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RESEARCH ARTICLE

Removal of heavy metals from waste water using amidoximated acrylonitrile grafted corn husks cellulose as an ion exchanger

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Abstract

The graft copolymerization of acrylonitrile (AN) onto the bleached dissolving pulp (yield from corn husks) under the initiation of potassium persulfate (KPS) was investigated. The relationships between the grafting efficiency percent and KPS concentration, monomer to pulp ratio, reaction time, as well as reaction temperature were established. The grafted cellulose has been characterized by FTIR and swelling studies. Sorption of Ni ions by grafted cellulose was investigated. The effect of Amidoximation of the grafted cellulose using hydroxylamine to convert nitrile group to amidoxime then its swelling properties and metal ion sorption were investigated. Amidoximation increases the sorption affinity of the grafted cellulose towards water and metal ions.

INTRODUCTION

Rapid human population and industrialization growth has increased environmental problems such as water, air and land pollution. Heavy metals can be considered as some of the most problematic pollutants due to their non-biodegradable nature. In recent years, water pollution by heavy metals has posed one of the most severe environmental problems. For example, cadmium, lead, cobalt, copper, mercury, chromium, nickel, selenium and zinc are carcinogenic to human beings if consumed in high quantities. Because of the high solubility and bioavailability of heavy metals in aquatic environments, they can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders such as developmental retardation, various cancers, kidney damage, autoimmunity, and in extreme cases, even death (1-3).The conventional methods for removal of hazardous metal ions from wastewater such as precipitation, ion exchange, activated carbon adsorption, and electrolytic method have limitations like high cost, low removal rate or difficulty for regeneration, and reuse. Therefore, many researches focused on the study of alternative low-cost-effective adsorbents (4).

The adsorption of metal ions can be achieved by using polymer materials containing specific functional groups, for example, amino, carboxyl, phosphoric, tetrazine and amidoxime, etc. To form strong complexes with metal ions via the coordination reaction. The adsorption of metals onto these materials mainly depends on the functional groups on the adsorbent surfaces. Amidoxime group, in particular, has exhibited superior adsorption ability (5). The synthesized amidoximated polyacrylonitrile chelating beads were evaluated, for their ability to adsorb uranium from aqueous solution, at different temperatures and pH values (6).

Cellulose can be modified by the introduction of chelating metal-binding functional groups in the cellulose backbone for the adsorption of toxic metal ions in various media. The chelating functional groups can be attached to the primary or secondary hydroxyl groups of cellulose through a variety of chemical reactions, including esterification, etherification, halogenation, and oxidation. An alternative method is the grafting of desired monomers to the cellulose backbone by either the direct introduction of a metal-binding ligand or the subsequent functionalization of these grafted polymer chains with known chelating moieties Abdel-Halim, E. S., El-Rafie, M.

H. & Al-Deyab, S. S. (2011). Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles. Carbohydrate Polymers, 85, 692–697.

The graft copolymerization reactions can be initiated by free-radical or ionic chemical groups, Radical formation can occur on either the cellulose backbone or the monomer to be grafted; this induces homopolymerization of the monomer. Therefore, initiators creating radicals at various sites on the cellulose backbone are the choice for desired graft copolymerization (7).

An adsorbent including double amidoxime groups was prepared by graft copolymerization of glycidyl methacrylate (GMA) onto poly(ethyleneterepthalate) (PET) fibers using benzoyl peroxide (Bz_2O_2) as initiator in aqueous solution. Grafted PET fibers were modified with iminodiacetonitrile (IDAN) in ethanol. Afterwards, the nitrile groups were amidoximated by using hydroxylamine hydrochloride in methanol solution and the removal of Cr(VI) ions from aqueous solution onto amidoximated fibers was studied (8)

2. Experimental

2.1. Materials

Cornhusk was kindly provided from Sharkia, Egypt. It was first dried in sunlight and then cut into small pieces (2– 3 cm). The industrial waste water was obtained from the national company for maize products after the production of sorbitol from dextrose solution by reduction with hydrogen and Nickel contains about 1500 ppm. Ni and was used as sample for treatment.

