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Enhanced Removal of Cobalt(II) Ions from Aqueous Solution Using Thiourea-Impregnated *Gigantochloa albociliata* Charcoal Powder

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ABSTRACT

The feasibility of *Gigantochloa albociliata* (Buluh Madu) charcoal as low-cost adsorbent, effective and locally available material for the removal of cationic of Co(II) ions was investigated. In this study, *Gigantochloa albociliata* charcoal was impregnated with thiourea as chelating agent. The modification involved impregnation of thiourea into *Gigantochloa albociliata* charcoal via retort process. The resulting impregnated of *Gigantochloa albociliata* morphological characteristics for both modified and unmodified were characterize using a Scanning Electron Microscope (SEM). The surface of modified *Gigantochloa albociliata* charcoal seems to be irregular and uneven, with the present of Thiourea. Energy-dispersive X-ray spectroscopy analysis (EDX) showing the presence of nitrogen and sulphur in modified of *Gigantochloa albociliata* charcoal indicating the impregnation successfully occurred. The percentage carbon, oxygen, silica exist in modified *Gigantochloa albociliata* charcoal slightly decrease compared to unmodified. Further analysis of adsorptivity was carried out by soaking the modified charcoal in Co(II) ions aqueous solution and measure using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES). To study the adsorptivity of adsorbent, effect of contact time, initial concentration, and pH was used as parameter. The results show that impregnated charcoal has the highest adsorption of Co(II) ions compared with unmodified of *Gigantochloa albociliata* charcoal. Further study was carried out by analyse equilibrium data using isotherm and kinetic. Freundlich isotherm shows an excellent fit of experiment data may describe the heterogeneous surface account for multilayer adsorption. For kinetic study, pseudo-second order kinetic model show better fit that involving of chemisorption indicates there is electron sharing or transfer between thiourea (N- and S-groups) and Co(II) ions. From the result obtained, it is describe that impregnation of charcoal with thiourea enhance the intake of Co(II) ions.

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1. INTRODUCTION

Heavy metal pollution has become a major concern around the globe, especially with industrial growth in line in generating and discharge numerous and different kind of heavy metal into the environment, making heavy metal become one of the crucial environmental problems until today. Large amounts of wastewaters already containing Cobalt discharged from different industries especially in semiconductor industries [4]. This issue may pose a threat to environmental, mainly for human health. With that various treatment of Cobalt removal containing in wastewater has gained worldwide attention. The development and numerous of effective methods for removing heavy metal has been carried out in different of ways, yet still challenging for some researcher [17]. Electrocoagulation [6][18], electrodialysis [18], solvent extraction [13], chemical precipitation [21] and adsorption, are among of methods has been carried out in wastewater treatment [14][19]. Among them, adsorption has attracted increasing attentional due to their conventional methods for wastewater treatment which is more viable, easy operation and advantageous compared to the other methods [16]. However, finding the best route and suitable adsorbent to enhance the capability in removing heavy metal in wastewater might be quite challenging unless there is further modification

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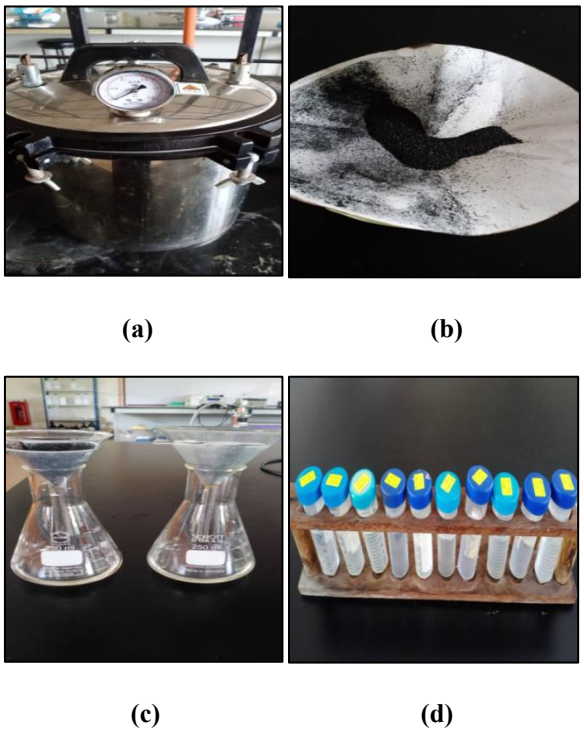
are involved. In this research study, the modification involved impregnation of Thiourea into *Gigantochloa albociliata* charcoal via retort process. The retort is tightly sealed to maintain a controlled environment, which may involve elevated temperature and pressure to enhance the interaction between the impregnating solution and the materials internal pores. This setup helps to promote deeper diffusion of the active compound into the materials structure, resulting in better surface modification and functional group attachment. The pressurized conditions in the retort also prevent the loss of volatile component and improve the efficiency of the impregnation, making it especially suitable for preparing chemically modified adsorbents with improved adsorption performance.

