

Adsorption of Cu(II) Ion onto Activated *Eupatorium Adenophorum* and *Acer Oblongum*: Thermodynamic, Kinetic and Equilibrium Studies

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Abstract: The performance of activated *Eupatorium adenophorum* (AEA) and activated *Acer oblongum* (AAO) biomass for removal of Cu(II) ion from aqueous solution was investigated. Adsorption was carried out by batch operation and different parameters applied were pH, contact time, temperature, adsorbent dose and initial metal ion concentration. The maximum adsorption for Cu(II) ions was found at pH 5.0. The equilibrium adsorption data were analyzed using Langmuir, Freundlich and Temkin isotherm models. The equilibrium data fitted well the Langmuir isotherm. The affinity of AEA is greater than AAO biomass. Kinetic studies were performed to understand the mechanistic steps of adsorption process. The rate kinetics for the adsorption of metal ions was best fitted with the pseudo-second-order kinetic model. The thermodynamic analysis indicated that the adsorption of Cu(II) metal ions onto AEA and AAO biomass was an exothermic process ($\Delta H^0 < 0$) and results in higher adsorption capacities at lower temperatures. The adsorption of Cu(II) metal ions onto AEA was more exothermic and spontaneous than AAO biosorbent. The negative value of ΔG^0 revealed that the adsorption was spontaneous. The feasibility of the process is evident from the positive value of ΔS^0 .

Keywords: Metal ions, Isotherm models, Kinetics, Biosorption, *Eupatorium adenophorum*, AEA, *Acer oblongum*, AAO, biomass

Introduction

Copper have important properties like thermal conductivity, electrical conductivity and non-corrosion properties. Therefore copper is widely used in many industries, like electroplating, paint, metal finishing, electrical, wood manufacturing pigment metal cleaning, plating bath, paper board, mining, paint and fertilizer^{1,2}. The effluents usually contain high concentration of copper ion. The heavy metals are non-biodegradable³. Heavy metal enters in ground and surface water which is responsible for water pollution as it is toxic in nature³. The heavy

metal accumulates in human body through the food chain. Copper is one of the most toxic heavy metal to living organism. The excessive intake of copper ions in human body may leads to several mucosal irritation, hepatic and renal damage, liver and brain damages, widespread capillary damages, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney^{2,4,5}. The world health organization recommended a maximum acceptable concentration of Cu(II) in drinking water⁶ is about 1.5 mg/L. There are various methods used to minimize the concentration of heavy metals from the effluent waste water. A wide range of processes such as chemical precipitation⁷⁻¹¹, liquid/liquid extraction^{12,13}, ion exchange^{7,14-16}, membrane filtration, electrolytic methods, coagulation, reverse osmosis and biosorption being used for removal of heavy metal ions from industrial effluents^{17,18}. Most of these methods suffer some drawback, some have high capital and operational cost, some faces problem of the disposal of the residual metal sludge and some are not suitable for low concentration of metal ions (10 mg/L). Among of these methods biosorption is the important procedure for the removal of low concentration heavy metal ions from the environment.

Researchers investigated the use of cheap, easily available and eco-friendly adsorbent which might be capable to removing significant quantities of heavy metal ions from industrial wastewater. Agricultural wastes and biomass such as peanut hull², sawdust^{4,5}, *urticadioica*¹⁹, *Artemisia vulgarise*²⁰ and *Diclipterabupleuroides*²¹ have been studied for copper adsorption from aqueous solution.

The object of this paper is to investigate comparative adsorption characteristics for removal of Cu(II) ion from aqueous solution using chemically treated AEA and AAO. SEM and FT-IR analysis were carried out to understand the surface and functional group of AEA and AAO biomass. Batch studies were conducted. Cu(II) solutions were used to assess adsorption isotherm, kinetic and thermodynamic models for the removal of copper from synthetic aqueous solutions. The influence of pH, adsorbent dosage, initial metal ion concentration, contact time and reaction temperature were the parameters selected to the study on adsorption of Cu(II) ions onto AEA and AAO activated biomass. Two kinetic models including pseudo-first and second order were used to investigate the mechanism of copper ion adsorption.

Experimental

All reagents used were of Analytical Reagent (A.R.) grade. 1000 mg/L stock solution of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was prepared in double distilled water. The pH of solutions were adjusted to 5 using 0.1 N NaOH or 0.1 N HCl solutions. Digital pH meter (Model: Systronic 361) was used to monitor the pH of the solution. The range of concentration of copper ions in synthetic wastewater varied between 10 to 50 mg/L.

Preparation of adsorbent

Eupatorium adenophorum leaves were collected from out skirts of town Almora, Uttarakhand, India. *Acer oblongum* leaves were collected from high altitude areas of Chopta, Rudraprayag, Uttarakhand. These leaves were thoroughly rinsed with double distilled water to remove dust and soluble materials and dried at room temperature. Leaves were kept in hot air oven (Popular Traders S.N.-1680) at 333 K for 24 h. The dried biomass was crushed to fine powder in an electric grinder. This powdered mass was treated with 0.1 N HNO_3 at room temperature for 24 hours then filtered and washed with doubled distilled water. Obtained biomass was dried in hot air oven at 333 K for 2 days. After crushing, the treated biomass was sieved to get particle size of 63 microns (170 bss shieve) and then stored in air tight

bottle which is used as an adsorbent later on. The surface functional groups of the activated biomass were identified by Fourier Transform Infrared Spectroscopy (Bruker Alpha S.N. 200855 made in Germany). The surface morphology of adsorbent was studied by Scanning Electronic Microscopy (Model- JEOL-JSM6610-JFC1600)

Adsorption experiments

The adsorption experiments were carried out with 100 mL of standard solution in 250 mL borosil conical flask. The solution was shaken at 170 rpm for 30 minutes. The filtrate was digested with concentrate HNO₃ and analyzed by atomic absorption spectrophotometer (Optima 4300DV ICP, Perkin-Elmer, Boston, MA). Each experiment was duplicated under identical conditions.

The effect of pH on the Cu(II) ions adsorption was studied²² over pH range from 1.0 to 9.0. The adsorbent dosage mass added was 1.0 g and the initial concentration of Cu(II) was 10 mg/L. The pH of Cu(II) solution was adjusted using either 0.1 M HCl or 0.1 M NaOH.

