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Synthesis, characterization of acrylamide grafted chitosan and its use in removal of copper(II) ions from water

Ahmed Jasim M. Al-Karawi[a,*], Zyad Hussein J. Al-Qaisi[a], Hussein Ismael Abdullah[a], Ali Mohamad A. Al-Mokaram[a], Dhafir T. Ajeel Al-Heetimi[b]

[a] Al-Mustansiriya University, College of Science, Department of Chemistry, PO Box 46010, Baghdad, Iraq
[b] University of Baghdad, College of Education/Ibn Al-Haitham, Department of Chemistry, Baghdad, Iraq

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ABSTRACT

The graft copolymerization of acrylamide onto chitosan in aqueous medium was investigated, using potassium persulfate (PPS) as initiator. The graft copolymer was characterized by Fourier transform infrared spectra analysis, differential scanning calorimetric and thermogravimetric analysis. The effects of polymerization variables, such as the initiator concentration, the ratio of monomer to chitosan, as well as, reaction temperature were studied, and the grafting conditions were optimized. The prepared polymers which have the highest percentage of grafting (PG) have been used in removal of Cu(II) ions from water by followed adsorption studies at pH = 7. The amount of metal ion uptake of the polymers was determined by using atomic absorption spectrophotometer. The effect of polymer mass and temperature on the adsorption of Cu(II) ions have been also reported. Langmuir and Freundlich isotherm models were used to fit the experimental data. The experimental data of the adsorption equilibrium from Cu(II) solution correlates well with the Langmuir isotherm equation.

1. Introduction

Chitosan is a linear polysaccharide composed of randomly distributed β-(1 → 4) linked D-glucosamine (deacetylation units) and N-acetyl D-glucosamine (acetylated units) and is represented as homopolymer (Fares & Al-Ta'ani, 2003; Radhakumary, Nair, Matthew, & Nair, 2005; Shaoyun et al., 2004; Tatjana et al., 2007). The outstanding chemical, biological and pharmaceutical applications of chitosan have attracted attention to the potential utility of chitosan-grafted polymers in different areas such as drug delivery system (Takahashi, Takayama, Machida, & Nagai, 1990) and hydrogel formation (Kweon & Kang, 1999). Industrial revolution has accelerated the release of pollutants into the environment and heavy metals are among the most important pollutants in our environment. Removal of heavy metals from water is important to protect public health, because of their toxic effect to the human being and other animals and plants in the environments (Bayrammoglu, Denizli, Sektas, & Arica, 2002; Gupta, 1998; Li & Bai, 2005; Nagah, Endud, & Mayanar, 2002; Zalloum, Al-Qadah, & Mubarak, 2009). In this work we report the modification of chitosan via chemical grafted of acrylamide monomer and study the Effect of polymerization variables (monomer, initiator and temperature) on grafting percentage. Thermal analyses (TGA & DSC) and FTIR spectroscopy have been used for characterization of prepared polymers. Also the adsorption of Cu(II) onto prepared polymers has been investigated. Batch adsorption experiments were carried out as a function of contact time, temperature and polymer mass at pH = 7. The amount of metal ion uptake of the polymers was determined by using atomic absorption spectrophotometry.

2. Experimental

2.1. Materials

All reagents were commercially available and used without further purification. Solvents used in this work were distilled from the appropriate drying agent immediately prior to use.

2.2. Measurements

FTIR spectra of the polymers were recorded with (8400) (FTIR) Shimadzu spectrophotometer in the range 4000–500 cm^{-1}. Thermal analyses (TGA & DSC) of the polymers were carried out by using PerkinElmer thermal analysis. Atomic absorption data were obtained with the aid of a Phoenix-986 AA spectrophotometer. Samples were shaken and thermostated using BS-11thermostated shaker.

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* Corresponding author. Tel.: +964 7901 333 232.
E-mail address: a_jasim2006@yahoo.com (A.J.M. Al-Karawi).

