal ion concentration in the aqueous phase equilibrium. Copper was extracted out of a solution with ion concentration of 6.56mg/L and adsorbed onto the chitosan surface, with an adsorption level of 8.80 mg of Cu(II)/g chitosan. The amount of copper adsorbed onto the chitosan surface was found to increase with increased concentration of the ions in the solution, until a maximum adsorption capacity was reached at 69.64 mg Cu(II)/g chitosan from solution with Cu(II) ions concentration of 108.96 mg/L.

On the other hand, the use of CTS-BTN as adsorbent showed an adsorption capacity of 10.65 mg Cu(II)/g CTS-BTN from solution with Cu(II) ions concentration of 6.56 mg/L.The adsorption capacity was also found to increase as the solution is more concentrated, until a maximum adsorption capacity was obtained at 77.54 mg Cu(II)/g CTS-BTN from solution with Cu(II) ions concentration of 108.96 mg/L. Similar result was also observed in the research conducted by Vasconcelos *et al.* (2007) on the equilibrium isotherm for Cu(II) ions by chitosan.

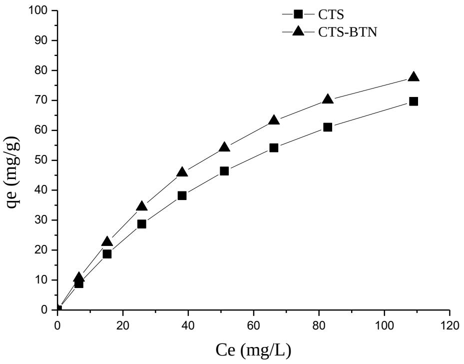

Figure 4. Relation between C_e and q_e by chitosan and CTS-BTN. Volume = 50 mL; C_0 = 10-200 mg/L; pH 6,mass of adsorbent = 50 mg; contact time 90 min; temperature 30ºC; stirring 200 rpm.

As seen on Figure 4, the amount adsorbed increased with the equilibrium concentration of the metal ion in solution, progressively reaching saturation of the adsorbent. The Langmuir and Freundlich isotherm models were usedfor interpretation of the adsorption data.

Langmuir and Freundlich isotherm models

The Langmuir and Freundlich isotherm models, as shown in Equation 2 and 5, are preferred in studies on adsorption in solutions and were used to fit the experimental data in this study. The linear form of the Langmuir isotherm model (eq.3) and the Freundlich isotherm model (eq.6) were used to calculate the parameters. The selection of isotherm model is based on the linearization that provided the best fit of experimental data, that is the best correlation coefficient value (R). The results of adsorption capacity Cu(II) ion for CTS and CTS-BTN are shown in Table 1.

The Langmuir and Freundlich model parameters are shown in Table 1. From Langmuir model were obtained K_L (1.27×10^{-2} mg/L) and q_m (142,86 mg/g) value of CTS-BTN were higher than K_L(1.15×10^{-2} mg/L) and q_m(142,86 mg/g) value of CTS.

Figure 5 demonstrates the linearization of Langmuir isotherm plot for sorption of Cu(II) by CTS and CTS-BTN adsorbent. The regression lines were obtained by plotting the relation of C_e vs C_e/q_e. The regression line of CTS has a higher slope than CTS-BTN, with a slope of 0.008 and 0.007 respectively. However, the correlation coefficient value (R) of CTS-BTN is 0.998, which is higher than the correlation coefficient value (R) of CTS that is 0.995.

Table 1. Parameters and coefficient of correlation for CTS and CTS-BTN of Langmuir and Freundlich model

Model	Adsorbent	Parameters	R^2
Langmuir	CTS	$K_L = 1.15\times10^{-2}$ mg/L q_m = 125mg/g	0.995
	CTS-BTN	$K_L=1.27\times10^{-2}$ mg/L q_m = 142,86 mg/g	0.998
Freundlich	CTS	K_F = 2.50 1/n = 0.727	0.992
	CTS-BTN	K_F = 3.13 1/n = 0.711	0.984

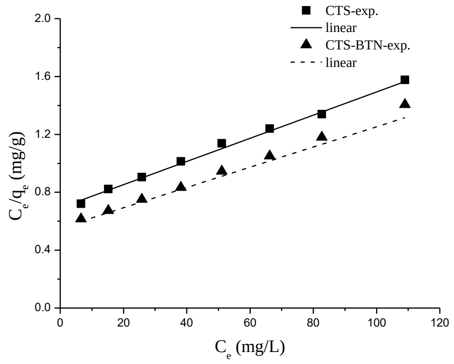

Figure 5. Relation between C_e vs C_e/q_e by CTS and CTS-BTN

Based on equation (4), the value of R_L was obtained, 0.19 for chitosan and 0.18 for CTC-BTN, which indicate that the adsorption processes are favourable (Ngah*et al.*, 2002; Futalan*et al*., 2011).

Figure 6 shows the linearization of Freundlich isotherm plot for sorption of Cu(II) by CTS and CTS-BTN adsorbent. The regression lines were obtained by plotting the relation of log C_e versus log q_e. The regression line of CTS has a higher slope than CTS-BTN, with a slope of 0.727 and 0.711 respectively. However, the correlation coefficient value (R) of CTS is 0.992, which is higher than correlation coefficient value (R) of CTS-BTN that is 0.984.