The effect of adsorbent dosage mass was conducted by different adsorbent dosage mass ranging from 0.5 to 2.5 g with Cu(II) solution (10 mg/L, pH 5.0) at 170 rpm for 30 minutes. The adsorption efficiency of the adsorbent at equilibrium was calculated using the equation:

$$\text{Adsorption efficiency} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

Where C_i is the initial metal ion concentration (mg/L) and C_e is the equilibrium metal ion concentration (mg/L). The adsorption capacity and the quantity of metal adsorbed at equilibrium were calculated by using the following equation:

$$Q_e = \frac{(C_i - C_e) \times V}{m} \quad (2)$$

Where C_i and C_e are the initial and final metal ion concentrations in mg/L, V is the volume of solution in (L), m is the mass of adsorbent (g) and Q_e is the metal quantity adsorbed at equilibrium (mg/g).

Adsorption equilibrium experiments were carried out 100 mL of different initial concentration Cu(II) solution (10, 20, 30, 40 and 50 mg/L) under the optimum conditions of pH 5.0, 1.0 g of adsorbent was shaken at 170 rpm for 30 minutes. For kinetic study, 100 mL of different initial concentration Cu(II) solution (10, 30 and 50 mg/L) with 1.0 g adsorbent were shaken at 170 rpm for a varied contact time in a range of 15-105 min at room temperature. For thermodynamic study, 1.0 g of adsorbent with 100 mL of different initial concentration of Cu(II) solutions were shaken for 180 min in a range of temperature from 288 K to 348 K.

Results and Discussion

Characteristics of the AEA and AAO biomass

Functional characteristics

In order to determine the main functional groups of AEA and AAO biosorbent which participate in Cu(II) ion sorption and gives the information of possible cell-metal ions interactions. FT-IR spectra were recorded before and after adsorption. The functional groups in unloaded and Cu(II) ion loaded AEA and AAO biosorbent corresponding to infrared absorption bands are shown in Figure 1 and Figure 2, respectively.

In Figure 1, the sharp absorption band at 3741, 2362 and 2922 cm^{-1} of AEA are due to stretching vibration band of N-H, aliphatic²³ C-H and NH_2 respectively. The absorption band at 3836, 3615 and 3515 indicates that the presence of O-H group in biosorbent. The peak at 1461, 1239 and 1023 are related to saccharide structure which is assigned to C-O, C-O-H and C-C bending vibrations²⁴. These absorption bands are shifted after biosorption of Cu(II) ion onto AEA biomass. These bands were especially involved in copper adsorption.

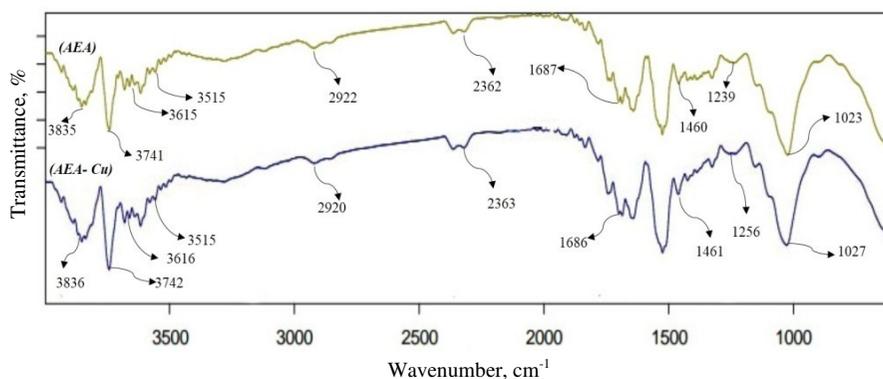


Figure 1. FT-IR spectrum of unloaded AEA biomass and Cu(II) loaded AEA (AEA-Cu) biomass

In Figure 2, the broad peaks in the region of 2916 and 2949 cm^{-1} are characterization of C-H group in the in aliphatic compound. The peaks at 1611, 1516 and 1438 cm^{-1} are related to the N-H stretching vibrations in ternary amine. Also, the formation of $-\text{CH}_2-\text{O}-\text{CH}_2-$ linkage is appeared²⁵ at 1085-1104 cm^{-1} . These shifts may be due to the changes in counter ions associated with the ether and amine group suggesting that these groups are predominant contributors in metal ion uptake²⁶. The absorption band of $-\text{C}-\text{O}$ was decreased due to the formation of complex between atom oxygen and Cu(II)²⁷. Obvious changes in the FTIR spectra were found at the wave numbers of 3810, 3742 and 3280 which appeared after Cu(II) adsorption²⁴. Which indicate that the metal ions adsorption on the adsorbent affected the chemical bonds in biosorbent. The result suggested that the sorption behavior of the bioadsorbent was affected by ion-exchange and mainly governed by chemical adsorption²⁴.

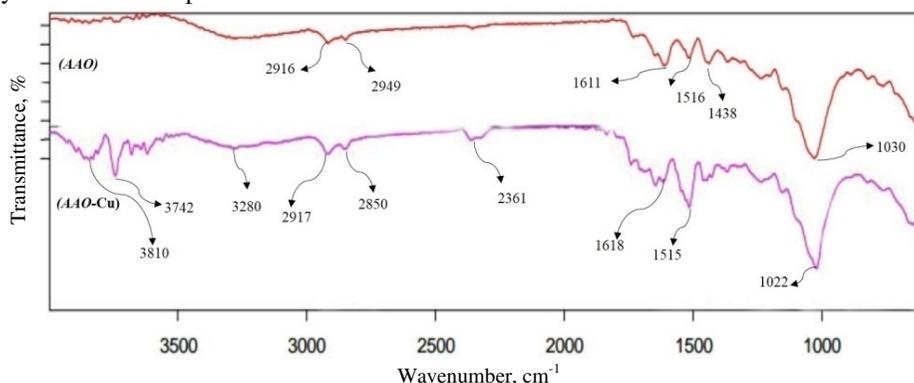


Figure 2. FT-IR spectrum of unloaded AAO biomass and Cu(II) loaded AAO(AAO-Cu) biomass

Morphology characteristics

Scanning electronic microscopy (SEM) is one of the most used characterization techniques applied for the analysis of surface morphology, properties, porosity and texture morphology of adsorbent^{19-21,28}. The surface morphology of AEA and AAO before and after metal ions adsorption is shown in Figure 3(a), Figure 3(b), Figure 3(c) and Figure 3(d). This revealed that AEA and AAO are mostly irregular in shape and contain many pores.