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2.3. Synthetic procedures

2.3.1. Graft copolymerization of chitosan with acrylamide

Grafting reactions were carried out in 250 ml polymerization flasks by first dissolving an exact amount of chitosan in 2% acetic acid solution followed by the addition of a solution of acrylamide. Finally a solution of potassium persulfate (PPS) was added as initiator. The polymerization flask was closed and placed in a thermostated bath at desired temperature for 2 h. The reaction product was precipitated in acetone. The precipitated was filtered off and then dried in vacuum to constant weight. The dried products were extracted with acetone–water (volume ratio = 40:60) mixture for 24 h to remove the homopolymer of acrylamide.

2.4. Adsorption studies

2.4.1. Sorption of copper(II) ion on the acrylamide grafted chitosan (AGC)

The copper(II) sorption characteristics of resins were investigated by the batch equilibrium method. 0.1 g of dry AGC was suspended in 15 ml of buffer solution pH = 7 (sodium acetate and acetic acid) for 1 h with continuous shaking to equilibrate. An amount of 15 ml of $CuCl_2$. $2H_2O$ aqueous solution (235 mg/L) was then added and the mixture was shaken at 30 °C for specific period of time. The samples were filtered off and the amount of Cu(II) ions remaining in solution was determined by atomic absorption spectrophotometry (AAS) at $\lambda = 324.7$ nm, using standard solution for calibrations. The effect of polymer mass on the adsorption of Cu(II) ion was also studied by using different masses of AGC polymers (0.2, 0.3 and 0.4 g) at 30 °C, for specific period of time. In order to know the effect of temperature on the adsorption of Cu(II) ion, and so to obtain the maximum percentage of Cu(II) uptake, all the above experiments have been repeated again at different temperatures (40 and 50 °C).

3. Result and discussions

3.1. Synthesis of AGC

A graft copolymer is a macromolecular chain with one or more species of block connected to the main chain as side chain(s) (Zohuriaan-Mehr, 2005). Chitosan was chemically modified by grafting with acrylamide in a homogenous aqueous phase by using potassium persulfate (PPS) as intiator (Scheme 1).

3.2. Effect of polymerization variables on grafting percentage of AGC

3.2.1. Monomer concentration

The starting point of this work was to study the effect of monomer concentration on the grafting of acrylamide (AA) onto Chitosan. The percentage of grafting was calculated as follows:

$$PG = \frac{W_P}{W_A} \times 100$$

where PG is the percentage of grafting %, W_P is the weight of product; W_A is the weight of acrylamide.

It can be observed in Fig. 1 that the percentage of grafting (PG) was found to depend on the relative amount of monomer to chitosan, i.e. the PG grows sharply to a maximum by 7 g and then tends to decrease (slightly decreased). This could be attributed to the consumption of monomer to form homopolymer.

3.2.2. Initiator concentration

When the other factors are kept constant, the effect of PPS concentration on graft parameters is shown in Fig. 2. With increasing PPS concentration the values of PG increase. However, beyond the optimum PPS concentration of 4.5×10^{-3} mol/L, they are found to decrease. This can be explained that a further increase in PPS concentration accelerates the reaction of PPS and radicals, which terminates the chain propagation reaction, hence decreasing grafting parameters. This observation indicates that the optimal PPS concentration is 4.5×10^{-3} mol/L.

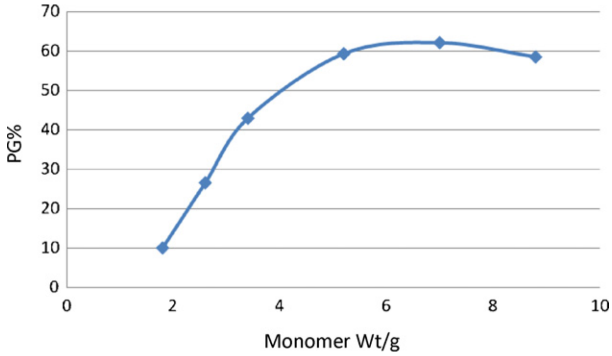


Fig. 1. The effect of monomer on the PG of AGC: chitosan = 1 g, [PPS] = 4.5×10^{-3} mol/L, t = 120 min, T = 60 °C.