2.2. Prehydrolysis

Cornhusks were prehydrolyzed to eliminate hemicelluloses that form an envelope around cellulose microfibrile. These hemicelluloses(sugars, sugar acids, and other polysaccharides of D.P ≈ 50-300) were eliminated by dilute acids where the raw material was refluxed with H_2SO_4 (6% related to the oven dry weight) and the liquid ratio is 1: 5 for six hours, washed and dried at 50^oC under vacuum till constant weight.

2.3 Pulping

Pulping was carried out using peracetic acid only (namely one stage pulping) or by using sodium hydroxide followed by peracetic acid (namely two stages pulping), as follows.

2.3.1 One stage pulping:

In a polyethylene bag the sample was mixed with peracetic acid (16% related to the O.D.W of the sample) with liquor ratio of 1:6 at 85^oC for two hours, washed with 80% A.A followed by distilled water till neutrality and dried at 50^oC under vacuum till constant weight (9,10).

2.3.2 Two stages pulping:

The sample was first treated with 10% NaOH (related to the O.D.W of the sample) liquor ratio of 1:3 at 90^oC for 1.5 hrs, washed with distilled water till neutrality. The sample was mixed with 16% peracetic acid, liquor ratio was 1:6 with acetic acid, in a bag. The bag was closed and immersed in water bath at 70^oC with continuous fluctuation for three hours, followed by filtration, washing with 80% A.A and distilled water till neutrality and dried at 50^oC under vacuum till constant weight (10, 11).

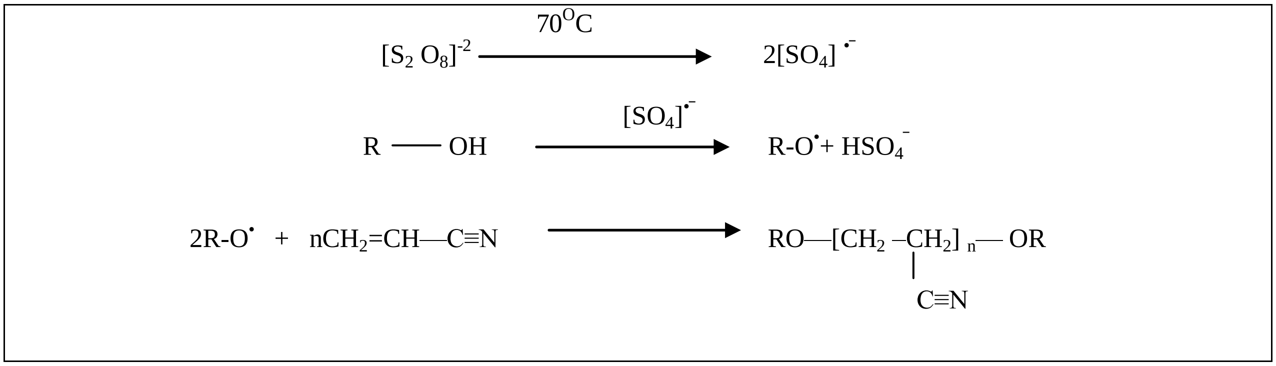
Peracetic acid (P.A.A) was prepared by reacting glacial acetic acid with 30 wt% hydrogen peroxide at room temperature for 48 hours. The volume ratio of acetic acid and 30 wt% hydrogen peroxide was selected as 1.5:1 (11). Sulfuric acid 1.5% (w/w) was added as a catalyst to form 16% P.A.A.

2.4. Bleaching

Bleaching process was carried out using alkaline hydrogen peroxide 20% water consistency. The bleaching solution contains 3% NaOH, 1% $MgSO_4$ and 2% H_2O_2 based on dry sample. This solution was mixed with the sample and placed in water at 70^{o}C for 1 hr with shaking and the sample was washed with distilled water till neutrality followed by drying at 50^{o}C under vacuum till constant weight (11).