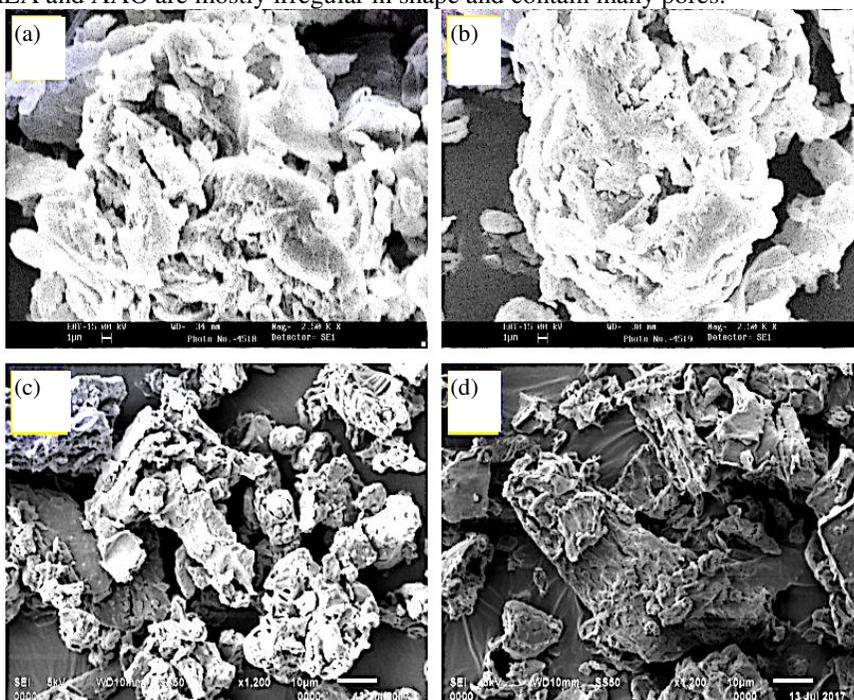


Figure 3 (a). SEM image of unloaded AEA biomass; (b) SEM image of Cu(II) loaded AEA biomass; (c) SEM image of unloaded AAO biomass; (d) SEM image of Cu(II) loaded AAO biomass

It is clearly seen that in Figure 3(b) and Figure 3(d) for AEA and AAO biomass respectively, the pores and surfaces of adsorbent were covered by the adsorbate.

Investigation of adsorption parameters

Adsorption of copper ions onto AEA and AAO were affected by various factors.

Effect of pH

The pH is one of the important factors for biosorption processes. It affects the surface charge of adsorbent and the degree of ionization of the adsorbate. The effect of pH in the initial solution of Cu(II) was examined at a different pH ranging from 1.0 to 9.0 onto *Eupatorium adenophorum* (AEA) and *Acer oblongum* (AAO) biomass. The results are shown in Figure 4 at pH 5 for the biosorption of Cu(II) maximum value was 89.5% and 83% for AEA and AAO biomass, respectively. Generally, metal biosorption involves complex mechanisms of ion-exchange, chelation, adsorption by physical forces, and ion entrapment in inter and intra cellular capillaries and spaces of the cell structural network of a biosorbent^{29,30}. There was minimum copper adsorption at pH 1.0 for AEA and AAO biosorbent. This was due to the

protonation of the functional groups were protonated at pH 1.0 as in an overall positive charge cannot be bind to positively charged metal ions³¹. In addition, Cu(II) ions enhanced competition for adsorption and ion-exchange sites with protons at low pH³¹. This could be also due to the protonation of the functional groups on adsorbent surface, inducing an electrostatic repulsion of Cu(II) ions and the surface active sites of AEA and AAO³¹. To avoid the occurrence of desorption, pH conditions of >5.0 must be maintained. It was perceived that there was no significant improvement in removal of Cu(II) when the initial pH of solution was greater than 5.0. At pH 5.0, Cu(II) solution consists of free Cu(II) ions that are mainly involved in adsorption process causing an increase in the amount of Cu(II) adsorbed. From Figure 4, it was observed that the adsorption percentage of Cu(II) decreased significantly from pH 7.0 to pH 9.0. This phenomenon is mainly caused by the presence of free ion species in the solution that the Cu(II) ions were presence in a very small quantity whereas $[\text{Cu}(\text{OH})]^+$ and $\text{Cu}(\text{OH})_2$ in a large quantities as suggested by Larous *et al.*,³². Therefore, at higher pH (>pH 5.0), Cu(II) are attached by the hydroxide ions to form $\text{Cu}(\text{OH})_2$ and soluble complex hydroxides^{33,34} $[\text{Cu}(\text{OH})_4]^{-2}$.

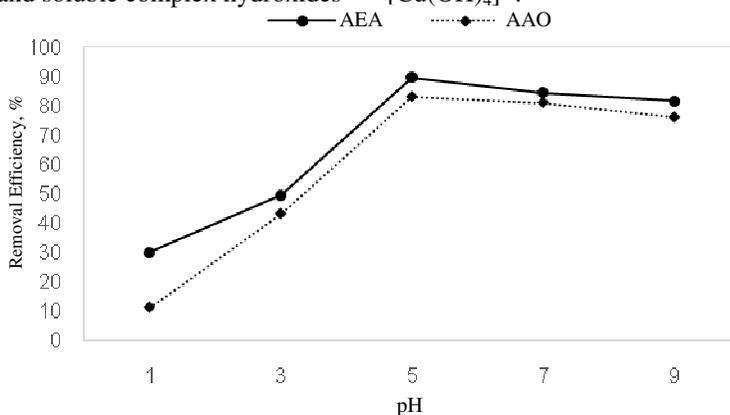


Figure 4. Effect of solution pH on adsorption of Cu(II), metal ions onto AEA and AAO (Adsorption conditions: initial concentration of metal ions 10 mg/L; 1 g AEA and AAO; contact time: 30 min.; temperature: 295 K; agitating speed: 170 rpm)

Effect of adsorbent dose

The amount of adsorbent plays an important role in the adsorption of Cu(II) ions from the aqueous solution. It is clear from Figure 5(a) & Figure 5(b) that quantity of Cu(II) ions adsorbed increases with varying adsorbent weight. On increasing adsorbent dose the removal percentage is increased from 48.9 to 89.9 and 40.5 to 65 for AEA and AAO respectively. These results suggest that the relationship between adsorbent dosage and removal percentage is related to increase the number of adsorption sites and this effect is not observed after 2.0 g of adsorbent dose. When the adsorbent dose is increased from 0.5 g to 2.0 g the adsorption capacity is decreased from 0.978 mg/g to 0.396 mg/g and 0.812 to 0.26 mg/g for AEA and AAO respectively. This phenomenon may be observed due to two reasons. First: an increase in adsorbent amount at constant Cu(II) ions concentration at constant volume may cause inoccupation of the adsorption sites. Secondly: due to the particulate interaction such as aggregation resulting from high adsorbent dosage³⁵. The further adsorption of Cu(II) ion is not observed as the adsorbent surface and metal ions have reached to an equilibrium^{36,37}. It is observed that the AEA have better adsorption capacity as compared to AAO.