2. METHODOLOGY

Gigantochloa albociliata species (Buluh Madu) was obtained from Universiti Teknologi MARA (UiTM). The chemicals for preparing modified adsorbent are Nitric Acid (HNO_3) (HmbG Chemicals), Thiourea (Sigma Aldrich), Multi elements standard mixture (Perkin Elmer), deionized water. Next, as for the apparatus and equipment used in characterization process were pH meter, Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) (Thermo Electron Corporation), and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) (Perkin Elmer). In this research paper, *Gigantochloa albociliata species* (Buluh madu) is used as starting material in the production of adsorbent. This bamboo was cut into small pieces, and burned into charcoal by using conventional method with the temperature around 500-900^{o}C. Then, the charcoal obtained was crushed into small particle size by using mortar and pestle, and were seizes to obtain size of 150µm - 250µm. Before used, the charcoal then was washed with deionized water to eliminate undesirable materials, by stirring for 10 minutes before drying process followed by oven dried at 50^{o}C for 24h.

2.1 Bamboo Charcoal-Thiourea Modification

The dried Bamboo charcoal (BC) was then undergoes pre-treatment process with Nitric Acid (HNO_3). HNO_3 solution was prepared by dissolving appropriate amount of concentration 15M HNO_3 in 500ml deionised water. Then, 50g of Charcoal was immersed in 300ml of 1M HNO_3 (solid liquid ratio=1:6) and stirred for 10 minutes. Then, it was retorted for 1h. After the immersion time ended, the sample then remained in the mixture at room temperature for cooling process for 24h. Then, the sample was filtered out from the solution and later put in the oven at 50^{o}C for drying process for 24h and stored in desiccators for further experiments. It is known as pre-treatment of Charcoal (HNO_3-BC). The HNO_3-BC then was modified using Thiourea as chelator. 10g pre-treated bamboo charcoal then was added into 5g in 200ml of Thiourea with constant stirring for 10 minutes, and undergoes retort for 1h. Then, the modified charcoal was remained in retort for cooling process for 24h. The residue was filtered, and dried at 50^{o}C for 24h. The sample then was stored in a reagent bottle (Identified as Thiourea-BC). Next, the resulting filtrate was collected, and the samples are stored in labelled test tubes for quantitative analysis. The final concentration of residual Co(II) ions after adsorption was determined using inductively coupled plasma–optical emission spectrometry (ICP-OES).



(a) **(b)**

(c) **(d)**

Figure 1. Shows the step of retort process and the preparation of adsorbent of Thiourea

2.2 Preparation of Aqueous Water Stock of Co (II) Solution

(1000 mg/l) was prepared by dissolving 4.2265g of Cobalt (II) acetate (Co(CH3COO)2.4H2O) in 1000 ml of deionized water. The solid compound of Co(II) was shook to make it homogenized and to ensure the solid compound was completely dissolved in 1000ml of deionized in volumetric flask. Lastly, the volume of stock solution metal ions of Co(II) solution was measure according to desired concentration.

2.3 Retort

Retort Figure 1 (a) used in impregnation of BC in the impregnation process for preparation of adsorbent, a retort serves as a sealed, high pressure vessel, and heated to 120 - 126^{o}C with 0.10 – 0.14MPa to ensure uniform penetration of modifying agents into the raw materials. During the process, the adsorbent such as bamboo are soaked or mixed with a chemical agent like HNO_3 and thiourea, then placed inside the retort.

2.4 Batch Adsorption Experiment

The order to study the optimal condition of thiourea adsorption, the effiency of the impregnation of BC as an adsorbent was investigated through batch adsorption experiments for the removal of Co(II) heavy metal ions from aqueous. The Co(II) heavy metal ions stock solutions having concentration of 1000 ppm were prepared by adding appropriate amounts of deionized water, the test solutions were prepared by diluting the stock solution at desired concentration. The adsorption isotherm study for Co(II) ions was carried out by preparing different concentration of 10, 20, 30, 50, and 80 ppm of Co(II) ions stock solution with fixed amounts of adsorbent (2g), volume (40ml), pH (6), and contact time (60) throughout the experiment.

Meanwhile, for the effect of contact time, the initial concentration (50ppm), adsorbent dosage (2g), volume (40ml),

and pH (6) were remained constant, while the contact time was varied which is 15, 30, 45, 60, and 90 minutes. At each of specified time, the adsorbent will filtered out from Co(II) ions solution, and the residual of Co(II) ions was determined by using ICP-OES. The adsorption capacity at each contact time was calculated to examine the highest adsorption rate before approaching equilibrium and to provide experimental data for kinetic study. Lastly, the effect of pH was prepared in range of 1, 2, 4, 6, and 8. The initial pH of each Co(II) ions solution was adjusted to the required of pH value before the addition of adsorbent. The initial concentration (50ppm), adsorbent dosage (2g), volume (40ml) and contact time (60 minutes), were kept constant to evaluate the influence of pH on the adsorption process.

