Removal of Cu(II) by Amidoxime-modified Polyacrylonitrile-grafted-Cassava Starch

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ABSTRACT

The presence of heavy metal ions in the environment is one of the serious threats to human health. Heavy metal pollutants have accumulating characteristics in nature, and they are non-biodegradable with high toxicity even at trace concentrations. Cu(II) is associated with kidney and liver damage, anaemia, central nervous system problem and affects enzymes in living organism due to its high affinity towards ligands containing nitrogen and sulphur donors. Adsorption is regarded as a practical treatment method due to its low cost, high capacity, easy metal recovery and reusability. In the present work, we utilized our 'in-house' amidoxime-modified poly(acrylonitrile (AN)-grafted (g)-cassava starch (CS)) for the removal of Cu(II) from an aqueous solution. It was found that the maximum adsorption capacity of amidoxime-modified poly(AN-g-CS) was 75.76 mgg^{-1} at pH 5. The adsorption kinetic study showed that the optimum time required for the Cu(II) ions to attain saturation level was 1 h. The adsorption kinetic and equilibrium data were well fitted to the pseudo-second order model and the Langmuir isotherm, respectively.

Keywords: cassava starch; amidoxime; chemical modification; graft copolymerization; heavy metal ions, hydroxylamine hydrochloride; ligands; oxime group; polyacrylonitrile.

INTRODUCTION

Due to the alarming rate of global industrialization, introduction of poisonous substance into the environment has become a threat to both animals and plants. Thus, heavy metal ions discharged into the surrounding have caused a serious challenge to the environment as a result of their ability to transform into serious poisonous living materials[1]. Examples of such poisonous heavy metal ions that cause serious challenge to health and are persistent during treatment of waste water include; copper, mercury, cadmium, zinc, lead, chromium and nickel[2, 3]. Copper is one of the most important elements in activities of the human body, however, copper that was ingested more than the required amount can lead to serious health problems such as; convulsion, vomiting, cramps and eventually death[4].

Filtration, chemical precipitation, ion exchange, electrode deposition and surface complexation have several drawbacks due to either high cost of chemicals, metal selectivity; low adsorption capacity for heavy metal ions and low potential for regeneration[5]. However, adsorption is regarded as one of the most vital techniques due to availability of raw materials, simplicity with sufficient adsorption of heavy metal ions[6].

Attention of many researchers has been drawn towards the use of polyacrylonitrile (PAN) for adsorption of heavy metal ions in industries due to its special features that include hardness and flexibility, chemical resistance, consistency with other polar materials, permeability[6] and the existence of nitrile functional groups along polymer chains that could be converted into other functional groups[7]. Hence, PAN performance has been improved *via* chemical modification with various reagents such as hydroxylamine, ethylenediamine, hydrazine, thioamide and imidazoline to develop new moieties that are vital for the removal of cationic metal ions in wastewater[8, 9].

Agricultural adsorbent is considered as low-cost, cheap and abundant in nature that requires little processing and is a byproduct of waste material from waste industry. Plant wastes are also considered as inexpensive as they have no or very low economic value[10,11]. Most of the adsorption studies generally focused on untreated plant wastes such as papaya wood [12], maize leaf [13], leaf powder[14], peanut hull pellets [15], rice husk ash and neem bark[16]. Some of the advantages of using plant waste for wastewater treatment include simple technique, good adsorption capacity, abundant availability, selective adsorption of heavy metal ions, easy regeneration, low cost and requires little processing [17, 18]. It was reported that metal ions binding by lignocellulosic biosorbents occurred through moieties such as carboxyl or phenolics[19]. Metal biosorption is a complex process involving chemisorption, complextion, adsorption-complexation of surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface and surface adsorption[20, 21].

As reported in our previous study, we have prepared an adsorbent by grafting cassava starch (CS) onto polyacrylonitrile (PAN). CS was incorporated into hydrophobic PAN system to weaken the nitrile-nitrile dipolar interaction, thus facilitated the penetration of reagents into cyano groups during chemical modification. The cyano functional group in poly(AN-grafted *(g)*-CS) was utilized to be converted into desired chelating group (oxime) to form amidoxime-modified poly(AN-*g*-CS) (Figure 1). The chemically modified poly(AN-*g*-CS) was expected to capture heavy metal ions *via* complex formation of 'polymer-metal ions coordination complex'[22]. In addition, CS consists of lignocellulosics that are hygroscopic and has good affinity for water. Water is easily penetrating the non-crystalline part of cellulose and all parts of hemicellulose and lignin due to their random and amorphous structure [19]. Hence, it is expected that the amidoxime-modified poly(AN-*g*-CS) has a potential to adsorb high capacities of heavy metal ions from aqueous solution.