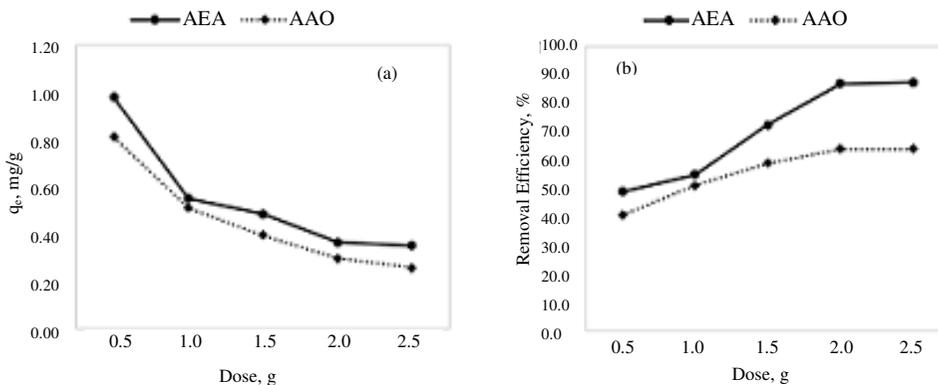


Figure 5(a). Effect of adsorbent dose on removal % of Cu(II) metal ions onto AEA and AAO (Adsorption conditions: initial concentration of metal ions 10 mg/L; pH: 5; contact time: 30 min; temperature: 295 K; agitating speed: 170 rpm) (b) Effect of adsorbent dose on unit adsorption capacity of Cu(II) metal ions onto AEA and AAO (Adsorption conditions: initial concentration of metal ions 10 mg/L; pH: 5; contact time: 30 min; temperature: 295 K; agitating speed: 170 rpm)

The effect of Cu(II) initial concentration and contact time

The effect of contact time is an important parameter for designing of biosorption experiment. The effect of contact time on the adsorption of Cu(II) ions onto AEA and AAO was investigated at various initial concentrations of Cu(II) ions, 10-50 mg/L which is shown in Figure 6, 7, 8 and 9. The adsorption capacity and % removal efficiency increase with increasing the contact time which reached to equilibrium within 90 min. After 90 min, the surface pores of adsorbent may be occupied and the copper ion requires more driving force to enter into the interior of the adsorption site after equilibrium³⁸. The equilibrium adsorption capacity of the AEA and AAO have increased with an increase initial Cu(II) ion concentration, while the percentage removal of Cu(II) ion showed the opposite trend. When the initial metal ion concentration increased from 10 to 50 mg/L, the adsorption capacity increased from 9.105 to 37.005 mg/g and 8.535 to 38.9 mg/g for AEA and AAO respectively, the percentage removal decreased from 91.05 to 74.01% and 85.35 to 77.8% for AEA and AAO respectively.

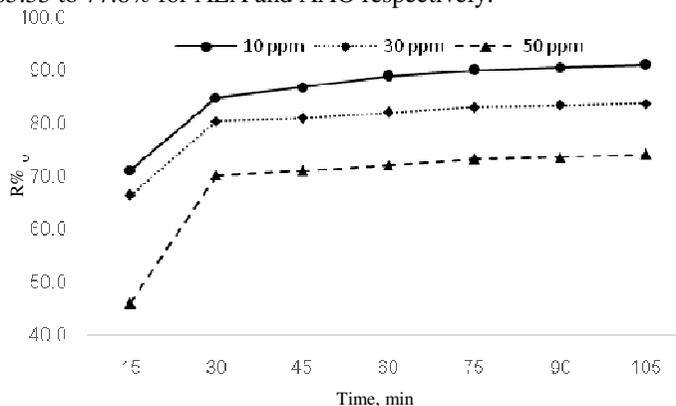


Figure 6. The effect of Cu(II) initial concentration and contact time metal ions onto AEA (Adsorption conditions: pH: 5; Temp: 295 K; agitating speed: 170 rpm; adsorbent dose: 1 g)

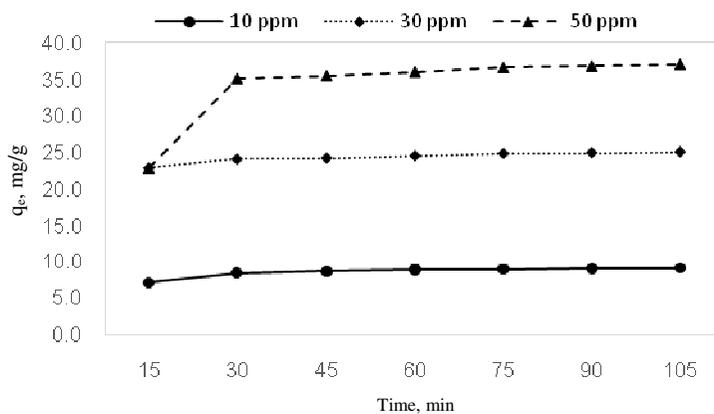


Figure 7. The effect of Cu(II) initial concentration and contact time metal ions onto AEA (Adsorption conditions: pH: 5; Temp: 295 K; agitating speed: 170 rpm; adsorbent dose: 1 g)

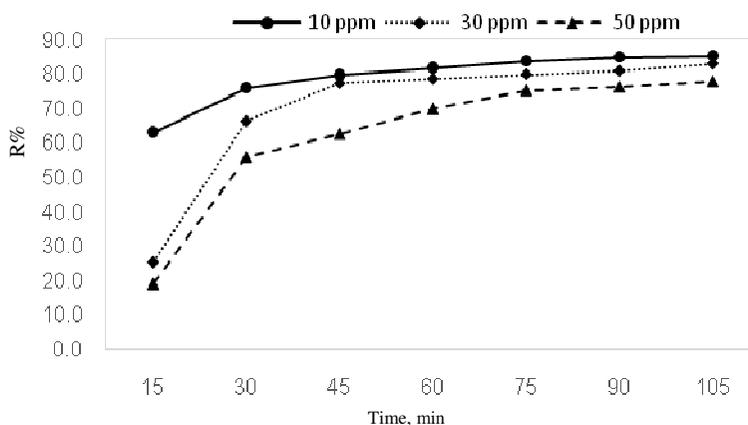


Figure 8. The effect of Cu(II) initial concentration and contact time metal ions onto AAO (Adsorption conditions: pH: 5; Temp : 295 K; agitating speed: 170 rpm; adsorbent dose: 1 g)

