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Cu (II), Mn (II) and Zn (II) Adsorption with Modified Grafted Cellulose from Aqueous Solution

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Abstract

Cellulose powder where modified by grafting with acrylamide to improve the swelling characters. The conditions of grafting such as monomer concentration, initiator ratio, time of grafting and grafting temperature were evaluated. The grafting efficiency, The swelling characters as water retention values and sodium binding capacity were determined and nitrogen content were also evaluated for grafting cellulose powder The structure of these compounds was investigated using FTIR. The optimum condition of grafting ratio of cellulose powder to acrylamide monomer1:1g/g, ratio of cellulose powder to initiator 1:0.3g/g, grafting time three hours and grafting temperature was 80˚C.

The obtained graft copolymers were used as adsorbents for the removal of Zn, Mn and Cu ions in an aqueous solution each one alone. The effect of pH value, contact time, initial metal ion concentration and polymer dosage on metal ions uptake were reported.

Keywords: Modified Grafted Cellulose, Adsorption, Cu (II), Mn (II), Zn (II)

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1. Introduction

Numerous studies have focused on the isolation of cellulose nanofibers (CNFs) from non-wood and bioresidue sources including , bagasse [1], rice straw [2], coconut husks [3] are some examples of non-wood sources for preparing cellulose nanocrystals (CNC).

CNFs extracted by a mechanical disintegration treatment of wood cells were first obtained [4]. This new type of cellulosic materials was named micro fibrillated cellulose (MFC). They worked with a Gaulin homogenizer and used a pressure of 8,000 psi. Cooling was used to maintain a product temperature in the range 70–80 ^{0} during the homogenization treatment. According to Bhatnagar and Sain [5] and Chakraborty et al. [6], the majority of cellulosic materials can generally be taken as a source to be used in producing CNF, as they had successfully isolated the cellulosic nanofibers from wood using a combination of chemomechanical treatments.

Besides being the cell-wall component of plants, cellulose fibers are also secreted extracellularly by some bacterial species such as Acetobacter, Agrobacterium, Alcaligenes, Pseudomonas, Rhizobium or Sarcina [7]. Bacterial cellulose is produced by cultivation in a culture medium. The most efficient producer of bacterial cellulose (BC) is Acetobacterxylinum (or Glucon acetbacterxylinus),a gram-negative strain of acetic acid producing bacteria [8].

Comparing plants and bacterial cellulose, BC network structure is secreted as a ribbon-shaped fibril less than 100 nm wide, which is composed of a bundle of much finer nanofibers, 2–4 nm in diameter [9]. To be more specific, the cellulose secreted from bacteria offers certain exceptional properties and produces a very fine and pure fiber network structure as well as higher mechanical strength [9].

Cellulose formed of repeating units (called cellobiose) resulting from connections of two anhydro-glucose rings joined via a β-1,4 glycosidic linkage, this linear homopolymer, depicted on Figure 1, is characterized by its extended and rather stiff rod like conformation, its significant hydrophilicity and its functional pendant groups. Cellulose –vinyl monomers grafted copolymers is an important tool for modification of swelling properties of cellulose [10], grafted cellulose copolymers have special importance in comparison to simple grafting of individual monomers [11].

The secondary and the primary hydroxyl groups of the anhydro-glucose rings are the basis for extensive intra- and intermolecular hydrogen bonding, allowing the formation of highly ordered three-dimensional crystal structures; therefore making cellulose a semi-rigid polymer which is not soluble neither in water nor in traditional organic solvents; additionally, no melting point.

Those multiple hydrogen bonds hold the chains firmly together side by side and form elementary microfibrils that have high tensile strength and confer an important rigidity to the cell walls. Depending on their origin, these microfibrils are generally constituted of fibrous structures, formed during the cellulose biosynthesis [12] also containing crystalline and noncrystalline domains located along their main axis.

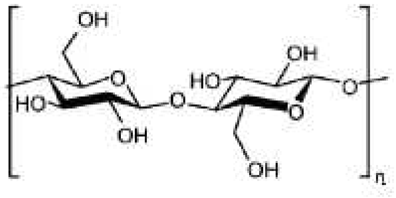

Fig (1): Structure of cellulose

The main aim of this study was to modify the structure of cellulose powder by addition a new groups in the cellulose backbone through grafting process. Grafting copolymer employed in this work was prepared cellulose powder-acrylamide grafting in presence of persulphate as initiator. The conditions of grafting such as monomer concentration, initiator ratio, and grafting temperature were evaluated.