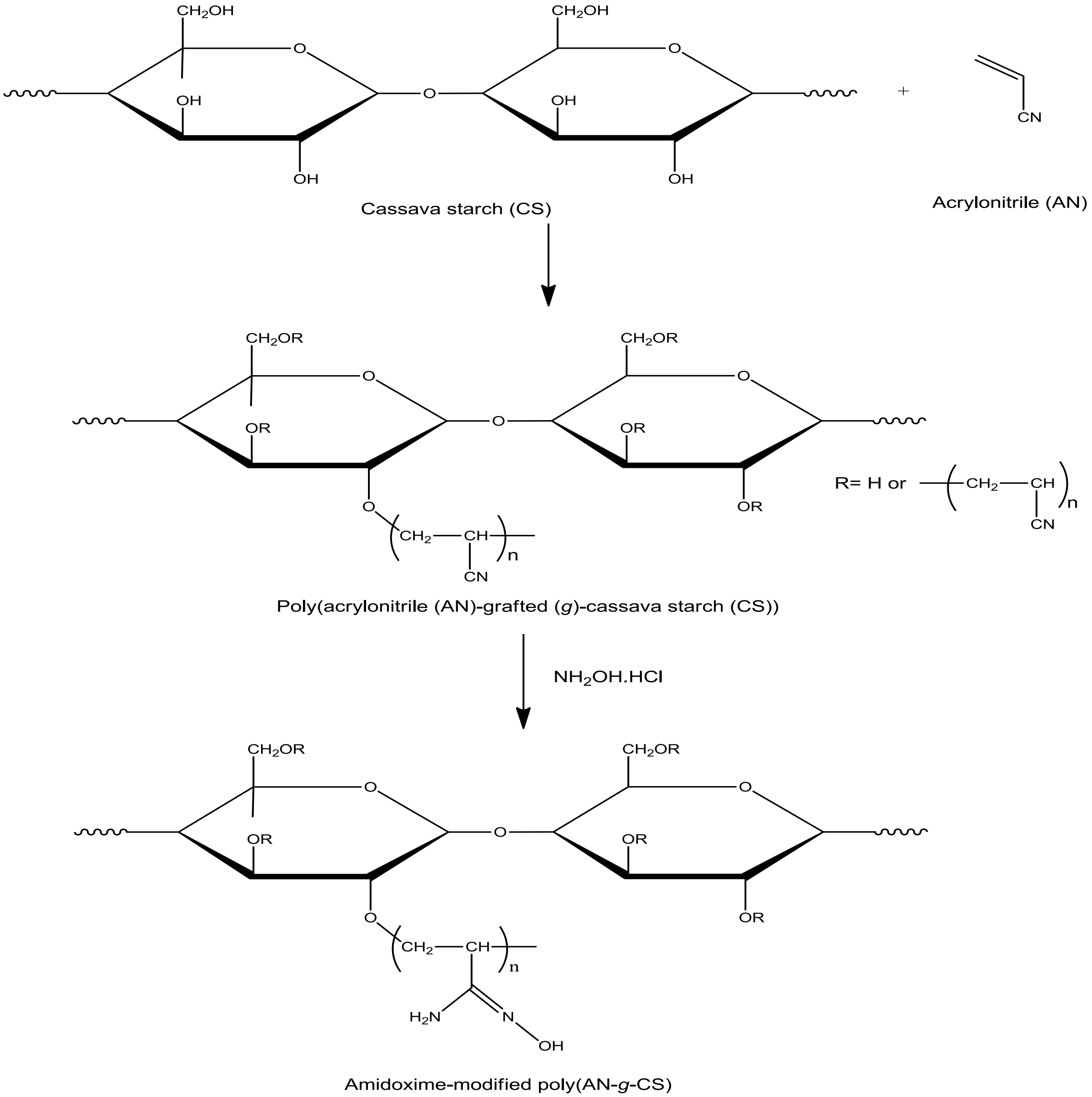

Figure 1. Formation of poly(acrylonitrile (AN)-grafted *(g)*-cassava starch (CS) and amidoxime-modified poly(acrylonitrile (AN)-grafted *(g)*-cassava starch (CS)

MATERIALS AND METHODS

Materials

The reagents used for the polymerization was acrylonitrile (99% grade) supplied by Merck Co. (United Kingdom) and cassava starch was bought from local market (Selangor, Malaysia). Potassium persulphate (KPS) and sodium bisulfite (SBS) were supplied by Systerm (Malaysia). Hydroxylamine hydrochloride (Acros organics, USA) was used for chemical modification. Sodium hydroxide (analytical grade) was supplied by R & M (U.K). Methanol (analytical grade) was supplied by ChemPur Systerm (Malaysia). Acrylonitrile was purified by passing the monomer through a short column of neutral alumina (grade for chromatography). All other reagents were used as received. Copper sulphate pentahydrate ($CuSO_4.5H_2O$) (99.8%, Merck) of analytical grade was used as heavy metal ion contaminant in this study.

Synthesis

The preparation of poly(AN-*g*-CS) has been reported in previous study [22]. Cassava starch (CS) was initially peeled and washed thoroughly with deionised water to remove the surface impurities. It was then dried under the sunlight for about 48 h before further drying in a vacuum oven at 50 ℃ overnight to eliminate the moisture. The particle size of CS was reduced by using mortar mill and was sieved to obtain a desirable size of about 10 μm. The final product was stored in a desiccator for further experimental use. 20 g of dried CS and 200 mL of deionized water were mixed in a three neck round bottom flask fitted with a water condenser under nitrogen atmosphere. The mixture was stirred for 1 h to form cassava slurry. The acrylonitrile (AN) (15 mL, 13.3 g) was added into the reaction medium, followed by SBS (2.09 g, 0.27 mol.L^{-1}) and KPS (2.16 g, 0.44 mol.L^{-1}). The graft copolymerization of poly(AN-g-CS) (ratio of AN:CS was 1:3) was performed at different condition parameters. The reaction temperature was varied to 40℃, 50℃ and 60℃ under constant stirring at 250 rpm. The reaction was terminated by pouring the product into 50 mL of methanol and left to precipitate for 1 h. The grafted copolymer was filtered and washed successfully with 50 mL of methanol and 100 mL of deionized water. The polymer was dried in a vacuum oven at 50 ℃ until a constant weight was obtained.

The removal of the homopolyacrylonitrile (homoPAN) from poly(AN-*g*-CS) was accomplished by stirring the poly(AN-*g*-CS) at 200 rpm in 25 mL of dimethyl sulfoxide (DMSO) for 24 h to dissolve the homoPAN. The poly(AN-*g*-CS) was filtered and washed successfully with 50 mL of methanol and 100 mL of deionized water. The purified poly(AN-*g*-CS) was dried in a vacuum oven at 50℃ until a constant weight was obtained[22].