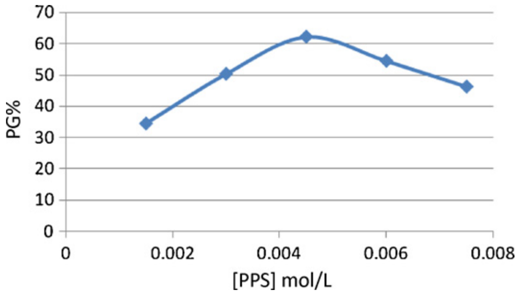


Fig. 2. Effect of PPS concentration on PG of AGC: chitosan = 1 g, monomer = 7 g, t = 120 min, and T = 60 °C.

3.2.3. Reaction temperature

The grafting reactions were carried out at different temperatures between 20 and 100 °C, keeping the other variables constant. As shown in Fig. 3, it is found that PG increase initially and then decrease to some extent with further increase in temperature. This is attributed to the fact that increasing the temperature favors the activation of macroradicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the backbone. However, a further increase in temperature decreases PG parameters, which can be ascribed both to the acceleration of termination reaction and to the increased chance of chain transfer reaction, accounting for the increase in the amount of homopolymer. This

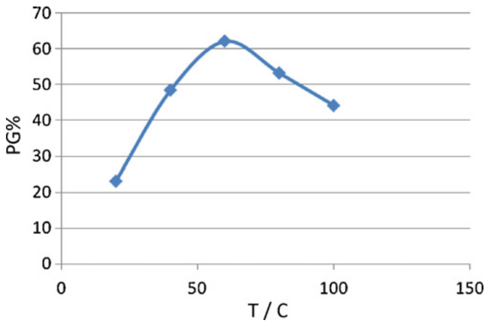
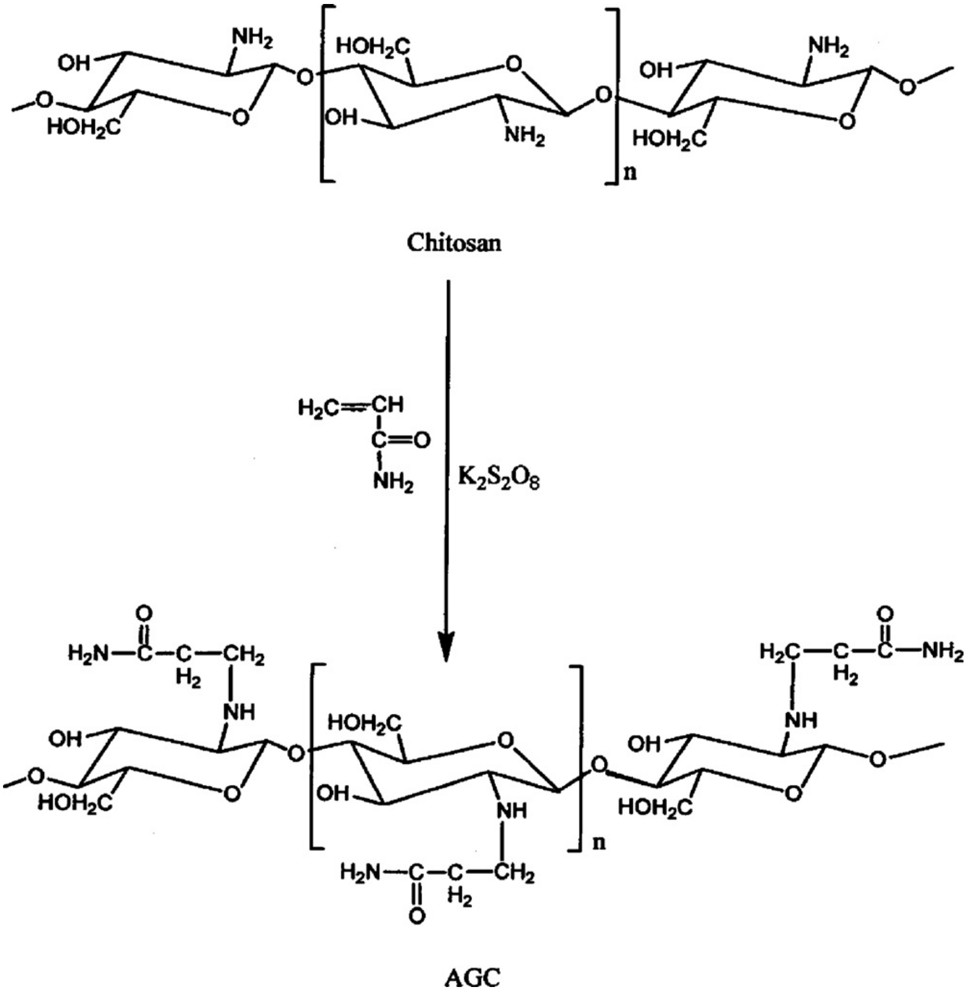


Fig. 3. Effect of temperature on PG of AGC: chitosan = 1 g, [PPS] = 4.5×10^{-3} mol/L, monomer = 7 g, t = 120 min.