The produced copolymers was used for removal of (Cu^{2+}, Mn^{2+} and Zn^{2+}) from aqueous solutions by adsorption. The effects of pH value, contact time, initial metal ion concentration and polymer dosage were reported.

2. Experiments and Materials

2.1. Materials

Cellulose powder, acrylamide, potassium per sulfate PPS, sodium hydroxide, salts of Cu, Mn, Zn ($CuSO_4.5H_2O$, $MnSO_4$ and $ZnSO_4.7H_2O$) obtained from EL-Naser Company, Egypt.

2.2. Grafting of acrylamide onto cellulose powder

Graft copolymerization of acrylamide onto cellulose powder was carried out with $K_2S_2O_8$ (PPS) as an initiator under vacuum. In a nicked 250 mL flask,$K_2S_2O_8$ is added to cellulose powder with a definite volume of distilled water then make activation in water bath at 100^{o}c for 15 minutes , leave it till cool then added aqueous solution of acrylamide ,put it in a water bath for a time with a shaking from time to another after close it .The reaction product was precipitated in acetone and dry it at 50^{0}c to obtain constant weight . To remove homopolymer of acrylamide coated polymer with distilled water for 24 hours then dry it.

2.3. Determination of metal uptake (Adsorption experiments)

Sorption was carried out by stirring 0.05 g of grafted cellulose as adsorbent in 25 ml solution containing different concentrations (5,10,15and 20) ppm ions of (Cu^{+2}, Mn^{2+}, and Zn^{2+}) at 2 hr. Then after filtration, the remaining metal ions in the filtrate were determined using Atomic Absorption (AA) spectrophotometer.

3. Results and Discussions

3.1. Synthesis of cellulose-acrylamide copolymers

Cellulose powder was chemically modified by grafting with acrylamide in a homogenous aqueous phase by using potassium persulfate (PPS) as initiator.

3.2. Effect of polymerization condition on grafting parameters

The grafting parameters (G.E, G, P, WRV, N_2 Content) varied by changing grafting process conditions as reaction temperature , persulphate (PPS) concentration, and monomer to cellulose ratio. So these factors were studied to reach the optimum conditions for grafting process.

3.2.1. Reaction Temperature

The grafting reaction was performed at different temperatures ranging from 50^{o}c to 80^{o}c, keeping the other variables and reagents constant.

Table (1): Effect of grafting reaction temperature on the grafting parameters

	Tempreature °C	P %	G %	G.E %	WRV	NaOH	N_2 %
1	50	122.5	15.48	12.64	619.9	820	3.06
2	60	136.5	57.33	42.00	625.0	870	5.18
3	70	137.0	74.50	54.30	660.0	930	7.30
4	80	188.5	113.1	60.00	673.0	995	7.80

Condition: 1:25 Liq. ratio, 1:1 cellulose/acrylamide, 0.3g pps/g cellulose, 3 hr, under vacuum.

Table (1) and Figure (1) show the effect of reaction temperature on different grafting parameters. From Table (1) and Figure (2) it is clear that the grafting parameter P% , G% , G.E% increase by increasing temperature from 50 °C to 80 °C , this can be attributed to that the increase in the mobility of chemicals and consequently it is causes an increase in the formation of the free radicals which increase of grafting process. Also from Table (1) and Figure (2) it is clear that the water retention value (WRV) of the produced grafted cellulose increase by increasing temperature due to the increase of grafting yield(increase of amide groups) which can be confirmed by increasing the nitrogen content of the grafted samples [13].

3.2.2 .Monomer concentration.

Table (2) shows the effect of different concentration of acrylamide on the grafting of cellulose powder. It is clear from Table (2) and Figure (3) that P % increases from 145.5%to 253.5% by increasing monomer to cellulose powder ration from 1:1 to 1:2, also the grafting percent increases from 76.00%to 136.85%.The increase of P %and G% can be associated with the high availability of acrylamide in the proximity of cellulose macromolecule with increasing acrylamide concentration.