Modification of poly(AN-g-CS) with hydroxylamine hydrochloride

The chemical modification of poly(AN-g-CS) with hydroxylamine hydrochloride to form amidoxime-modified poly(AN-g-CS) (Figure 1) has been reported previously [22]. 2 g of poly(AN-*g*-CS), 25 mL of methanol and 3 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) were added into a 250 mL three-neck round-bottom flask that was fitted with a reflux condenser. The mixture was stirred at room temperature for 2 h. 6 mL of sodium hydroxide solution (1 M) was added to the reaction mixture to neutralize the hydrochloric acid (HCl). The pH of the mixture was adjusted to pH 8. The reaction was allowed to proceed for 6 h at 70 °C under constant stirring. The amidoxime-modified poly(AN-*g*-CS) was then filtered and washed thoroughly with 50 mL of ethanol and 100 mL of deionized water. The polymer was allowed to dry in a vacuum oven at 50 °C till a constant weight was obtained [7].

Adsorption in batch experiment

A total of 3.93 g of $CuSO_4.(5H_2O)$ was dissolved in 1000 mL of distilled water to prepare 1000 ppm of Cu(II) standard stock solution. Dilution of the stock solution was made to prepare working solutions that contain different concentrations of metal ions, which were used in the adsorption studies. Batch experiment was performed at room temperature in order to establish the sorption capacity towards single-metal ion by mixing 0.10 g of the sorbent with 100 mL of heavy metal ion solution in a 250 mL conical flask. The mixture was magnetically stirred at 200 rpm for 2 h. 5 mL of sample was withdrawn from the bulk solution and filtered using membrane filter. The initial and final concentrations of metal ions were then analyzed using Atomic Absorption Spectrometer, S Series air pump, (U.S.A).

RESULTS AND DISCUSSION

Cu(II) adsorption

Effect of pH on adsorption

The effect of pH on adsorption was investigated because pH influences both the surface charge of the adsorbent and the level of ionization of heavy metal ions in aqueous solution [23]. Figure 2 shows the effect of pH on the adsorption of Cu(II) ions onto amidoxime-modified poly(AN-*g*-CS) with 100 $mg.L^{-1}$ of initial concentration of Cu(II) ions. On variation of the pH in the range of 2 to 5, the ions uptake was steadily increased for amidoxime-modified poly(AN-*g*-CS). At pH 5, the amidoxime-modified poly(AN-*g*-CS) demonstrated maximum uptake towards Cu(II) ions at 56 mgg^{-1}.

The amidoxime group has an amphoteric character [24]. At lower pH, the $–NH_2$ groups were protonated and resulted to the formation of $^{+}NH_3$ that hindered the ability of basic amino group to form complex with Cu(II) ions. In addition, lower dissociation of the acidic –OH at lower pH, results to lower Cu(II) uptake. As the pH was increased up to pH 5, decreased in positive surface charges resulted to lower competition between the proton and metal cations for the same active sites on the polymer phase and consequently reduced the electrostatic repulsion between the active adsorption sites on the polymer surface and the metal cations. Lower concentration of H^+ ions weaken the protonation of amino groups and resulted to the complex formation of $–NH_2$ with Cu(II) at higher pH [8, 24, 25, 26,].

As the pH was increased to pH 6, the adsorption of amidoxime-modified poly(AN-*g*-CS) towards Cu(II) ions was reduced to 25 mgg^{-1}. This is due to higher pH that increased the concentration of deprotonated groups and resulted to the hydrolysis of Cu(II) ions that precipitated as $Cu(OH)_{2.}$[27]. The soluble hydroxyl complexes weaken the coordination of the active sites with the metal cations and resulted to low adsorption towards Cu(II) at this condition. Based on this result, the adsorptions towards heavy metal ions were carried out at pH 5 for further analysis.

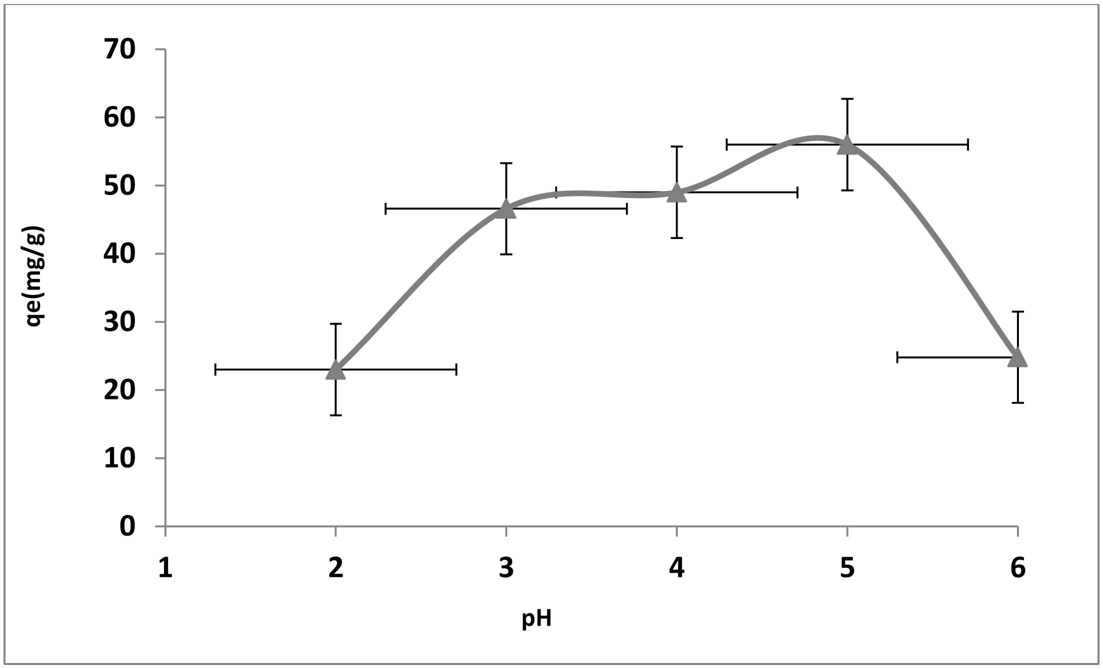

Figure 2. Effect of pH on the sorption capacity of Cu(II) by amidoxime-modified poly(AN-*g*-CS). Condition: 0.1 g of CS, poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) in 100 mL of 100 ppm Cu(II) solution at 200 rpm for 2 h at room temperature of 25±2℃. (Error bars represent the standard deviations of triplicate recordings).