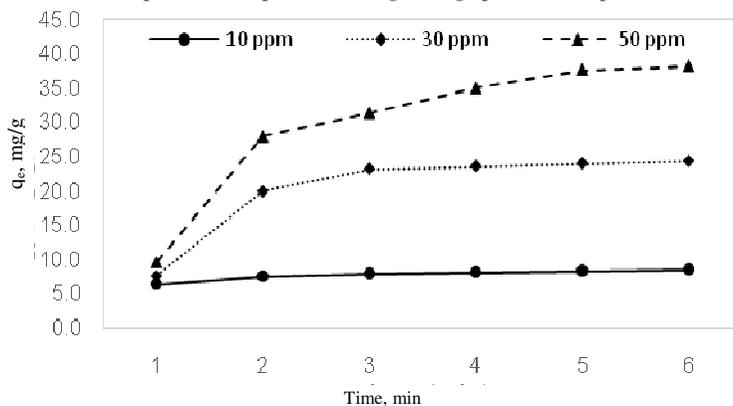


Figure 9. The effect of Cu(II) initial concentration and contact time metal ions onto AAO (Adsorption conditions: pH: 5; Temp 295 K; agitating speed: 170 rpm; adsorbent dose: 1 g)

This may be attributed to the initial concentration which provides an important driving force to overcome all mass transfer resistances of Cu(II) ions between the aqueous and solid phase, hence a higher initial concentration of Cu(II) ions will enhance the adsorption process³⁹. The result shows that for all of initial metal ion concentrations the equilibrium is reached in the same time. The time required attaining the equilibrium time and the amount of metal adsorbed at that equilibrium time reflected the maximum metal adsorption capacity under these particular conditions⁴⁰.

Effect of solution temperature and thermodynamic parameters

Adsorption of metal ions onto AEA and AAO biomass as an adsorbent was investigated at five different temperatures from 288 to 348 K. The initial Cu(II) ion concentration was 10 mg/L. The experiment showed that the adsorption capacity is increased till 333 K from 0.51 to 0.71 mg/g and 0.49 to 0.62 mg/g for AEA and AAO biosorbent, respectively. The adsorption process on both adsorbent was found to be exothermic when 10 mg/L of Cu(II) was used for adsorption.

The change in enthalpy ΔH^0 , during adsorption of Cu(II) was found to be -178.51 and -98.10 kJ/mole for AEA and AAO biomass, respectively. The entropy change ΔS^0 for AEA was +0.503 kJ/mole and that for the AAO was +0.335 kJ/mole. The values of ΔH^0 obtained shows that the adsorption of Cu(II) onto both adsorbents was exothermic with adsorption onto AEA adsorbent being more exothermic. The positive values of entropy may be due to some structural changes in the adsorbate and adsorbents during the adsorption process from aqueous solution onto the adsorbents. In addition, positive value of ΔS^0 indicates the increasing randomness at the solid-liquid interface during the adsorption of Cu(II) on the adsorbents.

$$\Delta G^o = -RTx \ln K_c \quad (3)$$

$$\Delta G^o = -\Delta H^o - T\Delta S^o \quad (4)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (5)$$

The variation in the biosorption process with respect to temperature has been explained on the basis of thermodynamic parameters, whether the process is spontaneous or not. The Gibbs free energy change (ΔG^0) is an indication of spontaneity of a chemical process and depends on enthalpy change (ΔH^0) and entropy change (ΔS^0)⁴¹.

Generally for physical adsorption the free energy change (ΔG^0) ranges from -20 to 0 kJ/mole and for chemical adsorption it ranges between -80 and -400 kJ/mole⁴². The ΔG^0 for Cu(II) adsorption was in the range of -1.893 to -24.479 kJ/mole and so the adsorption was predominantly physical adsorption. The degree of spontaneity of reaction increases with increasing temperature till 348 K for AEA and AAO biosorbent.

The K_c values calculated for the adsorption of Cu(II) for AEA and AAO are given in Table 1 and Table 2. As seen from the results, the K_c values decreased with increase in temperature which resulting a shift of equilibrium to the left *i.e.*, desorption of the adsorbed ions from the adsorbent is favored at higher temperatures. The ΔH^o and ΔS^o were obtained from the slope and intercept of the Van't Hoff plot of $\log K_c$ versus $1/T$. The values of these parameters thus calculated are recorded in Table 1 & 2. The negative values of standard enthalpy change (ΔH^o) for the intervals of temperatures showed the exothermic nature of the biosorption process. The low enthalpy values of ΔH^o is 20kJ/mole indicates that the physical sorption is involved in the process of adsorption²⁶. The estimated values of ΔH^o for the

present system were greater than 20 kJ/mole and hence, the process may involve a spontaneous sorption mechanism as ion exchange where chemical bonds are not of strong energies. The negative value of entropy change (ΔS°) corresponds to a decrease in degree of freedom of the adsorbed species and suggests the decrease in concentration of adsorbate in solid solution interface indicating there by increase in adsorbate concentration onto the solid phase. This is the normal effect of the chemical adsorption phenomenon, which takes place through ion exchange interactions.

Table 1. Thermodynamic parameters for biosorption of Cu(II) onto AEA

Temperature, $^\circ\text{C}$	ΔG° , kJ/mole	K_c	ΔH° , kJ/mole	ΔS° , kJ/mole
288	-1.893	1.083		
303	-8.029	1.381		
318	-16.162	1.857	-178.51	+0.503
333	-24.479	2.448		
348	-4.581	1.174		

Table 2. Thermodynamic parameters for biosorption of copper(II) onto AAO

Temperature, K	ΔG° , kJ/mole	K_c	ΔH° , kJ/mole	ΔS° , kJ/mole
288	0.946	0.961		
303	-1.991	1.083		
318	-9.502	1.439	-98.10	+0.335
333	-13.384	1.631		
348	-1.143	1.041		

Adsorption isotherms

An adsorption isotherm is characterized by certain constant values, which have to be investigated to understand the biosorption process. The surface properties and affinity of the adsorbent can also be used for the comparative study of the adsorbent for different pollutants⁴³. Adsorption isotherm is important to describe how the adsorbate ions interact with the active site of adsorbent. Three isotherm models, Langmuir, Freundlich, and Temkin were used in the analysis of adsorption results.