2.5. Grafting

Graft copolymerization of acrylonitrile onto cornhusks was carried out with $K_2S_2O_8$ (KPS) as an initiator under vacuum. In a two nicked 250 mL flask, cornhusks cellulose (1 g) was soaked in 30 mL of degassed distilled water for 24 hrs. The sample was stirred with magnetic stirrer for 15 minutes under vacuum. A separating funnel was conducted to the reaction vessel to be used for chemical additions. The sample was placed in water bath at desired temperature. $K_2S_2O_8$ solution 10 ml (2gm/100ml) was added. After 15 minutes 3ml acrylonitrile was added and the reaction was continued with shaking from time to time. After the reaction complete 100 ml methanol was added followed by washing with methanolic solution (4:1) then filtration and drying at 50^{o}C under vacuum till constant weight. For the purpose of removing the homopolymer, the crude grafting product was purified with Soxhlet extraction method with dimethylformamide for 12 h, after that 2h with acetone also with Soxhlet extraction method to remove excess dimethylformamide, then filtration and drying at 50^{o}C under vacuum till constant weight.



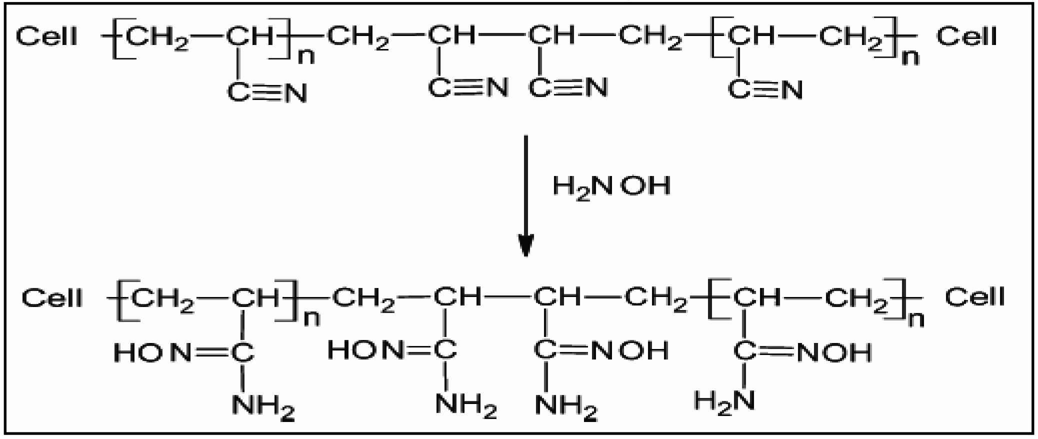
$$[S_2\,O_8]^{-2} \xrightarrow{70^{O}C} 2[SO_4]^{\bullet -}$$

$$R - OH \xrightarrow{[SO_4]^{\bullet -}} R\text{-}O^{\bullet} + HSO_4^{-}$$

$$2R\text{-}O^{\bullet} + nCH_2{=}CH{-}C{\equiv}N \longrightarrow RO{-}[CH_2 - \underset{C\equiv N}{\underset{|}{CH_2}}]_n{-}OR$$

2.6. Amidoximation of corn husks cellulose grafted-PAN

Exactly 20 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) was dissolved in 500 mL of methanolic solution (methanol/ water 4:1). The HCl of NH_2OH was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the reaction was adjusted to pH 10 by NaOH solution. A1-L, two-necked, round-bottomed flask was fitted with a stirrer, condenser, in thermostated water bath. Exactly 10 g of corn husks cellulose-graft-PAN was added to the flask with a hydroxylamine solution, and the reaction was maintained at 70^{o} C for 2 h. The hydroxylamine solution was decanted, and the polyamidoxime ligand was washed with a methanolic solution (4 methanol: 1 water). Then, the product was treated with 100 mL of methanolic solution of 0.1M HCl in (methanol : H_2O / 4:1) for about 15 minutes to convert the ligand into its hydrogen form. The ligand was washed several times with a methanolic solution (4:1) and dried at 50 C^{o} to a constant weight (12).