Effect of contact time

The adsorption capacity was determined as a function of time to evaluate the maximum contact time in the process of adsorption of Cu(II) towards amidoxime-modified poly(AN-*g*-CS). As shown in Figure 3, there were rapid uptakes towards Cu(II) at the first 20 min prior to saturation at 60 min with the highest Cu(II) uptake at 54 mgg^{-1}.

Higher heavy metal ions uptake in the case of amidoxime-modified poly(AN-*g*-CS) has been expected due to the synergistic role of CS as a good sorbent in aqueous solution [19] and the exploitation of nitrile functional group in AN units that was converted into oxime pendant groups to form ligand with Cu(II) ions.

Adsorption kinetics

The kinetic isotherm models have been widely explored to study the capacity rate controlling the adsorption[28]. The kinetic experiments of Cu(II) ions adsorption were performed using the optimum pH with chosen initial concentration of Cu(II) ions at room temperature. In present study, the sorption kinetic was compared using pseudo-first order and pseudo-second order kinetic models. The pseudo-first order kinetic model is based on the amount of solid received or contained and generally given by Equation 1.[29]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad [1]$$

where k_1 is the pseudo-first order rate constant (min^{-1}), q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t (min), respectively. This equation describes a reversible equilibrium between the solution and the adsorbent [30].

Figure 4 shows the pseudo-first order plot of log ($q_e - q_t$) against t of Cu(II) ions solution. The rate constant k_1 was calculated from the slope while the theoretical value of q_e was calculated from the intercept. As shown in Table 1, correlation coefficient (R^2) of amidoxime-modified poly(AN-*g*-CS) was found to be 0.932.

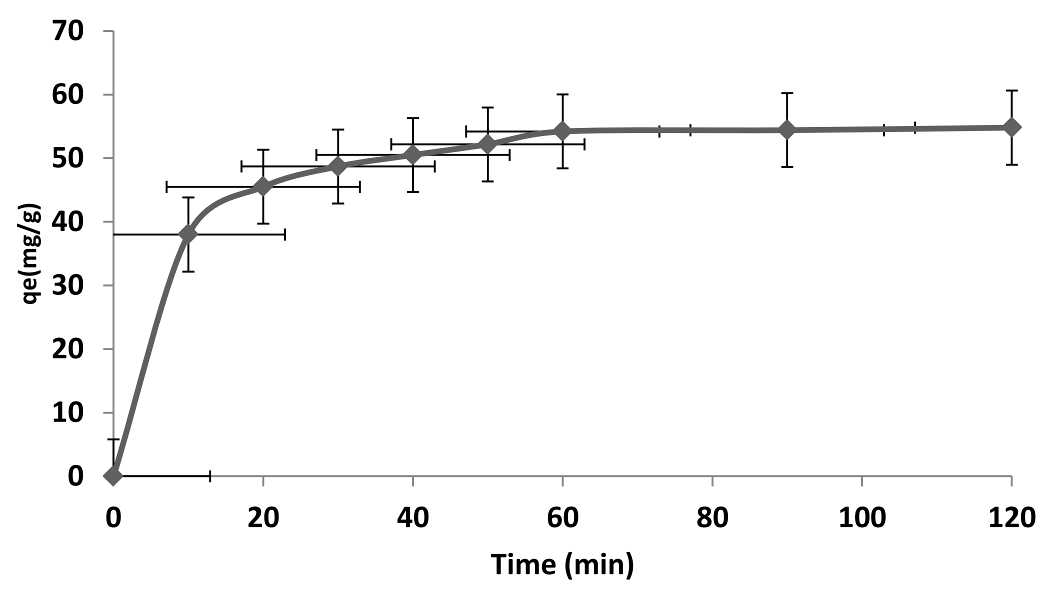

Figure 3. Effect of contact time on the adsorption capacity of Cu(II) by amidoxime-modified poly(AN-*g*-CS). Condition: 0.1 g of amidoxime-modified poly(AN-*g*-CS) in 100 mL of 100 ppm Cu(II) solution at 200 rpm at room temperature of 25±2°C. (Error bars represent the standard deviations of triplicate recordings).