2.5 Isotherm and Kinetic Study

The isotherm studies were correlated with Langmuir and Freundlich isotherm model. The percentage removal of Co(II) ions of each batch adsorption experiment were calculated by using following equation.

$$\text{Percentage removal (R\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{C_o - C_t}{m} \cdot V \quad (2)$$

$$q_e = \frac{C_o - C_e}{m} \cdot V \quad (3)$$

Where:

The C_o (mg/L) and C_e (mg/L) are the initial and final concentration of metal ions respectively. While the amount of adsorbate adsorbed per unit mass of adsorbent at time t (q_t, mg/g), and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (q_e, mg/g), C_t (mg/L) is the concentrations of adsorbates at time t, while V (L) is the volume of metal ions solution, and m (g) mass of adsorbent.

In this experiment, the equilibrium data obtained from batch experiment were analysed by using Langmuir isotherm model with the following equation.

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (4)$$

Where:

C_e is the concentration of solute at equilibrium (mg/l), q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), Q_0 is the monolayer adsorption capacity (mg/g), and b is the Langmuir constant related with the rate of adsorption (L/mg).

Then, Freundlich isotherm model was carried out followed by equation below.

$$q_e = K_f C_e{}^{1/n} \quad (5)$$

While in linear form of equation is:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

Where:

q_e is the amount of solute adsorbed per unit mass of adsorbent (mg/g), C_e is the concentration of solute at equilibrium (mg/l), K_f is the Freundlich constant related to adsorption capacity of adsorbent (mg/g), and 1/n are the heterogeneity factor indicating the adsorption intensity of adsorbent. The value of 1/n less than 1 indicates a normal adsorption and more than 1 represents the cooperative adsorption. Smaller the value of 1/n, greater is the probability of heterogeneity on the surface of adsorbent.

While, adsorption kinetic is the theory of the relationship between the adsorption process and time. In order to understand the kinetics of adsorption of solute onto adsorbent, pseudo-first order and pseudo-second order equations were applied using l inear equation of pseudo-first order is given as Eq. 7.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (7)$$

Where, qe is the adsorption capacity at equilibrium (mg/g), qt is the adsorption capacity at time (t), k1 is the rate constant of first pseudo adsorption (min^{-1}), and t is the time (min). While, the pseudo-second order equation can be represented as Eq. 8.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \left(\frac{1}{q_e}\right) t \quad (8)$$

Where, qe is the adsorption capacity at equilibrium (mg/g), qt is the adsorption capacity at time (t), k2 is the rate constant of second pseudo adsorption (g/(mg/min)), and t is the time (min).

3. RESULT AND DISCUSSION

3.1 FTIR Analysis

The elucidation of the component modified thiourea with bamboo charcoal before and after Co(II) metal ions adsorption by using FTIR, as shown in Figure 2, it is crucial to confirm the presence of functional group that attached on the surface of modified adsorbent. Thiourea-BC shows additional bands at 1080 - 1100cm^{-1} and 777 - 800cm^{-1} are attributed to C-N (cyanide) stretching thiourea and C=S thiocarbonyl stretching (NH2-C(=S)-NH2) indicating the incorporation of nitrogen and sulphide containing functional groups [2]. The introduction of –NH, and C=S act as soft base chelators that has the ability to binding or chelate well with metal Co(II) ions via acid-base interaction and complexation [23]. Meanwhile, the O-H of aqueous solution from Co(II) metal ions solution was found at 3351cm^{-1} in BC, while after the modification, there is overlapping of O-H and N-H (amine) in the range of 3300-3200cm^{-1} resulting in peak disappearance or intensity reduction, indicating the presence of amine group [2, 5], and C-H stretching presence at 2885cm^{-1} may suggest the new formation of function groups due to the modification process, possibly there is interaction with the charcoal on the surface upon [22]. This indicates, that impregnated of thiourea into the bamboo charcoal may successfully introduced S- and N- containing functional groups [22]. The functional group of C=O stretching vibration was found in the region 1700 cm^{-1}, C=C group at 1587 cm^{-1}, and C-O at 1060 cm^{-1}, confirming the presence of lignin and cellulose in the heterogeneous structure of bamboo charcoal [11].