2.7. Metal ion uptake

The two pulp samples were grafted with acrylonitrile and amidoximated then a batch technique was used for the adsorption of Ni from its solutions with pH ranging from 3 to 8. Exactly 0.5 gm of each was soaked into 50 mL of the buffered metal solutions, whose pH was adjusted for the desired value. The samples were fixed in a temperature-controlled shaking water bath and the adsorption experiments were carried out at different temperatures for different time intervals in a closed vessel for the adsorption test. At the end of experiment samples were removed by filtration. To determine the amount of metal ions adsorbed onto the amidoximated grafted cellulose, the metal ion concentrations remaining in the solution were determined by atomic absorption spectrophotometer at 232 nm by standard calibration curve method (13). Initial concentration of Ni in the buffered solution was 1.5 gm/lit (1500 ppm).

3. Results and discussion

The raw material used in this work (corn husks) has the following specification: α-cellulose% 61.7, ash% 3.5, and lignin 9.0%. The chemical analyses of both bleached and unbleached two pulps A, B (one stage and two stages pulp) are listed in table (1). It is clear from table (1) that pulp B has higher α-cellulose, lower ash content and produced with lower yield. This is due to the use of NaOH which facilitates the entrance of peracetic acid between cellulose fibers, so a great amount of lignin was eliminated. Also in the two stages pulping decreasing the temperature of the oxidation stage (PAA stage) decreases the oxidative degradation of cellulose. All that decreases the degradation and increases the ratio of α-cellulose in pulp B than pulp A. Also the penetration of NaOH to the crystalline regions in cellulose fibers in pulp B decreases the crystallinity percent (increase amorphous percent) so the fibers become more available for chemical reactions as we will see later.

Table 1
Analysis of the bleached and unbleached corn husks two pulp samples.

Pulp		Yield%	α-cellulose%	Cryst%	Amorph%	Ash%	Lignin %
A	Unbleached	48.7	74.7	-	-	1.80	4.2
	Bleached	46.6	91.6	83.2	16.8	0.06	-
B	Unbleached	45.2	83.8	-	-	0.24	2.3
	Bleached	43.1	93.2	79.0	21.0	0.01	-

Pulp A (one stage pulp): 16% peracetic acid with liquor ratio 1:6 at 85°C for two hrs.
Pulp B (two stages pulp): 10% NaOH, 1:3 liquor ratio at 90°C for 1.5 hrs **then** 16% peracetic acid with liquor ratio 1:6 at 70°C for two hrs.

3.1 Factors affecting grafting efficiency G.E% of acrylonitrile onto cornhusks cellulose.

The grafting efficiency of acrylonitrile grafting onto cellulose was varied by changing KPS concentration, monomer to substrate ratio, reaction time and reaction temperature. These factors were studied to reach the optimum conditions for grafting process.

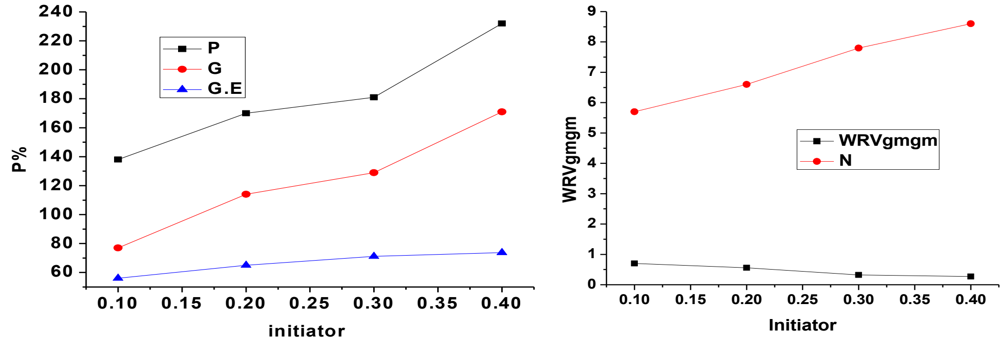
3.1.1. Effect of initiator concentration.