Scheme 1. General route of AGC synthesis.

observation indicates that the optimal reaction temperature is 60 °C.

3.3. Characterization of AGC

FTIR spectroscopy and thermal analyses (TGA & DSC) were used for characterization of AGC polymer. The FTIR spectrum, of AGC, shows characteristic band at 1660 cm^{-1}, which could be assigned to the stretching vibration of amide carbonyl group in grafted chain. This band is located at 1674 cm $^{-1}$ in the spectrum of acrylamide monomer. This shifting to lower frequency is may be due to inter and/or intra molecular interactions through hydrogen bonding. Naturally the insolubility of AGC in spite of containing a large number of amide groups is produced by the crosslinking (Pedram, Retuert, & Quijada, 2000). From the literatures (Mohy, Soliman, Hashem, & Tamer, 2008; Yinghai, Zhenghao, Yanzhe, & Kuilin, 2002), the TGA of pure chitosan shows a weight loss in two stages. The first stage ranges between 20 and 107 °C and shows about 13.08% loss in weight. This may be corresponding to the loss of adsorbed and bound water. The second stage of weight loss starts at 197 °C and that continues to 380 °C during which there was 40.55% of weight loss due to the degradation of chitosan. Whereas the TGA of the grafted product Fig. 4 is different from it. It is observed the latter has three stages of distinct weight loss between 80 and 500 °C. The first stage ranges between 80 and 200 °C with 9.50% of the adsorbed and bound water weight loss. The second stage of weight loss starts at 220 °C and that continues to 320 °C during which there was 22.12% of weight loss due to the degradation of ungrafted chitosan. There is 52.04% weight loss in the third stage from 350 to 500 °C that contributes to the decomposition of chitosan-g-PAA. So, it is evident that grafting acrylamide onto chitosan could enhance the stability of pure chitosan at higher temperature. Fig. 5 shows the DSC thermograms of pure chitosan (A) and AGC (B). The first endothermic peak in (A) at 102.2 °C is the glass transition temperature (T_g) of chitosan. However, the glass transition temperature of AGC has appeared at 87.8 °C (Fig. 5B). This may be explained that acrylamide grafting onto chitosan lowered the Tg of chitosan. The exothermic transition of chitosan is at 313.1 °C, which may correspond to the decomposition of the polysaccharide. Compared with 337.7 °C, which is the second exothermic transition temperature of AGC, it indicates that the degradability of chitosan has been improved through grafted acrylamide. The DSC thermogram of AGC also exhibited new endothermic peaks at 237.5 and 381.0 °C, which could be attributed to decomposition of graft moiety (acrylamide).

3.4. Rate of metal ion uptake as a function of contact time

The prepared polymers which have the highest PG were selected to study their ability for removing Cu(II) ion from water. The PG of AGC1, AGC2 and AGC3 are 54.4, 59.3, and 62.12, respectively. The rate of interaction of Cu(II) ions with polymers (AGC1, AGC2 and AGC3) was investigated by a batch equilibration technique as a function of contact time at pH = 7. Fig. 6 shows a typical dependence on metal ion uptake on contact time for all polymers (AGC1, AGC2