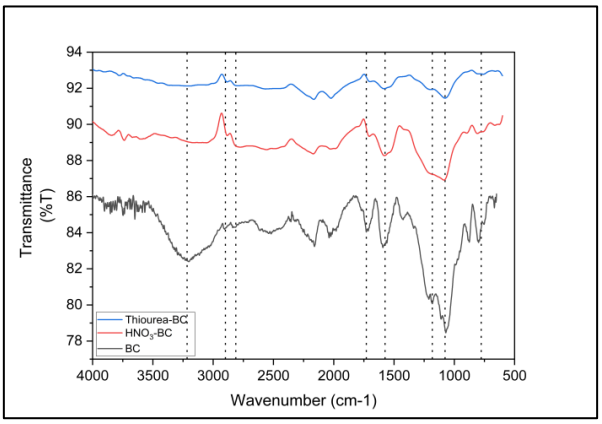
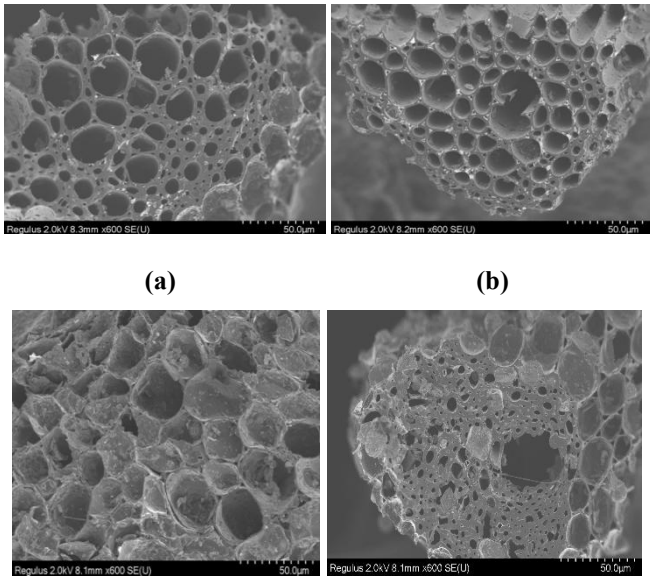


Figure 2. Shows FTIR Spectra of BC, HNO_3-BC, and Thiourea-BC

3.2 SEM-EDX Analysis

The different morphologies between modified and unmodified bamboo charcoal as well as after the adsorption process of Co(II) metal ions was analysed by using SEM-EDX. The SEM image as shown in Figure 3 revealed the morphologies change occurring upon the modified and adsorption of metal ions. Figure 3 (a) shows pure structure of BC showing roughness and lots of pore on the surface, whereas, Figure 3 (b) shows the surface of BC after the pre-treatment of BC with HNO_3 (HNO_3-BC) as oxidizing agent. Meanwhile, Figure 3 (c), shown the heterogeneous surface and pore blockage on the surface of bamboo charcoal adsorbed by thiourea molecules and most of pores were fully loaded with thiourea at 600x magnification [23]. The differences and changes on the surface of bamboo charcoal after the modification suggest the impregnation thiourea with bamboo charcoal are may successfully occurred. Therefore, Figure 3 (d) showing the modified thiourea after the adsorption of Co(II) metal ions. The intake of Co(II) metal ions its can be clearly seen on the surface of adsorbent [24].



(a) **(b)**

(c) **(d)**

Figure 3. SEM image of (a) Bamboo charocal, (b) HNO_3-BC, (c) Thiourea-BC, and (d) Thiourea-BC after the adsorption of Co(II) metal ions.

Elemental analysis of percentage compound were observed by using EDX analysis, as shown in Figure 4. As presented in Table 1, the percentage of Carbon (C) were 73.75%, slightly decrease after the impregnation with thiourea, could be due to the introduction of new elements that possibly attach on the surface of BC. The presence of new functional groups such as nitrogen (N) and sulphide (S) elements with 12,51% and 6.62% respectively, on the surface of adsorbent may indicates the impregnation of BC with thiourea are successfully occurred.

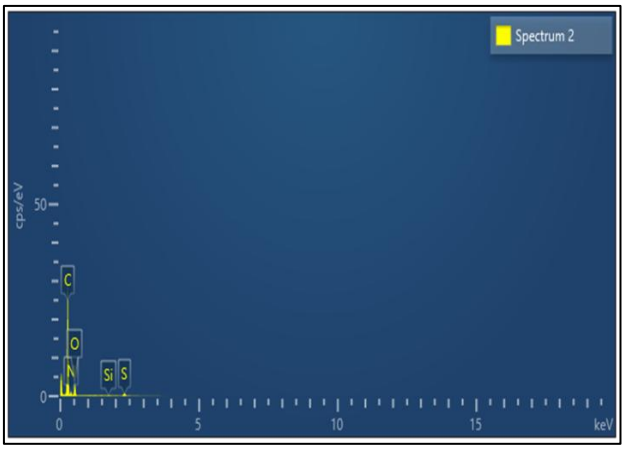


Figure 4. SEM-EDX Spectrum of modified bamboo charcoal with Thiourea

Table 1. The percentage comparisons of Bamboo charcoal, Pre-treatment of Bamboo charcoal and modified Bamboo Charcoal with Thiourea.