Potassium persulphate $K_2S_2O_8$ was used as an initiator for grafting of acrylonitrile onto corn husks cellulose with concentration ranging from 0.1 to 0.4gm. The effects of increasing the initiator concentration on the grafting factors (polymer loading and grafting efficiency) were listed in table (2). It is clear from table(2) that increasing KPS concentration from 0.1 to 0.3gm causes a significant increase in the grafting quality such as P%, G%, G.E%, and Nitrogen%. This is because of the presence of free radicals on cellulose molecules which enhances the grafting process. Further increase in initiator concentration up to 0.4gm causes a slight increase in the G.E% value that may be due to the enhancing of the homopolymerization reaction (14) while the P% increases on the expense of G%. Also we note that the water retention value (WRV) decreases after acrylonitrile grafting onto cellulose because of the hydrophobic behavior of the nitrile group, so the WRV decrease by increasing the G.E% while the N% increase. All this was illustrated in fig 1.

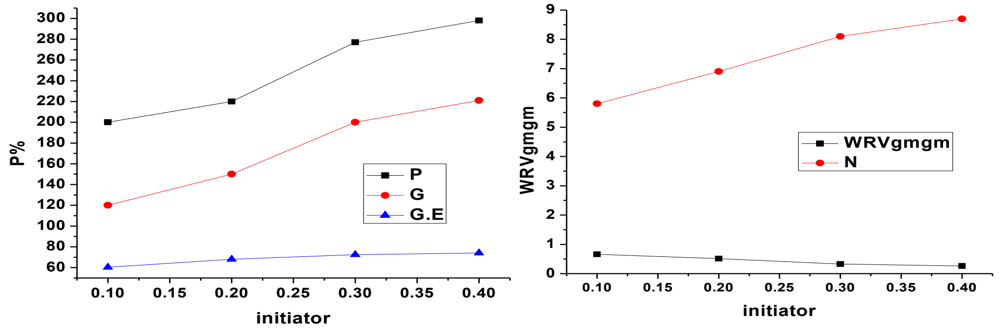
Table 2
Effect of initiator concentration on the grafting parameters.

sample	Initiator (gm/1 gm pulp)	P%	G%	G.E%	WRV gm/gm	N_2%
A	0.1	138	77	56.1	0.7	5.7
	0.2	170	114	65	0.56	6.6
	0.3	181	129	71.2	0.32	7.8
	0.4	232	171	73.8	0.27	8.6
B	0.1	200	120	60.3	0.66	5.8
	0.2	220	150	68.1	0.51	6.9
	0.3	277	200	72.5	0.33	8.1
	0.4	298	221	74.1	0.26	8.7

Conditions: 1 gm pulp, 1:50 liquor ratio, 3ml monomer, at 70^{0}C for 2 hrs under vacuum.



Effect of initiator sample A



Effect of initiator sample B

Fig. 1. The effect of KPS conc. on G.E% at the following conditions: 1 gm sample, 1:50 l.r, 3 gm monomer, for 2 hrs at 70^{o}C under vacuum and different initiator concentrations.

3.1.2. Effect of monomer ratio.

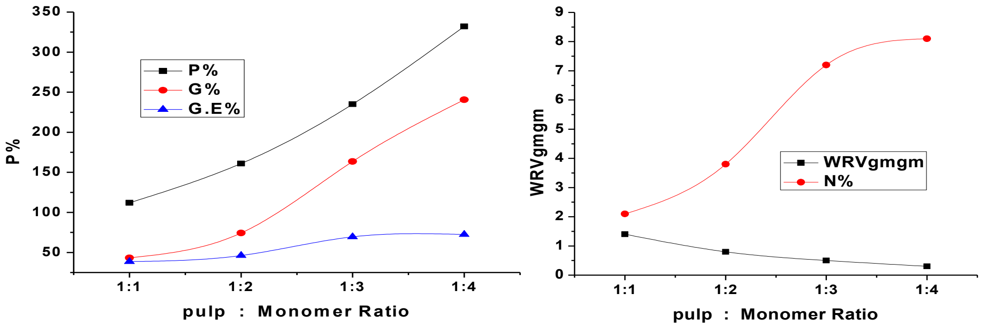
The monomer to substrate ratio was varied from 1:1 up to 1:4 with fixing other conditions and the values of P%, G%, G.E%, WRV and N% were listed in table (3). It is clear from table(3) that increasing monomer ratio increases

G.E% till the ratio of 1:3 but after that the value G.E% increases slowly. This is because homopolymerization increase on the expense of copolymerization (15-17) this was illustrated in fig.2.