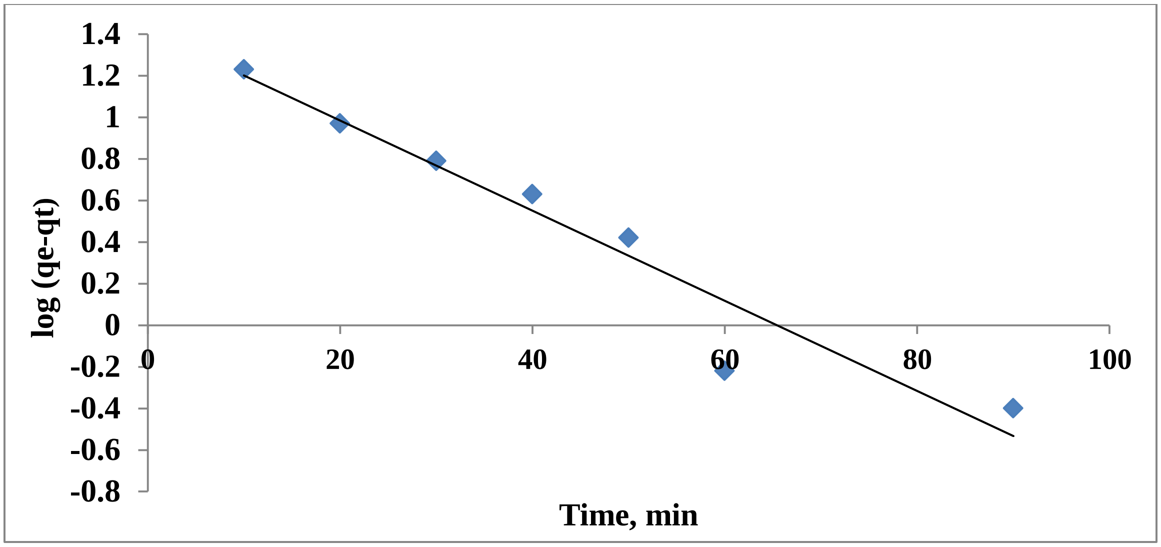

Figure 4. Pseudo-first -order rate for the adsorption of Cu(II) ions by amidoxime-modified poly(AN-*g*-CS).

$$\frac{dq}{dt} = k_{2,ad}\,(q_e - q)^2 \qquad [2]$$

where $k_{2,ad}$ is the rate constant of second-order-adsorption (g.mg^{-1}.min^{-1}). For the same boundary conditions the integrated form of Equation 2 is expressed as,.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad [3]$$

The initial sorption rate, h (mg/g. min), at t = 0 is given by,

$$h = k_{2,ad} q_e^2 \qquad [4]$$

where $k_{2.ad}$ and *h* were determined from the slope and intercept of the plots of *t/q* against *t* respectively.

Figure 5 shows the plot of the pseudo-second order kinetics for the adsorption of Cu(II) by amidoxime-modified poly(AN-*g*-CS). The linear graph with regression coefficient *(R^2)* value of 0.999 was obtained for amidoxime-modified poly(AN-*g*-CS). As shown in Table 1, the correlation coefficient (R^2) of the second order kinetic is higher (0.9997) as compared to the correlation coefficient obtained from the first order kinetic (0.9330). In addition, the equilibrium adsorption capacity $q_{e(cal)}$ of pseudo-second order has better agreement with the experimental value $q_{e(exp)}$ (Table 1). Hence, the pseudo-second order kinetic model is better to represent the experimental data than that of the pseudo-first order kinetic model. The pseudo-second order kinetic model is preferred to reflect the chemical process during adsorption of Cu(II) ions towards amidoxime-modified poly(AN-*g*-CS). Similar results have been reported for the biosorption of Cu(II) ions towards sugar beet pulp[23,31] and $H_3PO_4^-$ activated rubber wood sawdust[28] that obey the second order kinetic equation as well.

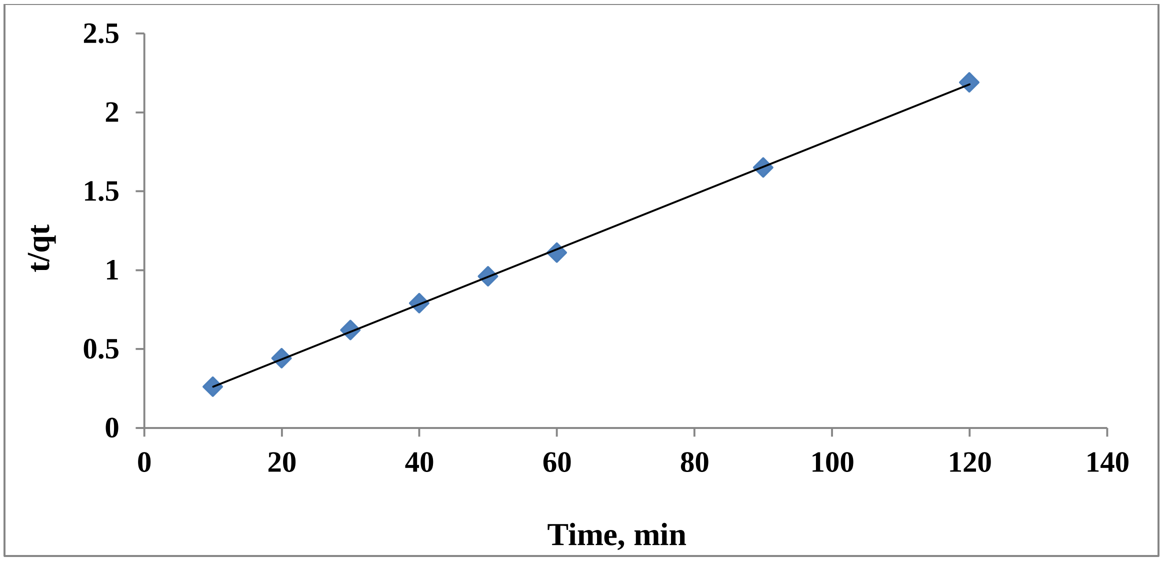

Figure 5. Pseudo-second-order rate for the adsorption of Cu(II) ions by amidoxime-modified poly(AN-*g*-CS)

Table 1. Pseudo first order and pseudo second order sorption rate constants and q_e values

First order kinetic equation				Second order kinetic equation			
$q_{e(exp)}$ (mg/g)	k_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	R^2	k_2 [g/(mg.min)]	$q_{e(cal)}$ (mg/g)	R^2	h [mg/(g.min)]
54.80	0.0499	26.18	0.9330	3.43×10^{-3}	57.47	0.9997	11.330

Effect of initial metal concentration

The effect of heavy metal ions concentration was studied by varying the initial concentration of Cu(II) ions at 25, 50, 75, 100 and 200 ppm, respectively. Figure 6 shows the effect of varying initial concentration with respect to the sorption capacities of Cu(II) ions. It reveals that the sorption capacity of amidoxime-modified poly(AN-*g*-CS) increased as the initial concentration of Cu(II) ions (25 ppm) was increased up to 100 ppm and reached their saturation point after 100 ppm. The adsorption capacity of amidoxime-modified poly(AN-*g*-CS) was increased from 18 mgg^{-1} (at 25 ppm of initial Cu(II) ions concentration) to 54 mgg^{-1} at 100 ppm of initial Cu(II) ions concentration. This implies that the adsorption of Cu(II) ions are dependent on the initial concentration of heavy metal ions [7]. The adsorption capacity increased as the number of possible binding sites increased and this is mainly due to the presence of more available solute and electrostatic interactions between the solute and the active sites [32].