Langmuir adsorption isotherm

The Langmuir adsorption is based on the assumption that all adsorption sites are homogeneous and independent of whether the adjacent active site is occupied or not, meaning monolayer therefore adsorption can take place at a binding site of the adsorbent surface and no further adsorption can happen at that site^{44,45}. The adsorption is constant and there is no transmigration of adsorbate in the plane of surface⁴⁶. The linear form of Langmuir isotherm⁴⁵ equation is given by following Eq. 6.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (6)$$

Where Q_e and C_e correspond to the mg of metal adsorbed per g of AEA and AAO biomass and residual metal concentration in the solution when in equilibrium. K_L (L/mg) and Q_{\max} are Langmuir constant and maximum capacity of adsorption (mg/g), respectively. Values of Langmuir parameters Q_{\max} and K_L were calculated from the slope and intercept of linear plot of C_e/Q_e versus C_e and given in Figure 10. The values of Q_{\max} , K_L and correlation coefficient R^2 are listed in Table 3.

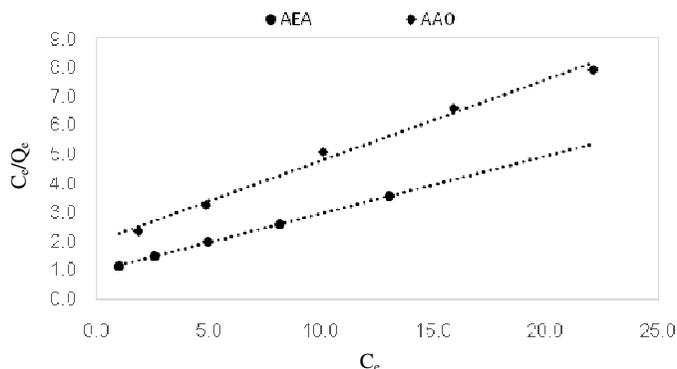


Figure 10. Langmuir isotherm model for biosorption of Cu(II) on to AEA and AAO

Freundlich isotherm

The Freundlich model (Figure 11) assumes that the uptake of metal ion occur on a heterogeneous adsorption surface by multilayer adsorption and the energy of adsorbent-adsorbate increases with increase in concentration of adsorbate solution⁴⁷. The linear form of Freundlich isotherm⁴⁷ is given by following Eq. 7.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Where K_f and n are Freundlich constants for the systems and represent adsorption intensity and adsorption capacity, respectively. The Freundlich constants K_f and n are obtained from the plot of $\log Q_e$ versus $\log C_e$ that should give a straight line with a slope of $1/n$ and intercept of $\log K_f$. From these plots the values of K_f and n were found to be 1.014 and 1.8 for Cu(II) on to AEA and 1.519 and 0.499 for Cu(II) on to AAO. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics⁴⁷. However, the R^2 values were found to be 0.981 and 0.984 for Cu(II) on to AEA and AAO, respectively. These results indicate that the Freundlich model was not able to adequately to describe the relationship between the amounts of sorbed metal ions and their equilibrium concentration in the solution.

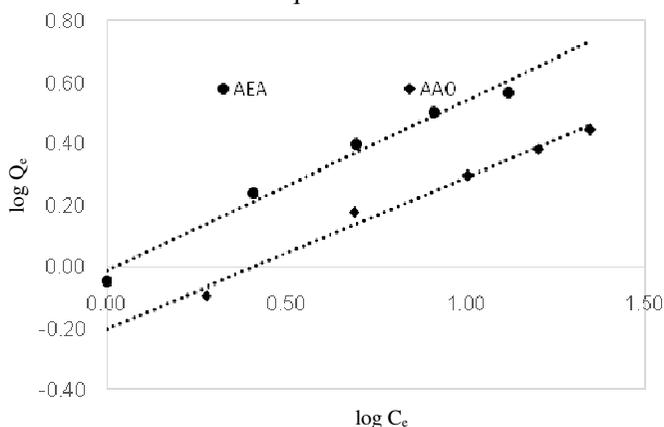


Figure 11. Freundlich isotherm model for biosorption of Cu(II) on to AEA and AAO

Temkin isotherm

Temkin isotherm takes into account the heat of adsorption all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbent interaction⁴⁸. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy⁴⁸. The linear form of Temkin isotherm model is given by the Eq. 8:

$$q_e = b_T \ln A + b_T \ln C_e \quad (8)$$

Where b_T is the Temkin constant related to heat of sorption (J/mole) and K_T the adsorption isotherm constant in (L/g). Values of b_T and K_T were calculated from the slope and intercept of the linear plot of q_e versus $\ln C_e$ as shown in Figure 12 are given in Table 3.

Table 3. Biosorption isotherm constants for sorption of Cu(II) onto AEA and AAO biomass

Isotherm model	AEA	AAO
Langmuir		
Q_{\max} , mg/g	5.007	3.358
K_L , L/mg	0.152	0.212
R^2	0.999	0.991
Freundlich		
K_F , mg/g, L/mg ^{1/n}	0.6512	0.1239
N	7.55	7.83
R^2	0.925	0.1239
Temkin		
b_T , mg/g	1.12022	0.784
A	3.6559	1.233
R^2	0.994	0.991

The isotherm constant for Langmuir, Freundlich and Temkin isotherm models studied and the correlation coefficient R^2 with experimental data are listed in Table 3. The correlation coefficients for Langmuir isotherm are highest in comparison to the value obtained for Freundlich and Temkin isotherms. Therefore the Langmuir isotherm is best fit isotherm for adsorption of Cu(II) on to AEA and AAO biomass. Q_{\max} is the monolayer saturation at equilibrium. K_L which corresponds to the concentration at which the amount of Cu(II) ion bound to the AEA and AAO biomass is equal to Q_{\max} indicates the affinity of the Cu(II) ion adsorption onto AEA and AAO. A high value of K_L indicates high affinity of Cu(II) adsorption on to AEA and AAO biomass. Show higher monolayer adsorption capacity. K_F and $1/n$ indicate the adsorption capacity and adsorption intensity, respectively. The higher value of $1/n$ indicates that the higher affinity and heterogeneity of the adsorption sites. The linear plots for Temkin adsorption isotherm (Figure 12), which consider chemisorption of adsorbate onto the adsorbent, fit quite well with correlation coefficients ($R^2 > 0.99$).