Grafting efficiency G.E% decreases by increasing acrylamide concentration over the monomer to cellulose powder ration 1:1.5. The continous decrease in G.E% Indicate the more homopolymer occurs, but the monomer concentration influences more the grafting reaction.

It is seems that WRV, NaOH and nitrogen content increases by increase the acrylamide concentration, and monomer ratio 1:1.5 is an ideal ratio.

Table (2): Effect of monomer concentration on grafting parameters.

	Monomer (g)	P %	G %	G.E %	WRV	NaOH	N_2 %
1	2.0	145.5	76.00	52.26	547.3	714.6	7.80
2	2.5	158.0	73.95	58.00	665.9	852.0	8.03
3	3.0	188.5	113.1	60.00	673.0	995.0	9.04
4	3.5	240.5	134.65	56.00	636.3	775.0	8.00
5	4.0	253.5	136.85	54.00	566.3	730.3	7.90

Condition: 1:25 Liq ratio, 2g cellulose, 0.3g pps/g cellulose, 3hrs under vacuum at 80 °C.

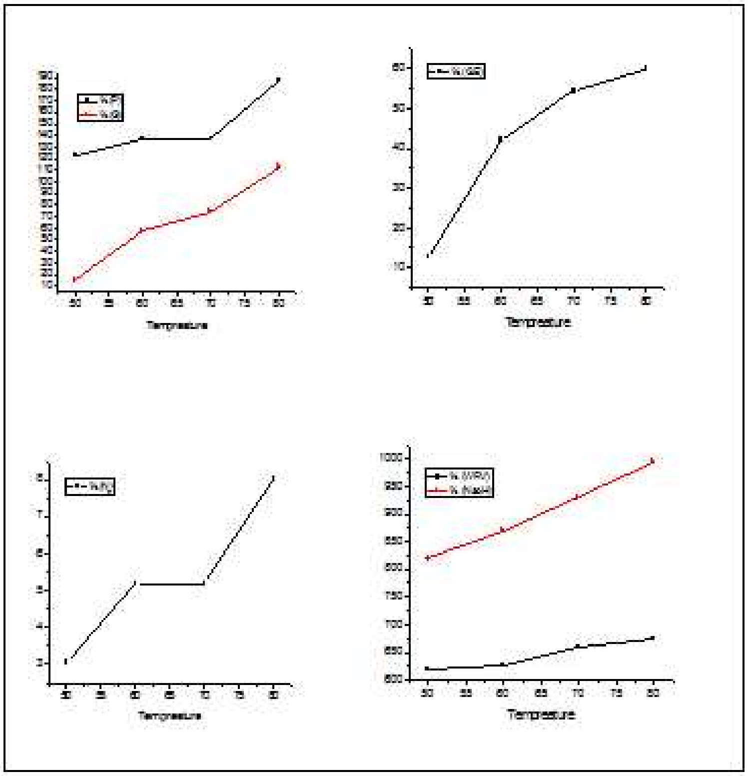

Fig (2): Effect of temperature on grafting parameter, swelling properties, and N_2 content.