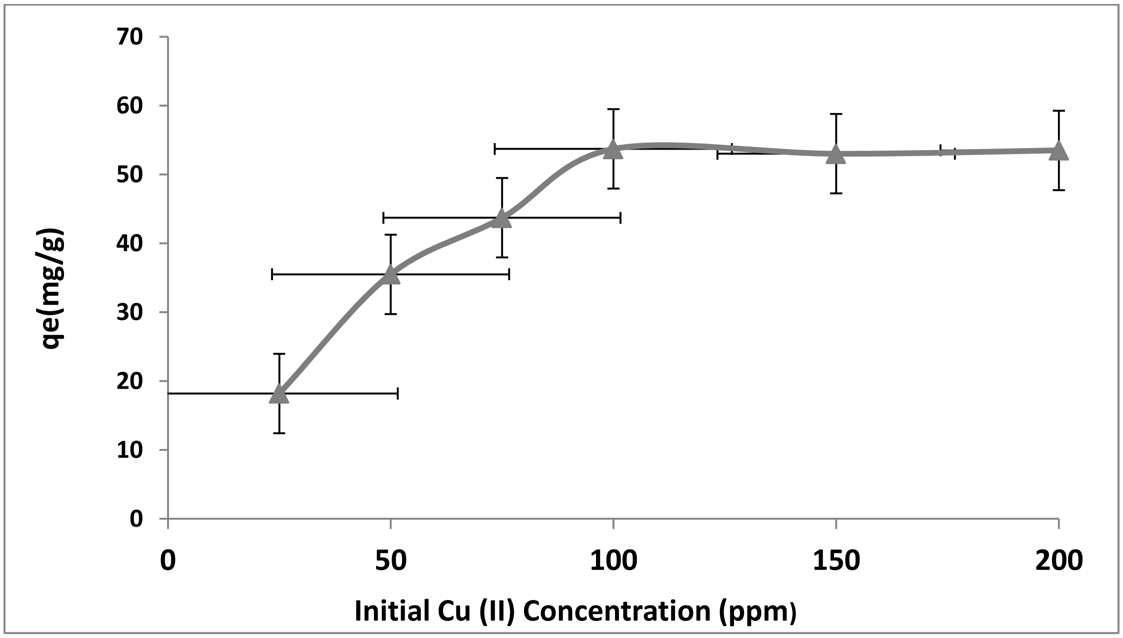

Figure: 6 Effect of initial Cu(II) concentration on the adsorption capacity of Cu(II) by amidoxime-modified poly(AN-*g*-CS). Condition: 0.1 g of amidoxime-modified poly(AN-*g*-CS) in 100 mL with different initial Cu(II) concentration at 200 rpm at room temperature of 25±2℃. (Error bars represent the standard deviations of triplicate recordings)

Adsorption isotherm

The equilibrium adsorption isotherms are part of the most favorable parameters used to explain the adsorption process and provide dependent relationship between the amount of heavy metal ions adsorbed and the heavy metal ions concentration in the equilibrium solution[33]. Generally, the importance of adsorption isotherms is to provide information on how the adsorbate molecules dispersed between solution and the adsorbent molecule at a given equilibrium conditions [34]. Langmuir and Freundlich adsorption isotherms are the two isotherms applied in the present study.

Langmuir isotherm describes an adsorption occurring on the surface that has a finite number of sites with similar energy levels. This model was generated based on the assumption that homogeneous adsorption occurred on a monolayer surface coverage and without net interaction between the adsorbed species [35].

The linearized Langmuir isotherm equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \quad [5].$$

where C_e is the equilibrium concentration of Cu(II) (mgg^{-1}), q_e is the adsorption capacity at equilibrium (mgg^{-1}), Q_{max} is the maximum adsorption capacity monolayer coverage (mgg^{-1}), b is termed as Langmuir constant that describes the affinity of the sorbent to the binding sites of the adsorbent (mL.mg^{-1}). The linear plots of C_e/q_evs C_e that was represented in Figure 7 was used to obtain the value of b (L.mg^{-1}) and Q_{max} (L.mg^{-1}) from the slope and intercept, respectively. The calculated value of the Langmuir isotherm constant and Q_{max} are tabulated in Table 2.

Table 2. Langmuir and Freundlich isotherm constants and their correlation coefficients for the adsorption of Cu(II)

Langmuir isotherm				Freundlich isotherm			
Q_{max} (mg/g)	b (L/mg)	R^2	$R_{L\ 25,100}$	K_f(L/mg)	$1/n$	n	R^2
75.76	0.049	0.9822	0.45, 0.17	6.94	0.544	1.84	0.9661