Elements %	BC	HNO_3-BC	Thiourea-BC
Carbon, C	91.79	89.18	73.75
Oxygen, O	7.29	9.73	12.51
Nitrogen, N	-	0.69	6.74
Silica, Si	0.92	0.40	0.38
Sulphide, S	-	-	6.62

3.3 Adsorption Isotherm

The Langmuir and Freundlich isotherm equation were used to describe the data obtain from the adsorption of Co(II) metal ions from Thiourea modified of BC.

3.3.1 Langmuir Isotherm

The Langmuir equation was used in this experimental data and the adsorption parameters obtained from the data such as Langmuir constant K_L (mg/L) and maximum capacity, q_{max} (mg/g) were shown in Table 2.

From the Langmuir data in Table 2, the Co(II) metal ions was adsorbed on the surface of the impregnated of Thiourea bamboo charcoal. The correlation coefficients of (R^2= 0.802) value which assessed the moderate fit for Langmuir model, compared with Freundlich model, may suggests a poor agreement of Langmuir model assumption proving the adsorption may possibly occur on multilayer adsorption or surface heterogeneity might be involved, considered the heterogeneous surface as shown in SEM result Figure 3 (c), indicating that Langmuir might be non-ideal to interpret of this adsorption behaviour.

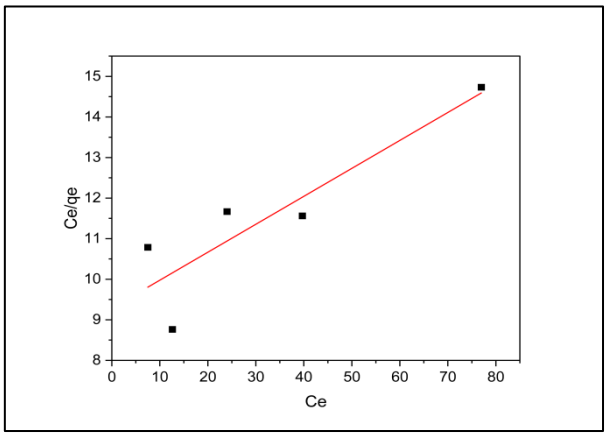


Figure 5. Langmuir isotherm plots of the adsorbed Co(II) metal ions on the Thiourea-BC.

Table 2. The adsorption parameters of Co(II) metal ions with modified Thiourea with bamboo charcoal.

q_e (mg/g)	q_{max} (mg/g)	K_L (L/mg)	R^2
12.35	14.512	0.074	0.802

3.3.2 *Freundlich Isotherm*

The freundlich isotherm model below describes the adsorption on the surface heterogeneous and account for multilayer adsorption.

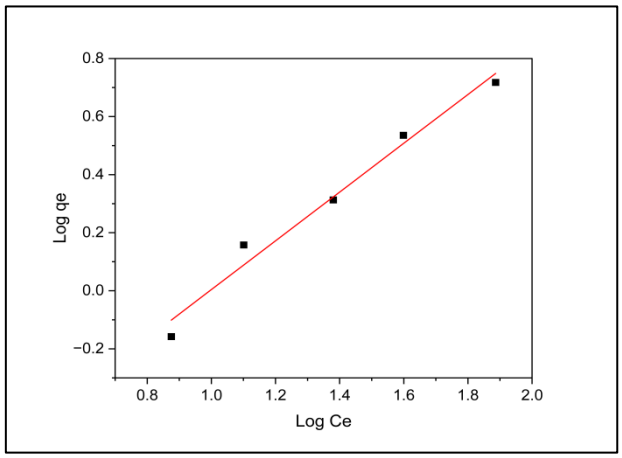


Figure 6. The Freundlich isotherm plots of the adsorbed Co(II) metal ions with Thiourea-BC

Table 3. The adsorption parameters of Co(II) metal ions with modified Thiourea with bamboo charcoal.

n	K_f	R^2
1.190	0.146	0.978

The Table 3 explained the Freundlich isotherm model of $1/n_f$ values, which indicates heterogeneity of surface and adsorption intensity. Generally, the n's value (1.190) which higher than 1, showing the favourable value of adsorption condition, suggest that some of the Cobalt (II) metal ions were adsorbed on the surface of modified thiourea via internal surface account for multilayer adsorption.

Thus, the finding showed that Langmuir and Freundlich isotherm can be used to describe that Co(II) metal ions can be adsorbed by monolayer or multilayer [7]. From the R^2 value with 0.802 and 0.978 for Langmuir and Freundlich isotherms respectively. Since the Freundlich isotherm model shows the higher of R^2 value compared with Langmuir isotherm, it is suggest that Co(II) metal ions adsorption is better describe by multilayer adsorption rather than monolayer adsorption [5, 8]. Moreover, the image of SEM for modified thiourea in Figure 3 (c) showing the uneven of pores which suggest for heterogeneous surface, proven in Freundlich fitting parameters. With that, the results experimental data indicates that Co(II) metal ions adsorption may follows the Freundlich isotherm model perfectly, suggest the multilayer adsorption on heterogeneous surface [2].