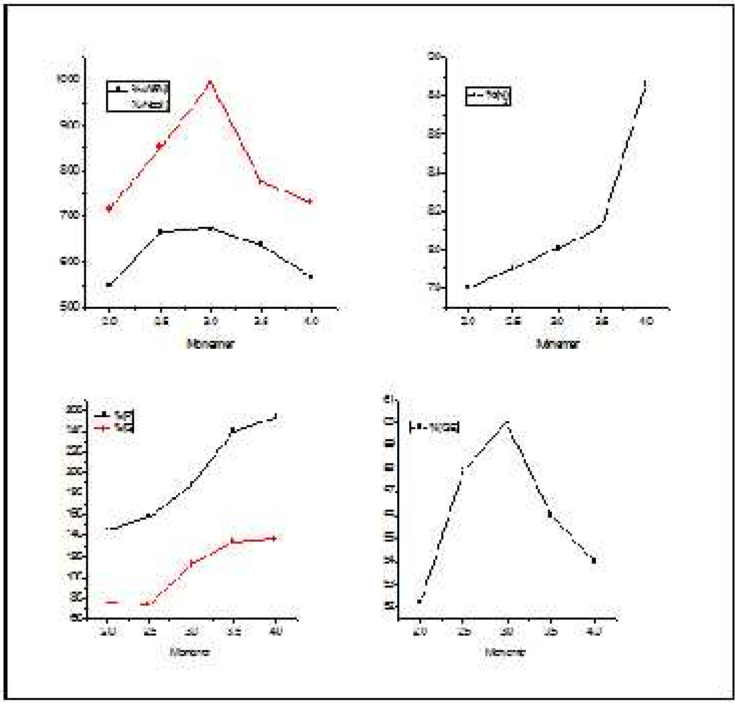

Fig (3): Effect of monomer concentration on grafting parameter, swelling properties and N_2 content.

3.2.3. Initiator Concentration

Potassium persulphate was used as initiator for grafting process with the concentration of 0.2 to 1.2 g/g cellulose. The effects of increasing the initiator concentration on the grafting factors were illustrated in Table (3) and Figure (4).

Table (3): Effect of initiator concentration on the grafting parameters

	pps	P %	G %	G.E %	WRV	NaOH	N2 %
1	0.2	104.0	-ve	-ve	-ve	-ve	-ve
2	0.4	123.0	53.50	43.49	368.0	849	7.42
3	0.6	188.5	113.1	60.00	673.0	995	7.80
4	0.8	138.5	74.50	53.79	567.8	890	8.40
5	1.0	156.0	81.00	51.92	466.0	881	8.26
6	1.2	173.0	85.00	49.10	464.0	863	7.07

Condition: 1:25 Liq. ratio, 2g cellulose, 2g acrylamide, 3hr, under vacuum at 80 °C.

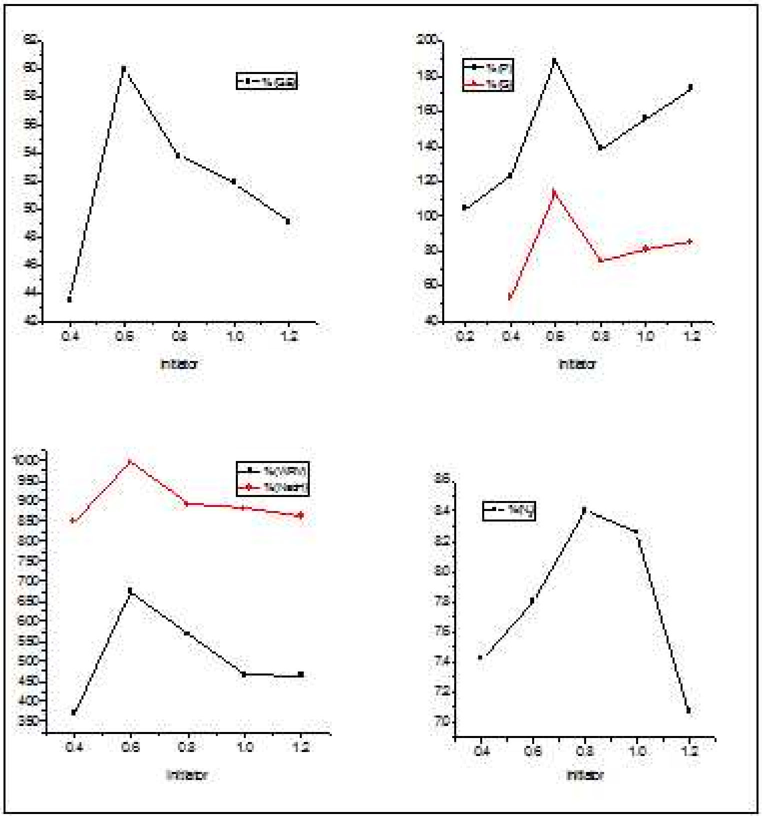

Fig (4): Effect of initiator concentration on grafting parameter, swelling properties and N_2 content.

It's clear that increasing of persulphate concentration from 0.1 up to 0.3 g/g cellulose causes a significant increase in the grafting parameters G.E%, G%, P %, WRV and Nitrogen content, this is because the presence of free radicals on cellulose molecules enhances the grafting process. Further increase in initiator concentration causes a decrease in the G.E% value that may be due to the consumption of accessible sites on cellulose [7].