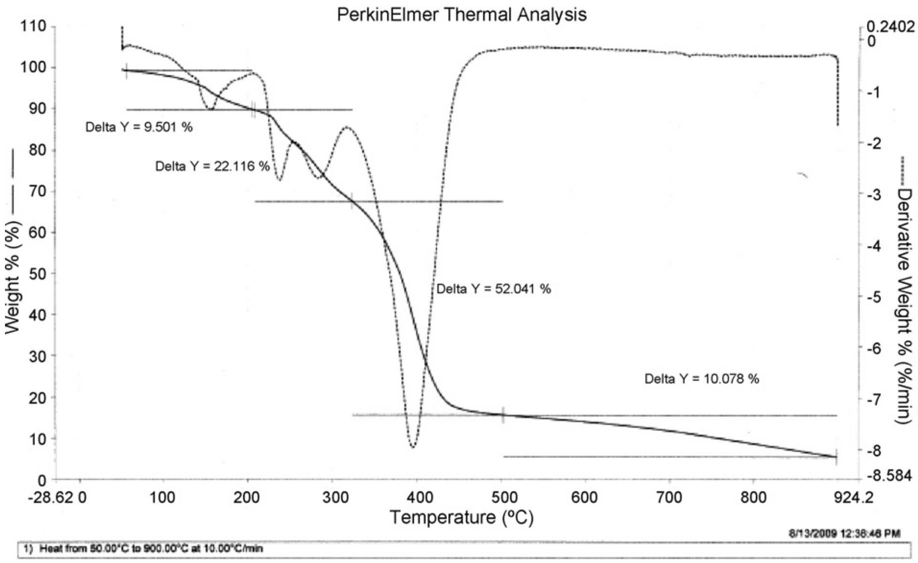


Fig. 4. Thermographmetric analysis TG and DTG of AGC.

and AGC3). Results indicate that a fast rate of equilibration, about 31–42% of metal ion uptake were achieved after 6 h and reaches a steady state after 12–18 h. Moreover AGC3 polymer has a highest uptake capacity of Cu(II) ion, while AGC1 has the lowest uptake capacity. This may be depends on the percentage of grafting of acrylamide onto chitosan. The increasing of grafting percentage of Chitosan-g-PAA leads to increase the functional groups in the chain of backbone structure and consequently increase the uptake capacity of Cu(II) ions.

3.4.1. *The effect of polymer mass on the adsorption of Cu(II) ion*

Fig. 7 shows that the percentage of Cu(II) ion adsorption increases with the increasing of polymer mass. This could be explained by the increasing of polymers sites available for adsorption. This is the same for all polymers (AGC1, AGC2 and AGC3).

3.5. *Adsorption isotherms*

The most common sorption models used to fit the experimental data are the Langmuir and Freundlich isotherms (Tan, Hameed, & Ahmed, 2007). The Langmuir isotherms model assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturated the adsorbent. The linear form of Langmuir model is given as:

$$\frac{C_e}{Q_e} = \frac{1}{b\,Q_0} + \frac{1}{Q_0}C_e \tag{1}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), Q_0 is Langmuir constant related to adsorption capacity and b is a constant related to the affinity between the adsorbent and the adsorbate. The values of Q_0 and b could be determined by plotting C_e/Q_e vs. C_e. Q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at equilibrium. The value of Q_e can calculated by using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 is the initial concentration of adsorbate (mg/L), V is the volume of solution (L), W is the mass of dry resin used (g). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (Weber & Chakravorti, 1974) which is defined as follows:

$$R_L = \frac{1}{1 + b\,C_0} \tag{3}$$

The value of (R_L) indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The widely used empirical Freundlich model is the most important multi-site adsorption isotherm for heterogeneous