3.3.3 *Effect of Contact Time*

The graph below showing the differences of Co(II) metal ions removal efficiency over contact time. The trends from the graph also showing rapidly increase in first period of time, which then gradually stabilizes over time.

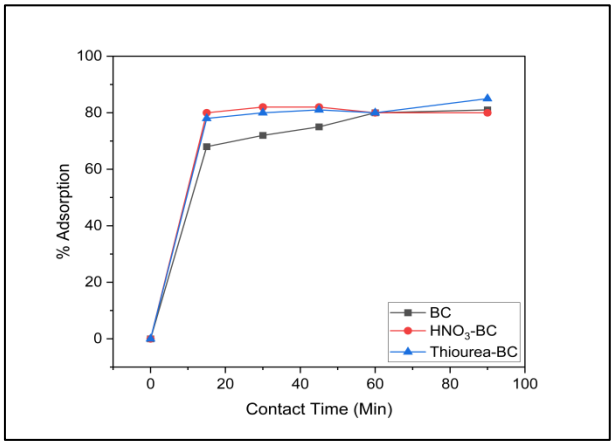


Figure 7. Removal percentage of Co(II) metal ions at different of contact time.

As shown in Figure 7, the effect of contact time on Co(II) metal ions removal reach the stability at 60-90 minutes range of time, within the first 15 minutes to 45 minutes, Co(II) metal ions removal significantly increase indicating that the adsorption process are fast at the beginning of adsorption process and almost reach the equilibrium at 90 minutes [2]. This happens because, initially there are many available of adsorption site on the surface of adsorbent allowing and giving the opportunity to Co(II) metal ions interact and easily attached to, leading to the fast of adsorption rate [14, 20]. As the time increase, the pores of adsorbent almost saturated because more adsorbent molecule already bind on the surface of adsorbent and becomes limited number of active sites due to saturated with Co(II) metal ions [3].

From Figure 7, in the same period of time at 90 minutes, the impregnated of BC with Thiourea showing the highest adsorption rate with 83% compared with BC and HNO_3-BC which showing stabilizes of removal percentage indicates that equilibrium has been reached. It is shown that the modified thiourea-BC has the ability to enhance the adsorption capacity. This improvement can be attributed to new functional groups such as Sulphide and Nitrogen that provide additional binding sites on the surface of adsorbent [23]. The presence of both

Sulphide and Nitrogen could altered the surface and has the potential in increasing the surface area and contribute to enhance the adsorption capacity compared with raw BC and HNO_3-BC.

3.3.4 *Effect of Initial Concentration*

The adsorption efficiency of Co(II) metal ions removal was evaluated as a function of initial concentration, as shown in Figure 8. The graph was illustrated the Co(II) metal ions percentage removal for the sample over an initial concentration with 10, 20, 30, 50, 80 ppm. From the results below, it is evident that Co(II) metal ions removal efficiency are crucially influenced by initial concentration which at low concentration of metal ions in aqueous solution [1, 3].

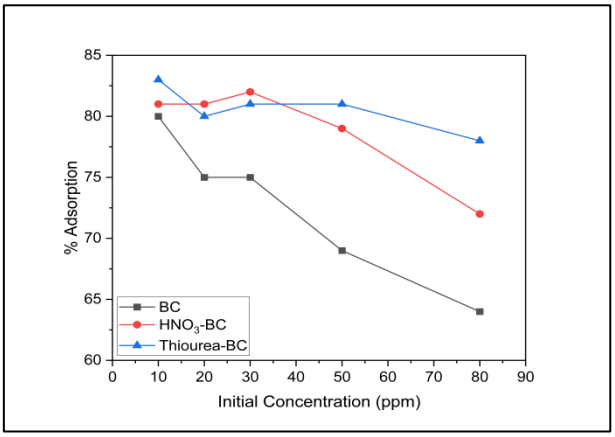


Figure 8. Removal percentage of Co(II) metal ions at different of initial concentration.

This is due to, at low concentration of initial metal ions, there are high of surface area and more available of active sites on the surface of adsorbent relative to the number of metals ions, making it easier for the Co(II) metal ions to interact and bind, so the Co(II) ions were easily adsorbed, and removed causing the adsorption occurs efficiently [15]. Meanwhile, as the initial concentration increase, the number of metal ions exceeded the available of the adsorption sites that leading to saturation of the adsorption surface and causing a decreasing in the percentage removal [1]. This phenomenon owing to the driving force which occurred because there is huge different between concentration of Co(II) metal ions in the solution, and the surface adsorbent dosage used, leading to a higher interaction rate and greater uptakes of ions per unit mass of adsorbent [3]. However, at certain point, after reaching their saturation where all the active binding sites are occupied, further in increasing the initial concentration of metal ions there will be no longer result in higher adsorption, and the equilibrium was established [9]. Therefore, adsorption improves with increasing metal ions initially but, eventually becomes stabilizes due to site saturation.