R_L Values at different initial metal ion concentrations

The effect of isotherm shape can be used to predict whether an adsorption system is favorable or unfavorable⁴⁹. The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined⁴⁹ by the following Eq. 9:

$$R_L = \frac{1}{1 + K_L x C_o} \quad (9)$$

Where R_L is dimensionless separation factor, C_0 is initial concentration of metal ions (mg/L) and K_L is Langmuir constant (L/mg). The parameter, R_L indicates the adsorption nature to be either irreversible if ($R_L=0$), favorable if ($0 < R_L < 1$), linear if ($R_L=1$) and unfavorable if ($R_L > 1$)⁴⁹. In this study, the values of R_L obtained for Cu(II) ions onto AEA and AAO biomass at 293 K are given in Table 4 and are greater than 0 and less than 1. This indicates that the adsorption of metal ions onto TAC is favorable. In this study, all R_L values fall between zero and one as shown in Table 4.

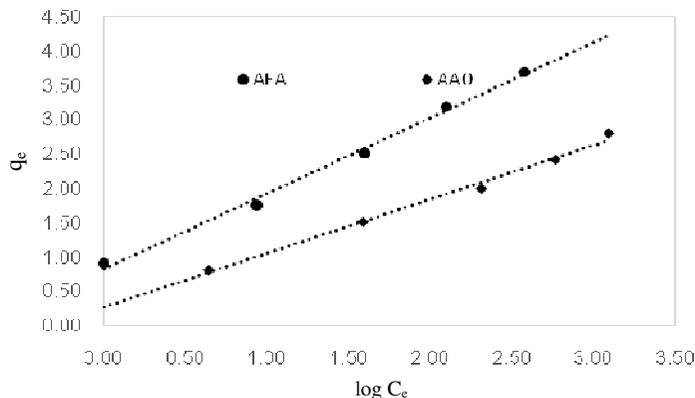


Figure 12. Temkin Isotherm model for biosorption of Cu(II) on to AEA and AAO

Table 4. R_L values based on the Langmuir isotherm

C_0 , mg/L	R_L Value	
	AEA	AAO
10	0.868	0.713
20	0.721	0.491
30	0.571	0.318
40	0.447	0.229
50	0.334	0.176

Kinetics of adsorption and model fittings

Adsorption kinetics elaborate the rate of adsorption of solute Cu(II) ion onto solid adsorbent in solution interface and provides valuable information about the reaction pathways and mechanisms. The kinetic of Cu(II) ion adsorption on AEA and AAO biomass are analyzed using two kinetic models, which are pseudo-first-order and pseudo-second-order models. The mechanism is identified on the basis of Q_{max} calculated value which is nearer Q_{max} experimental value with R^2 the correlation coefficients. The relatively high R^2 value indicated that the model successfully follows the kinetics of Cu(II) adsorption.

Pseudo-first-order kinetics

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models were used to experimental data. The pseudo-first order model of Lagergren is based on the rate of the adsorptive interaction can be investigated⁵⁰. This model describes the rate of adsorption to be proportional to the number of unoccupied sites by the solutes and can be expressed in a linear form as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (10)$$

Where q_e and q_t are the amounts of Cu(II) adsorbed (mg/g) at equilibrium and at time t (min), respectively and K_1 is the pseudo-first-order adsorption rate constant (L/min) (Figure 13 & 14). The values of K_1 , q_e calculated from the equation and the correlation coefficient (R^2) values of fitting the first-order rate model at different concentrations are presented in Table 5 and Table 6.

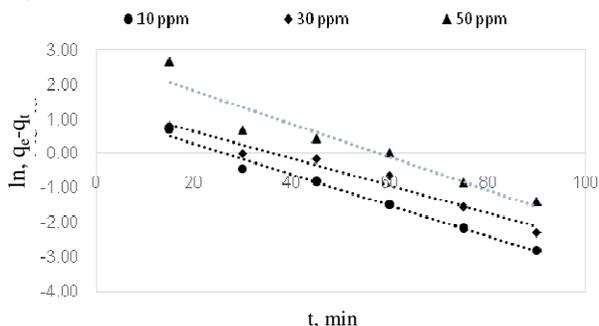


Figure 13. Pseudo-first-order sorption kinetics of Cu(II) ions onto AEA biomass

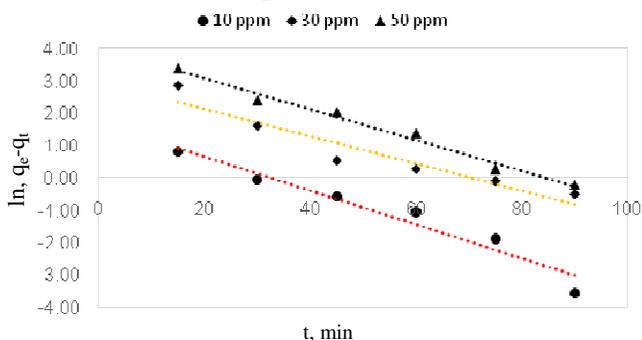


Figure 14. Pseudo-first-order sorption kinetics of Cu(II) ions onto AAO biomass

This model elucidate the adsorption capacity of adsorbent in liquid/solid system and assumes that the rate of metal ion (adsorbate) uptake with time is directly proportion to the difference of number of occupied site and the amount of adsorbate uptake with time. The pseudo-first order works well only where adsorption process occur very rapid adsorption period⁵¹. Ho mentioned that, the use of the Lagergren model for prediction of the adsorption kinetics is not suitable for the entire adsorption period⁵².

Pseudo-second order kinetics

Pseudo-second order kinetic model (Figures 15 & 16) assumes that, the rate of occupation of adsorption sites is proportional to the square of the number of vacant active sites. The adsorption rate is depends on the concentration of the activated sites on the surface of adsorbent. The overall rate of Cu(II) sorption process appear to be controlled by chemical process through sharing of electrons between biosorbent and metal ion, or covalent forces, through exchange of electrons between the particles involved^{53,54}. The pseudo-second order kinetics can be expressed in a linear form as follows:^{51,52}:

$$\frac{t}{qe} = \frac{1}{K_2 q_e^2} + \frac{t}{qe} \quad (11)$$

Where K_2 is AEA equilibrium rate constant of pseudo-second order (g/L AAO min), q_e is the amount of adsorption equilibrium, K_2 is the rate constant of the equation (L/min), q_e (cal.) is the calculated amount of adsorption equilibrium and R^2 is the coefficient of determination are present in Table 5 & 6.