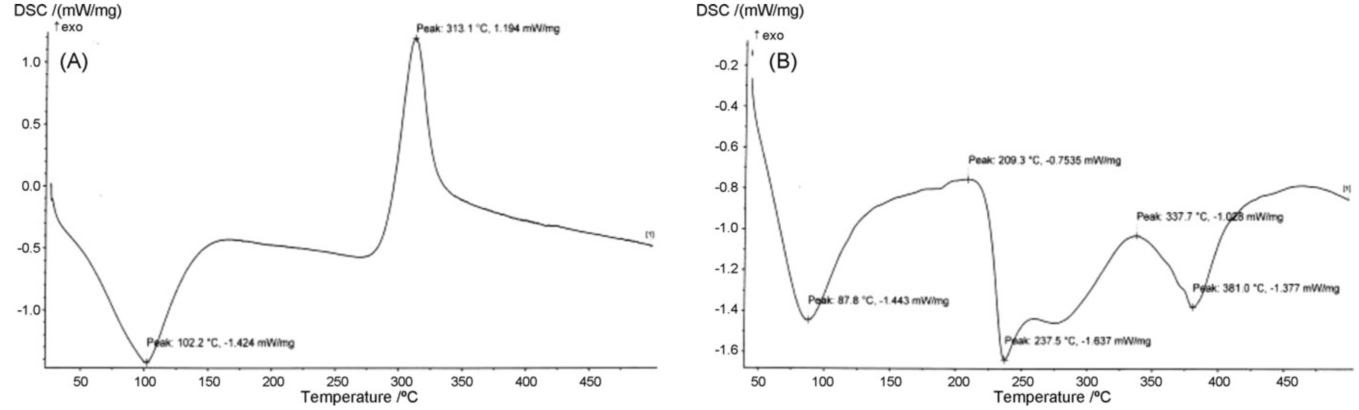


Fig. 5. DSC thermograms of (A) chitosan (B) AGC.

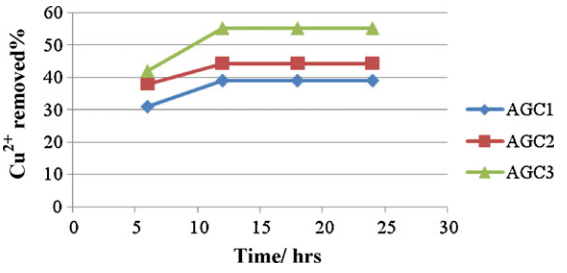


Fig. 6. Cu(II) ion uptake by AGC1, AGC2, AGC3 polymers as a function of contact time.

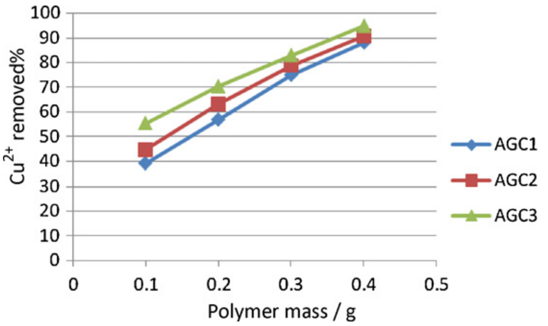


Fig. 7. Effect of polymer mass on Cu(II) ions removed % by polymers.

surfaces. It assumes an initial surface adsorption followed by the condensation effect resulting from extremely strong solute–solute interaction. The linear form of Freundlich model is as follows:

$$\text{Log}\ \ Q_e = \text{Log}\ \ K_F + \left(\frac{1}{n}\right)\ \text{Log}\ \ C_e \tag{4}$$

where K_F is Freundlich isotherm constant and correlated to maximum adsorption capacity. n is a Freundlich isotherm exponent constant which gives an indication of how favorable the adsorption process is (Hosseini, Mertens, Gorbani, & Arshadi, 2003). The values of K_F and n could be obtained by plotting Log Q_e vs. Log C_e. The significance of the adsorption isotherms is that they show how the adsorbate molecules are distributed between the solution and the adsorbent at the equilibrium conditions and the effect of equilibrium concentration on the loading capacity of the polymer at different temperatures. Fig. 8 shows the adsorption of Cu(II) ions using AGC 1 at three different temperatures (30, 40 and 50 °C). Results show that for the same equilibrium concentration, the loading capacity of the adsorbent increases with the increasing of temperature. This result confirms the endothermic nature of the adsorption of Cu(II) ions onto AGC polymer. Langmuir and Freundlich isotherm models were used to fit the experimental data, Figs. 9 and 10, respectively. The figures indicate that the Langmuir isotherm model gives the best fit of the experimental data compared to Freundlich isotherm model. The results demonstrate that the adsorption of Cu(II) ions by AGC is characterized by monolayer coverage of the Cu(II) ions on the adsorbent outer surface. In addition the adsorption process has a homogenous nature or equal activation energy for each adsorbed molecule. Furthermore, the values of separation factor R_L are in the range of $(0 < R_L < 1)$, this indicates that the adsorption of Cu(II) ions on the polymers particles is favorable (Fig. 11).