3.3.5 *Effect of pH*

The adsorption efficiency of Co(II) metal ions was evaluated as a function of pH as shown in Figure 9. The graph below was illustrate the percentage of Co(II) metal ions removal for the across from pH 1 until pH 8.

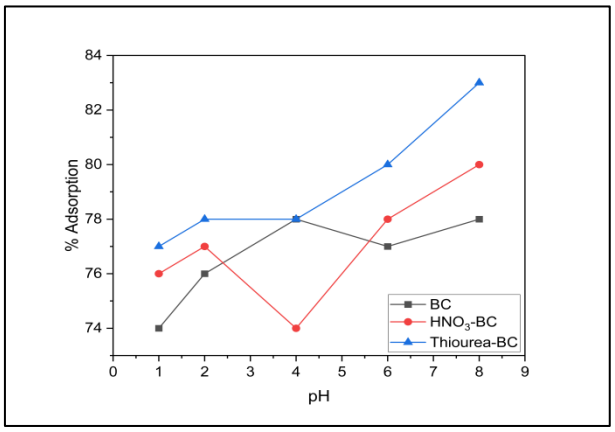


Figure 9. Removal percentage of Co(II) metal ions at different of pH solution.

From the graph above, as a result shown, it is evident that the efficiency Co(II) metal ions removal are crucially influenced by the effect of pH. The maximum removal (R%) and adsorption capacity (qe) of modified bamboo charcoal occurred at the pH 6.0 with 80%. Although higher percentage removal was observed at pH 8, this could be attributed to the formation of $Co(OH)_2$ precipitation rather than adsorption [2]. Therefore, pH 6 was selected as optimum to ensure the removal efficiency is dominated by adsorption [2]. Meanwhile, at lower pH value (1-4), the percentage removal of Co(II) metal ions are respectively low [15]. This may be due to the high concentration of hydrogen ions (H^+) that competing with Cobalt (II) metal ions (Co^{2+}) on the surface of adsorbent, causing the limiting the adsorption of Co(II) metal ions.

As the pH increase in range 6 until approaching neutral pH, the percentage removal of Co(II) metal ions showing significantly high percentage compared in the low pH (acidic condition), which reaching the highest peak [10]. This may be attributed to the high concentration of hydroxide ions (OH^-) in basic condition, the adsorbent surface exhibits the favourable interaction with Cobalt (II) metal ions (Co^{2+}) leading to maximum adsorption. These behaviour indicates that the condition of solution either in acidic or basic condition plays a crucial role in determining the effectiveness of Co(II) metal ions adsorption [26].

3.4 *Kinetic Adsorption*

3.4.1 *Pseudo First Order Kinetic*

Kinetic study for pseudo first order was plotting the linear plot of log (qe – qt) versus time (min) was used to evaluate the adsorption rate of behaviour of Thiourea-BC, for removal of Co(II) ions. Based on figure 10, the moderate fit of R^2 values, and poor linearity indicating the partially of conformity which not adequately well described of pseudo first order kinetic, leading to insufficient to represent the adsorption process for modified BC. This could be due to the adsorption process may involving chemisorption or interactions between the adsorbate and adsorbent on the surface of adsorbent, or the adsorbent surface being heterogeneous, leading to variations in adsorption energies and kinetics [2].

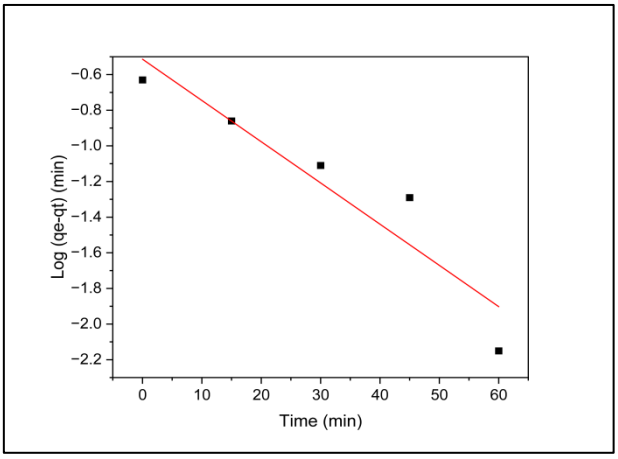


Figure 10. Pseudo first order kinetic model for the adsorption of Co(II) metal ions

3.4.2 Pseudo Second Order Kinetic

Adsorption kinetic pseudo-second order was conducted to investigate the chemical interactions between the adsorption surface of adsorbent and Co(II) metal ions, and showing the experiment data of kinetic was well followed the pseudo-second order. The value of pseudo-second order rate constant (K_2) and the adsorption capacity (q_e) are showed in the Table 4 and Table 5.