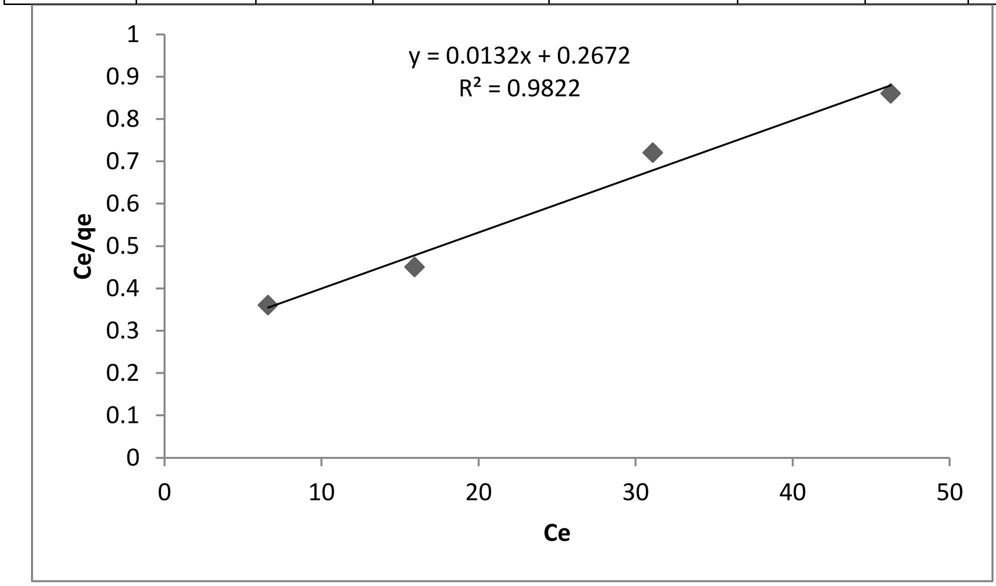

Figure: 7 Langmuir isotherm for the adsorption of Cu(II) by amidoxime-modified poly(AN-*g*-CS)

We proposed the important properties and feasibility of the Langmuir isotherm on the dimensionless constant, R_L, which is expressed as[36, 37]:

$$R_L = \frac{1}{1+bC_o} \quad [6]$$

where b is the Langmuir equilibrium constant (L.mg^{-1}) and C_O is the initial concentration of Cu(II) (mg.g^{-1}) [30]. The R_L value indicate the adsorption feasibility condition; for unfavorable ($R_L > 1$), irreversible ($R_L = 0$) and favorable ($0 < R_L < 1$) [26].

The R_L value that was calculated from two different initial concentration of Cu(II) ions (25 ppm and 100 ppm) are tabulated in Table 2. The result indicates that the R_L value of amidoxime-modified poly(AN-*g*-CS) were 0.45 and 0.17 L.mg^{-1}, which is less than 1, and implies the feasible adsorption of Cu(II) ions onto amidoxime-modified poly(AN-*g*-CS).

In contrast, the Freundlich adsorption isotherm assumes that the uptake or adsorption of heavy metal ions occurred on heterogeneous surface [8]. It assumes an initial surface adsorption followed by the condensation effect which occurred from extremely strong solute-solute interaction [34]. It is expressed based on the relationship between equilibrium liquid and solid phase capacity based on multilayer adsorption. The general form of Freundlich isotherm is given by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad [7]$$

The plot of *log* q_e vs *log* C_e is presented in Figure 8 that gave a straight line and the values of n and K_f were obtained from the slope and intercept, respectively.

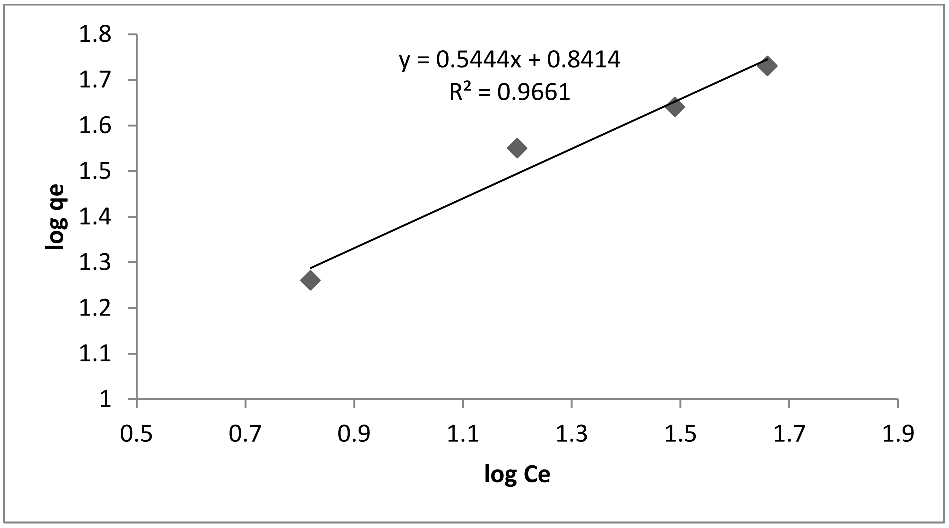

Figure 8. Freundlich isotherm for the adsorption of Cu(II) by amidoxime-modified-poly(AN-*g*-CS)

The values of Freundlich isotherm constant (K_f), Freundlich constant for intensity *(n)* and correlation coefficient (R^2) are presented in Table 2. As shown in Table 2, the value of *n* is in the range of 1-10 (*i.e. 1/n* less than 1) that represent favorable adsorptions *via* Freundlich isotherm.

As shown in Table 2, the Langmuir isotherm graph provided higher correlation coefficient *(R^2)* values as compared to that of Freundlich isotherm. This indicates that the sorption of Cu(II) onto amidoxime-modified poly(AN-*g*-CS) is fitted well with the Langmuir isotherm model.

Effect of sorbent dosage

Figure 9 shows the effect of varying adsorbent dosage (0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g) by fixing the 100 ppm of initial concentration of Cu(II) ions at pH 5. The adsorption capacity was decreased from 55.01 mgg^{-1} to 18.2 mgg^{-1} as the amount of amidoxime-modified poly(AN-*g*-CS) was increased from 0.1 g to 0.5 g, respectively. This was due to the lower utilization of the adsorbent that results to the less commensurate increase during the adsorption process[8]. Most probably, higher concentration of sorbent leads to the agglomeration of sorbent particles that decreased the surface area and availability of the active sites to form ligand with metal cations [38].