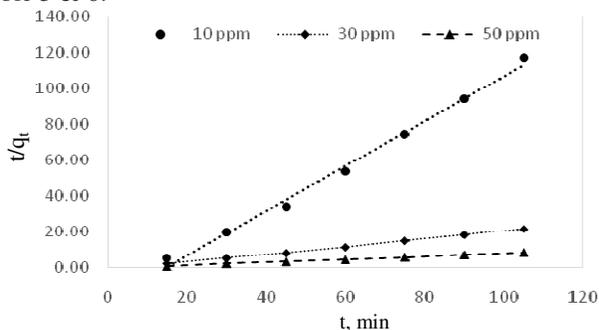


Figure 15. Pseudo-second-order sorption kinetics of Cu(II) ions onto AEA biomass

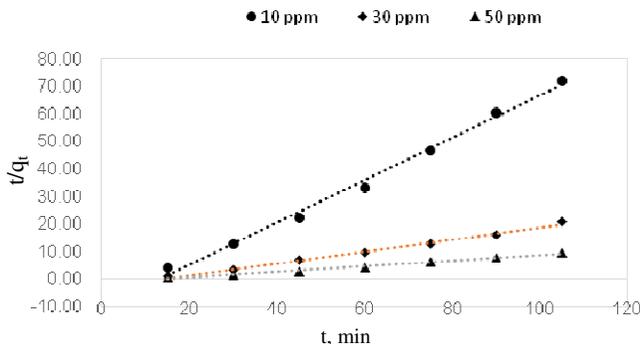


Figure 16. Pseudo-second-order sorption kinetics of Cu(II) adsorption on AAO biomass

As seen in Table 5 and Table 6, the correlation coefficients of pseudo-first order kinetic were calculated to be in a range of 0.913-0.985 and 0.903-0.983 for AEA and AAO, respectively. It shows the applicability of pseudo-first order kinetic model on the experimental data for AEA and AAO biosorbent. The theoretical and experimental equilibrium biosorption capacity q_e are given in Table 5 and Table 6. However, the values of q_e for pseudo-first order are not in an agreement with the experimental q_e values. This indicates that pseudo-first order equation might not be sufficient to describe the interaction between Cu(II) ion-adsorbent. The R^2 values in Table 5 and Table 6 suggest that biosorption of Cu(II) onto AEA and AAO do not follow pseudo-first order kinetics. The correlation coefficient R^2 for pseudo-second order kinetic is greater than 0.99 and its calculated q_e values agree with the experimental values, q_e for AEA and AAO biosorbent. This confirms that the adsorption data are well represented by the pseudo-second order kinetic model. From Table 5 and Table 6, it was observed that the pseudo-second order kinetic rate constants decreased with the increase of Cu(II) initial concentrations. This is because of less competition of sorption surface active sites at lower concentration. The rate of Cu(II) ion onto AEA is greater than AAO biomass. At higher concentration, the competition for the adsorption active sites will be increased and consequently the adsorption rate will become slower. A similar result was reported for the adsorption of Cu(II) on chitosan coated sand⁵⁵, sugar beet pulp⁵⁶ and *Cinnamomum camphora leaves*³⁰.

Table 5. The comparison of pseudo-first order, pseudo-second order rate constants and calculated and experimental q_e values obtained at different Cu(II) ion concentration data for AEA

Kinetic model	C_0 , mg/L		
	10	30	50
q_t (Exp.)	0.895	4.899	12.995
Pseudo-first order			
q_e cal., mg/g	3.197	4.105	15.922
K_1 , 1/min	4.47×10^{-2}	3.93×10^{-2}	4.81×10^{-2}
R^2	0.985	0.966	0.913
Pseudo-second order			
q_e cal., mg/g	0.798	4.63	12.12
K_2 , g/mg min	8.59×10^{-2}	3.1×10^{-2}	1.26×10^{-2}
R^2	0.993	0.998	0.999

Table 6. The comparison of pseudo-first order, pseudo-second order rate constants and calculated and experimental q_e values obtained at different Cu(II) ion concentration data for AAO

Kinetic model	C_0 , mg/L		
	10	30	50
q_t	1.465	5.1	11.1
Pseudo-first order			
q_e cal., mg/g	5.533	19.97	56.97
K_1 , 1/min	5.26×10^{-2}	4.23×10^{-2}	4.77×10^{-2}
R^2	0.946	0.909	0.984
Pseudo-second order			
q_e cal., mg/g	1.302	4.602	9.702
K_2 , g/mg min	3.267×10^{-2}	2.507×10^{-3}	3.08×10^{-4}
R^2	0.9933	0.992	0.9863

Conclusion

In this study, AEA and AAO were used and investigated as possible biosorbent for the removal of Cu(II) ion from its aqueous solution using batch sorption technique. The adsorption of Cu(II) onto AEA and AAO biomass was affected by pH, adsorbent dose, contact time and temperature. Spectroscopic analyses involving Fourier transform infrared (FTIR) and Scanning Electronic Microscope (SEM) were also important in order to have a better understanding on the mechanism of the Cu(II) metal ion adsorption on modified biomass leaves. Sorption capacity be governed by the pH and the biosorbent dose. The optimum pH which gives higher % removal of Cu(II) is 5. At optimum conditions of pH 5.0, contact time of 30 min and temperature of 293 K. The thermodynamic parameters ΔH^0 , ΔG^0 and ΔS^0 give information about spontaneity of adsorption process. The results indicated that Cu(II) biosorption onto AEA and AAO was found to spontaneous exothermic and irreversible. The equilibrium data have been analyzed using Langmuir, Freundlich and Temkin isotherm models. The Langmuir adsorption isotherm was best correlation coefficient for biosorption of Cu(II) ions onto AEA and AAO biomass, thus indicating the applicability of monolayer coverage of Cu(II) on AEA and AAO surface. The biosorption capacity of Cu(II) found to be 5.008 and 3.358 mg/g for AEA and AAO biomass respectively. The equilibrium data were also well described by the Temkin equation further supporting Cu(II) adsorption on to AAO as a chemisorption process. The biosorption capacity AEA is greater than AAO biomass. The kinetic results provided the best correlation of the experimental data of biosorption of Cu(II) ions onto AEA and AAO

biomass by the pseudo-second-order kinetic model. The pseudo-second order kinetic model assumes that, the rate-determining step may be chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. This study demonstrated that it is possible to remove copper ion from aqueous solution with AEA and AAO adsorbent.

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