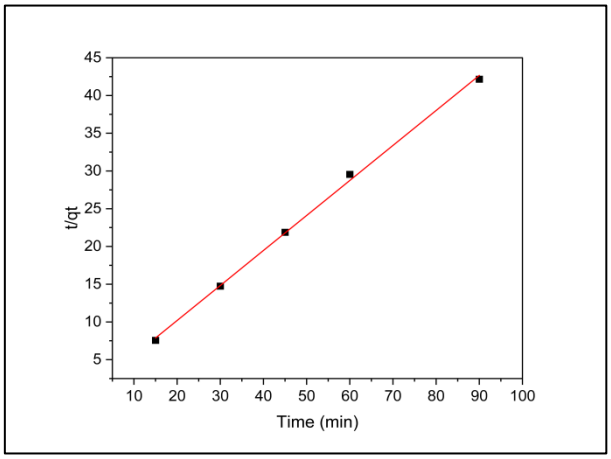


Figure 11. Pseudo-second order kinetic model for the adsorption of Co(II) metal ions.

The graph plot of t/qt versus time (min) as shown in Figure 11 for the modified Thiourea adsorbent showing excellent fit of experiment data with high correlation coefficients (R^2=0.99). The second order-rate constant obtained from this is 1.068 x 10^{-2} g/(mg/min). The rate constant indicates that higher dosage of adsorbent was required less time to achieve the initial adsorption of Co(II) metal ions owing to their high potential surface area. As for the equilibrium adsorption capacity, qe is 8.180 mg/g that obtained from the graph below also indicates that the overall of dosage are capable to uptake more adsorbate on the surface of adsorbent. This result shows that the rate controlling step in the adsorption process chemisorption are directly involve, where there are interaction of electrons sharing or transfer between adsorbent and adsorbate [12, 25]. In conclusion, the best fit of pseudo-second order and freundlich isotherm from kinetic study and the adsorption isotherm, respectively showing the support there involvement of the chemisorption in the adsorption process between thiourea (N- and S- groups) and Co(II) metal ions [5].

Table 4. The parameters of the adsorption kinetic of Co(II) metal ions.

Pseudo First Order			Pseudo Second Order		
q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/(mg/min)	R^2
0.321	0.011	0.62	8.190	1.068 x 10^{-2}	0.99

Table 5. Comparison between experimental of adsorption capacity, and adsorption capacity kinetic for pseudo second order.

$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	% error
7.970	8.190	2.9

4. CONCLUSION

In conclusion, used of retort as newly method that proposed in this research study to prepare the impregnated of thiourea into the bamboo charcoal has been successfully employed. To the best our knowledge, impregnation method via retort assist method has not been reported for this precursor, demonstrating its potential as a new sustainable and low cost alternative for preparing modified carbon-based adsorbent. Basically, the method was effectively proven in enhancing the surface functionality, as well as adsorption capacity under mild hydrothermal conditions without the need for expensive autoclave equipment. Introduction of new functional groups such as nitrogen (N) and sulphide (S) with 6.74% and 6.62% respectively, after the impregnation process, may indicates the impregnation are occurred, aligned with result of SEM-EDX analysis in Figure 3 and Figure 4, shows the pore blockage and possibly fully loaded with thiourea on the surface. Moreover, the result of the modified *Gigantochloa albociliata* charcoal with Thiourea as chelator are able to adsorb Co(II) metal ions and showing promising potential to act as adsorbent in heavy metal removal. From the result, based on different parameters for contact time at 90 minutes, the optimum adsorption of removal Co(II) metal ions is 83%, while at pH 6, the highest efficiency for the removal of the ions was observed is 80%. By using Langmuir and Freundlich isotherm model at different of initial concentration, data revealed that Freundlich model showing the perfectly fit that Co(II) metal ions are absorb with multilayer adsorption on heterogeneous surface. Besides that, the best fit of pseudo-second order indicates the support there is involvement of the chemisorption in the adsorption process between thiourea and Co(II) metal ions. Thus, impregnation of thiourea into the bamboo charcoal proving the ideal performance for the adsorption of Co(II) metal ions.

5. RECOMMENDATION

Based on the limitation of this research study, the following recommendations are proposed for future research work which should focus on the regeneration and reusability

of modified BC as desorbing agent for at least 5 cycles. Addition EDX analysis after the adsorption of Co(II) ions are recommended to further strengthen the proposed adsorption mechanism by confirming the presence of cobalt species on the adsorbent surface. Besides that, BET analysis should be included as the evidence of surface area and pore changes after the modification, and correlate structural properties with adsorption performance, as well as testing with real industrial of wastewater containing heavy metal ions would be a good practical for the adsorbent application.

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