The crosslinked treatment of chitosan was found to reduce the adsorption capacity on metal ions due to a decrease in accessibility to internal sites or blockage of some adsorption sites (Ngah*et al.*, 2002). Based on Figure 5, the value of K_F and n were 2.50 mg/g and 1.38, while R^2= 0.992. The higher value of correlation coefficient obtained suggests that the Langmuir model represent the sorption process better than the Freundlich model in this study (Hanif*et al.*, 2007).

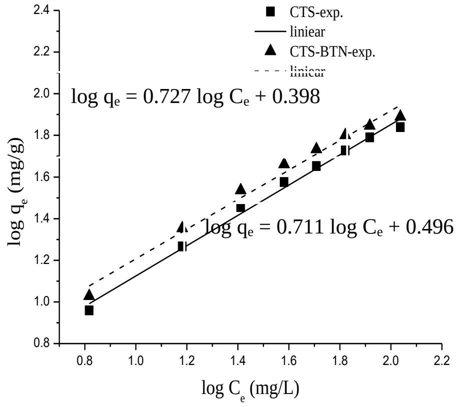

Figure 6. Relation between log C_e vs log q_e plot by CTS and CTS-BTN

Pseudo First Order and Pseudo Second Orderfor IsothermModels

Figure 7 shows the pseudo-first-order by plotting time in minutes vs log (q_e-q_t). The regression of CTS and CTS-BTN have the same slope value of -0.001. However, the correlation coefficient value (R^2) of CTS, (0.983) is higher than CTS-BTN (0.810). Figure 8 shows the pseudo-second-order by plotting time in minutes vs t/q_t. The regression line of CTS has the slope value of 0.012, which is higher than CTS-BTN slope value of 0.009. However, the correlation coefficient value (R^2) of CTS-BTN, which is 0.995 higher than CTS, which is 0.991. First-order sorption rate constant ($k_{1,ads}$), second-order sorption rate constant ($k_{2,ads}$) and q_{eq} values were determined from the slope and intercept of the plots using equation (7) and (8).

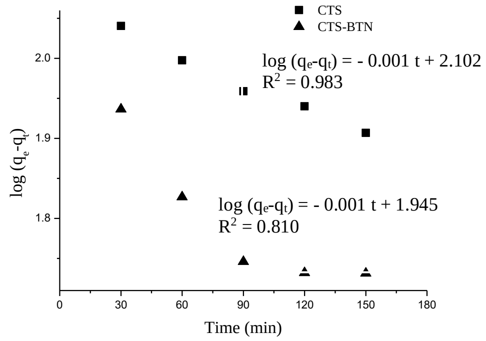

Figure 7. Relation between time vs log (q_e-q_t) of plot pseudo first order onto CTS and CTS-BTN

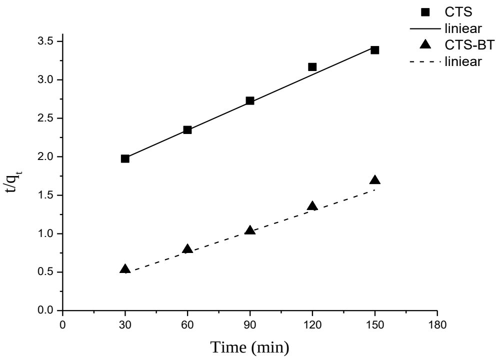

Figure 8. Relation time vs t/q plot of pseudo second order onto CTS and CTS-BTN

Table 2. Q_e, $k_{1,ads}$, $k_{2,ads}$ and coefficient of correlation associated to the Lagergren pseudo first order and pseudo second order kinetic model

	CTS	CTS-BTN
Pseudo first order kinetic		
q_e, (mg/g)	126.47	88.31
$k_{1,ads}$ (1/min)	2.30×10^{-3}	2.30×10^{-3}
R^2	0.983	0.810
Pseudo second order kinetic		
q_e, (mg/g)	83.33	111,11
$k_{2,ads}$ (g/mg min)	8.85×10^{-5}	3.72×10^{-4}
R^2	0.991	0.995

The values of the parameters $k_{1,ads}$,$k_{2,ads}$, q_e, and correlation coefficients are presented in Table 2. The correlation coefficients of CTS for the second-order kinetic model aobtained are greater than the first-order kinetic model, which R^2 for the second-order is 0.991 and the first-order is 0.983. On the other hand, the correlation coefficients of CTS-BTN for the second-order kinetic model obtained are greater than the first-order kinetic model, which R^2 for the second-order is 0.995 and the first-order is 0.810. These indicate that the sorption system is a second-order model and not a first-order model, based on the assumption that the sorption may be the rate-limiting step (Aksu, 2001; Robati, 2013; Kowanga, 2016).

CONCLUSIONS

Commercial chitosan and chitosan-bentonite were used in this study as an adsorbent to remove copper ions from dilute solutions. It was observed that the pH of the solution was the most significant parameter determining the adsorption capacity. The maximum equilibrium uptake value found was 43.75 mg/g for CTS at pH 6. The Langmuir model was fit better than Freundlich model to describe the isotherm models for the adsorption capacity in this study. Based on the Langmuir model, the adsorption capacity of chitosan was 125 mg/gand chitosan-bentonite was 142.86 mg/g. For the studied systems, adsorption kinetic followed the pseudo-second-order equation mechanism, giving the best correlation of the experimental data.

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