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

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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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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.

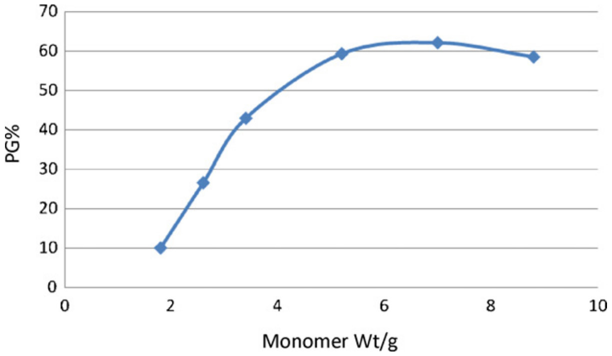

Fig. 1. The effect of monomer on the PG of AGC: chitosan = 1 g, [PPS] = 4.5×10^{-3} mol/L, *t* = 120 min, *T* = 60 °C.

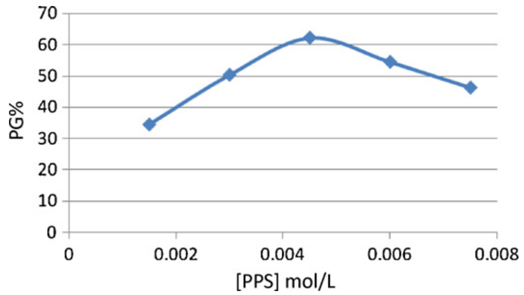

Fig. 2. Effect of PPS concentration on PG of AGC: chitosan = 1 g, monomer = 7 g, *t* = 120 min, and *T* = 60 °C.

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

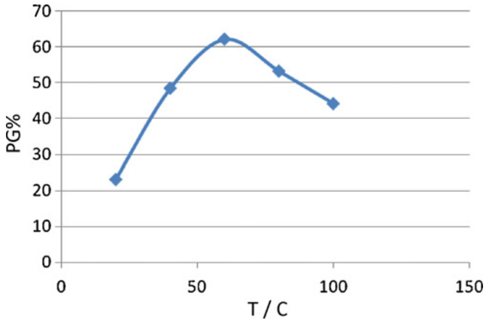

Fig. 3. Effect of temperature on PG of AGC: chitosan = 1 g, [PPS] = 4.5×10^{-3} mol/L, monomer = 7 g, *t* = 120 min.