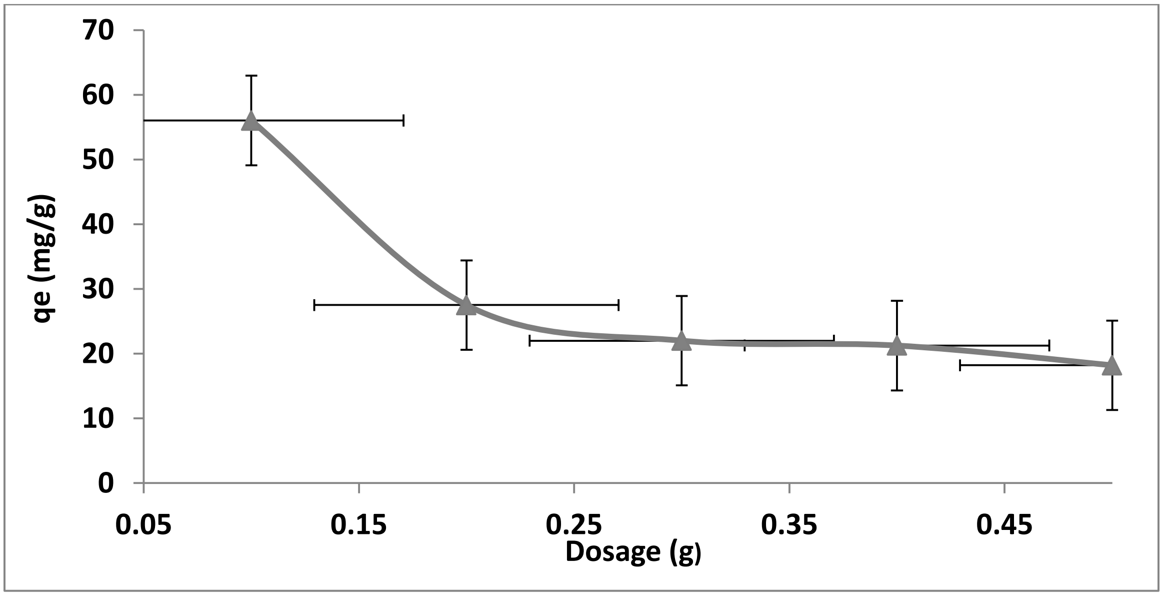

Figure 9. Effect of varying dosage on the sorption capacity of Cu(II) by amidoxime-modified poly(AN-*g*-CS). Condition: different dosage of amidoxime-modified poly(AN-*g*-CS) in 100 mL of 100 ppm Cu(II) concentration at 200 rpm for 2 h at room temperature of 25±2℃. (Error bars represent the standard deviations of triplicate recordings).

Mechanisms for Cu(II) uptake by amidoxime-modified poly(AN-g-CS)

Due to the porous nature of the amidoxime-modified poly(AN-*g*-CS), the intra-particle transport is suggested to be the rate controlling steps; where the rate constant for the transfer of the sorbate to the active site inside the particles is slower compared to the adsorption onto the surface of the adsorbent[38]. As proposed in Figure 10, adsorption of Cu(II) ions towards the active sites on the surface of chelating resin (chelate formation) occurred between amidoxime and metal cations, which form square-planar chelates. This formation is expected to contribute to the efficiency of heavy metal ions uptake by the adsorbent [39].

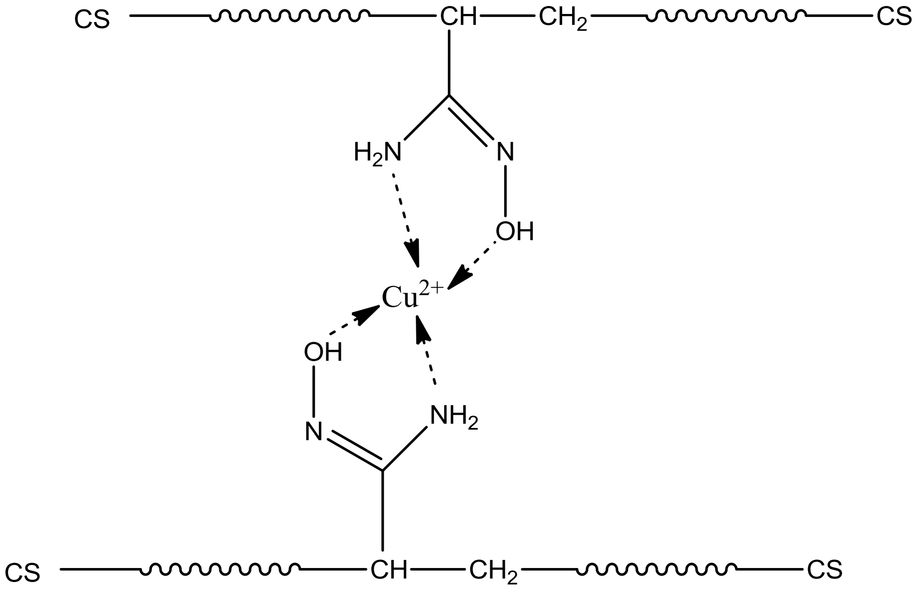

Figure 10. Proposed mechanism of complex formation of amidoxime-modified poly(AN-*g*-CS) and Cu(II) ion

CONCLUSION

The maximum Cu(II) ions removal by the amidoxime-modified poly(AN-*g*-CS) was observed to occur at pH 5. It was established that the adsorption capacities of Cu(II) ions were increased as the dosages of the adsorbent were decreased. In addition, the adsorption capacities of Cu(II) ions were increased with increasing initial concentration of Cu(II) ions. The highest removal of Cu(II) ions was recorded as 75.76 mgg^{-1}. This was achieved by applying low adsorbent dosage at 0.1 g in an acidic condition (pH 5). The isotherm and kinetic studies showed that the adsorption of Cu(II) onto amidoxime-modified poly(AN-g-CS) fitted well the Langmuir isotherm and pseudo-second-order kinetics, respectively.

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