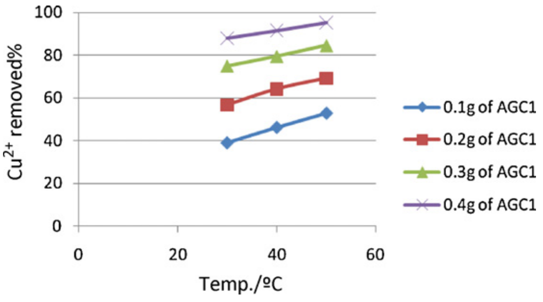


Fig. 8. Effect of temperature on Cu(II) ions removed % by AGC1 polymer.

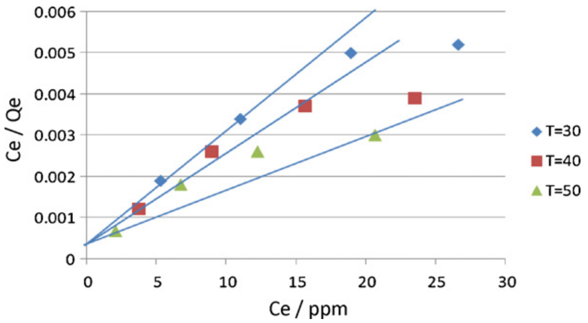


Fig. 9. Linearized Langmuir for Cu(II) ions adsorption by AGC1 polymer at different temperature.

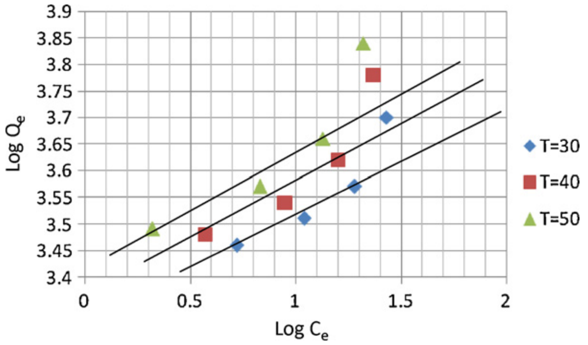


Fig. 10. Linearized Freundlich for Cu(II) ions adsorption by AGC1 polymer at different temperature.

The thermodynamic parameters (the standard free energy ΔG°, the standard enthalpy ΔH° and the standard entropy ΔS°) for the adsorption process were calculated using the following equations (Ho & Mckay, 1998):

$$\ln\ \ K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_d is the distribution coefficient

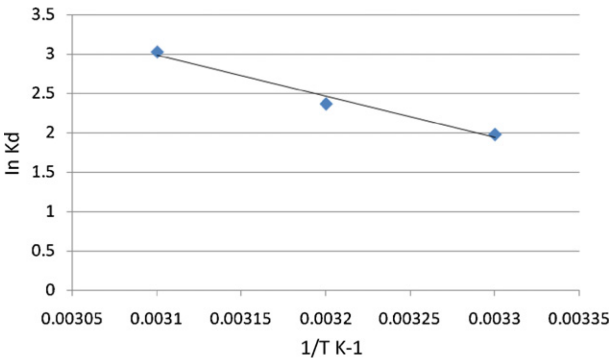


Fig. 11. Variation of thermodynamic parameters with temperature for the adsorption of Cu(II) ions on AGC1 polymer.

which could be calculated as shown below:

$$K_d = \frac{C_{Ae}}{C_e} \tag{6}$$

where C_{Ae} (mg/L) is the amount adsorbed on the resin at equilibrium and C_e (mg/L) is the equilibrium concentration. The values of ΔH° and ΔS° were calculated from the slop and intercept respectively of the plot between $\ln K_d$ vs. $1/T$. ΔG° was calculated using the relationship below:

$$\Delta G^\circ = -RT \quad \ln \quad K_d \tag{7}$$

The values of ΔH° and ΔS° of AGC1 polymer are 51.47 kJ/mol and 27.03 J/mol K respectively. The positive values of standard entropy of activation ΔS° indicate the affinity of acrylamide grafted chitosan for adsorbates such as Cu(II) ions as a result of the increased randomness at the interface between the solid liquid phases. The values of ΔG° are −4987 J/mol at 303 K, −6167 J/mol at 313 K and −8136 J/mol at 323 K. It can be seen from results that the value of ΔG° decreases as the temperatures increases. This indicates the spontaneous nature and feasibility of the process (Zalloum et al., 2009).

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