On the other hand, the grafting efficiency decreases by increase of the PPS concentration although the p% increase this means that the increase in the PPS concentration increase the homopolymer formation rapidly that finally decrease the G.E% value.

3.2.4. Infrared spectra of the pure cellulose and grafted samples.

FT- IR technique was used to identify the functional groups present in cellulose powder and grafted cellulose-acryl amide copolymer, the spectra of ungrafted cellulose(fig.5, a)showed bands at 1157.94 cm^{-1} ,1080.39 cm^{-1},which were attributed to C-O band stretching. Additional characteristic adsorption band appeared at 560.25 cm^{-1}, which were due to anhyroglucose ring stretching vibrations. Abroad band due to hydrogen bonded –OH groups appeared at 3424.81 cm^{-1}, and a 2878.91 cm^{-1}, for C-H stretches and CH_2 symmetric bending respectively. A small sharp peak at 896.17 cm^{-1}, corresponded to the glucosidic C-H deformation with ring vibration contributions and OH bending.

IR spectrum of grafted cellulose (Fig.5,b, c and d) with acrylamide exhibited the new absorption band at 1649.15 cm^{-1} which attributed to carbonyl group (C=O)of the amide group, also the OH band and C-O-C band intensities at 3423.81 cm^{-1}, 1080.39 cm^{-1}, respectively decrease after grafting this is because of the degradation of the glucose units.

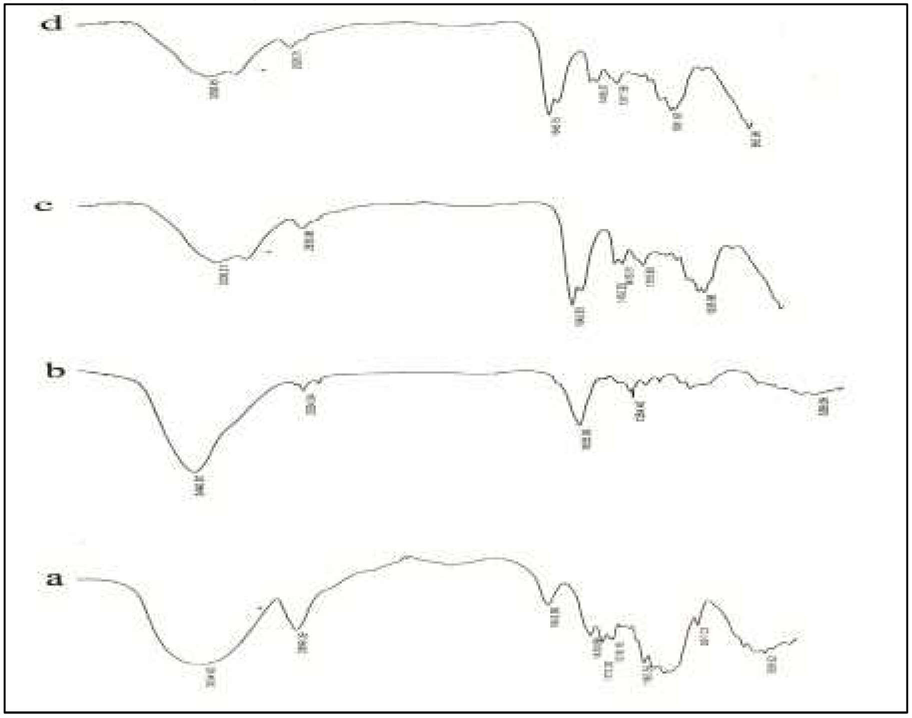

Fig (5): FTIR spectra of cellulose powder (a) and grafted cellulose (b,c,d,) with acrylamide.

3.3. Analytical Applications

The ability of the resulting polymer to remove Cu^{2+}, Mn^{2+} and Zn^{2+} ions from aqueous media was examined and optimized by considering the following parameters:

3.3.1. pH

The pH of the aqueous solution of metal ion is an important operational parameter in the adsorption process as it affects the solubility of the metal ion, concentration of the counter ions on the functional groups of the adsorbent as well as the degree of ionization of the adsorbate during reaction [14]. The effect of pH on Cu^{2+}, Mn^{2+} and Zn^{2+} adsorption was investigated in the pH range 2.5 to 6.2 to prevent the precipitation of metal ions as hydroxides. As shown in Fig.6, the uptake of all metal ions increases with increasing pH.This behavior is expected [15-17] and may be due to the electrostatic attraction between metal ions and the functional groups on the adsorbent surface which increases with decrease of H^+ ions as the solution acidity decreased. The low removal values found at acidic solutions may be attributed to the competition between H^+ and metal ions for the same adsorbing sites [18].

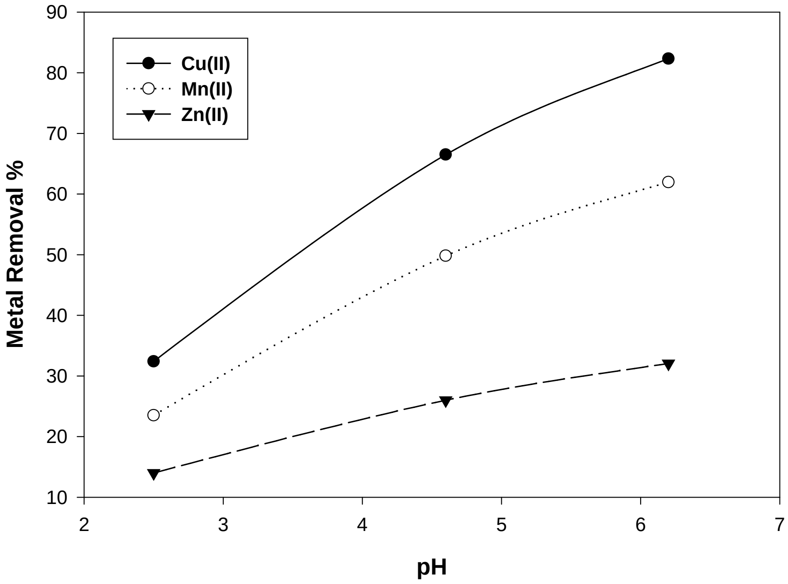

Fig (6): Effect of solution pH on the removal efficiency of Cu^{2+}, Mn^{2+} and Zn^{2+} by grafted polymer.

3.3.2. Contact time

The effect of contact time was depicted in Figure (7). As can be seen from the figure, the adsorption increased with increasing contact time. The rapid adsorption at the initial stage is probably due to the abundant availability of active sites on the surface of grafted polymer. With a gradual decrease of these sites, the adsorption capacity of metal ions becomes less and the equilibrium was achieved within 120 min, so an equilibration period of 120 min was selected for all further experiments.

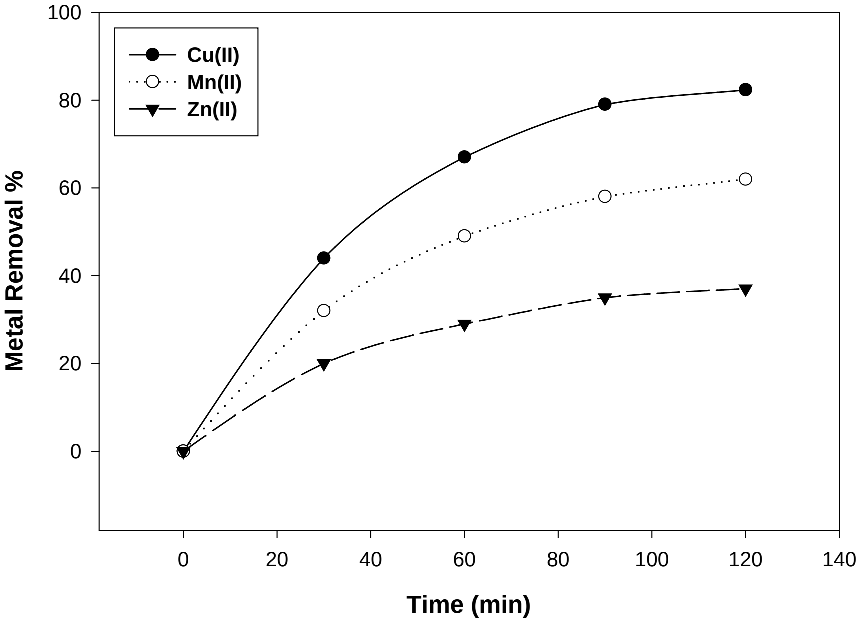

Fig (7): Effect of contact time on removal efficiency of Cu^{2+}, Mn^{2+} and Zn^{2+} by grafted polymer.

3.3.3. Initial metal ion concentration

The initial concentration of metal ions is an important factor for effective adsorption process. The removal percent of metal ions Cu^{2+}, Mn^{2+} and Zn^{2+} at different metal ion concentration (5 - 20 mg/L) were performed by keeping all other parameters constant. As shown in Fig. 8, the removal percent decreased for all metal ions by increasing the initial metal concentration.

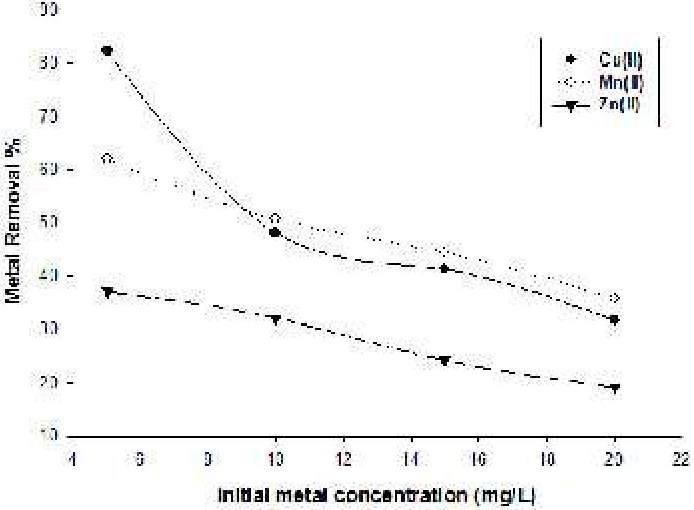

Fig (8): Effect of initial metal concentration on removal efficiency of Cu^{2+}, Mn^{2+} and Zn^{2+} by grafted polymer.

3.3.4. Polymer dosage

The effect of adsorbent dosage on Cu^{2+}, Mn^{2+} and Zn^{2+} adsorption was investigated by changing the adsorbent dosage from 0.1to 0.4 g/L. The results(Fig.9)show that the removal capacity decreased from 6.97 to 0.94 mg/g for Cu^{2+}, from 7.59 to 1.42 mg/g for Mn^{2+} and from 4.65 to 0.37 mg/g for Zn^{2+}, when polymer dose increased from 0.1 to 0.4mg/L, respectively. This was due to increased adsorbent surface and availability of more adsorption sites with a fixed amount of metal ions. This decrease in adsorption capacity may be attributed to overlapping or aggregation of adsorption sites causing a decrease in total adsorbent surface area available to the metal ion and an increase in diffusion path length [19].

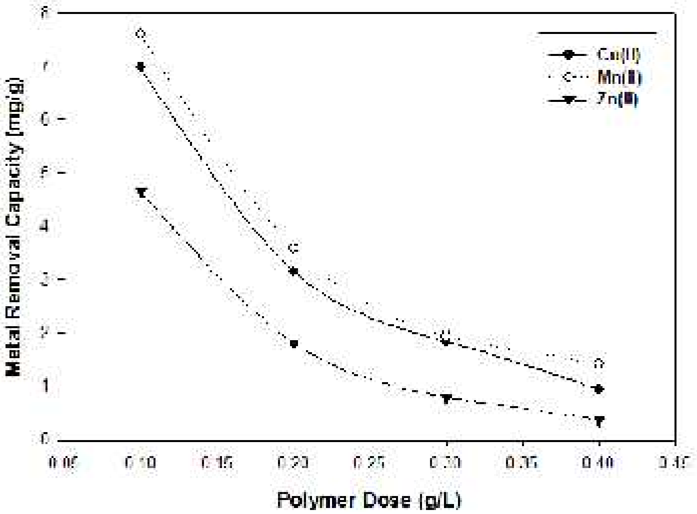

Fig (9): Effect of polymer dosage on removal efficiency of Cu^{2+}, Mn^{2+} and Zn^{2+} by grafted polymer.

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