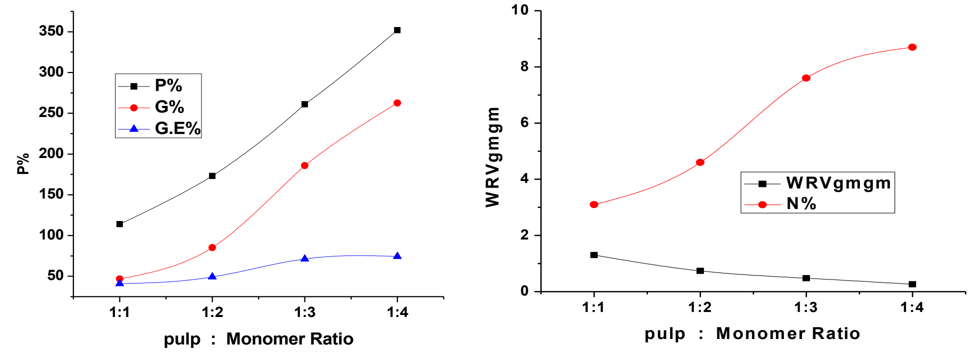
Table 3
Effect of monomer ratio on the grafting parameters.

sample	pulp : Monomer Ratio	P%	G%	G.E%	WRV gm/gm	N_2%
A	1:1	112	43.2	38.6	1.4	2.1
	1:2	161	74.3	46.2	0.8	3.8
	1:3	235	163.5	69.6	0.5	7.2
	1:4	332	240.7	72.5	0.3	8.1
B	1:1	114	46.7	41	1.3	3.1
	1:2	173	85.1	49.2	0.74	4.6
	1:3	261	185.8	71.2	0.48	7.6
	1:4	352	262.5	74.3	0.26	8.7

Conditions: 1 gm pulp, 1:50 liquor ratio, 0.3gm initiator, at 70^{0}C for 2 hrs under vacuum.



Effect of monomer ratio sample A



Effect of monomer ratio sample B

Fig. 2. The effect of monomer conc. on G.E% at the following conditions :(1 gm sample, 1:50 l.r, 0.3 gm initiator ($K_2S_2O_8$), 2 hrs at 70^{o}C under vacuum)

3.1.3. Effect of reaction time.

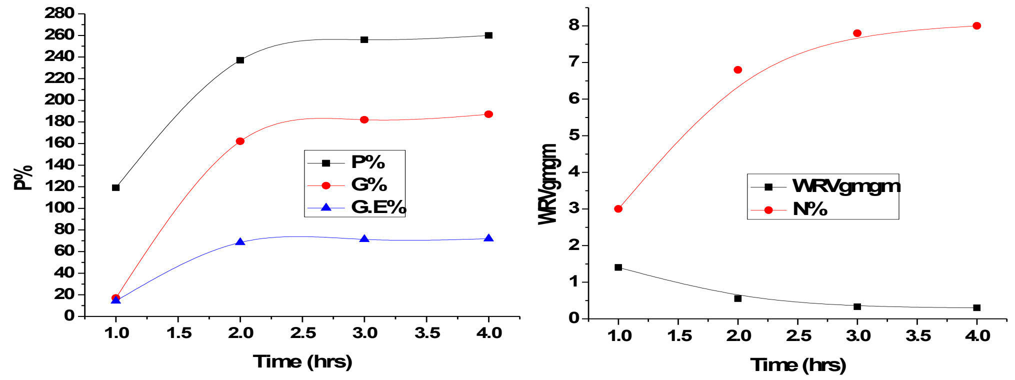
From table (4) it is clear that in the first hour the G% is very low so the corresponding G.E% also has a small value this is because a few number of active sites have been formed. By increasing reaction time G.E% increases till 2 hrs then it starts to increase slowly because the reactant concentration decrease (initiator and available sites on the cellulose backbone) and the medium viscosity increase that retards diffusion.

Table 4

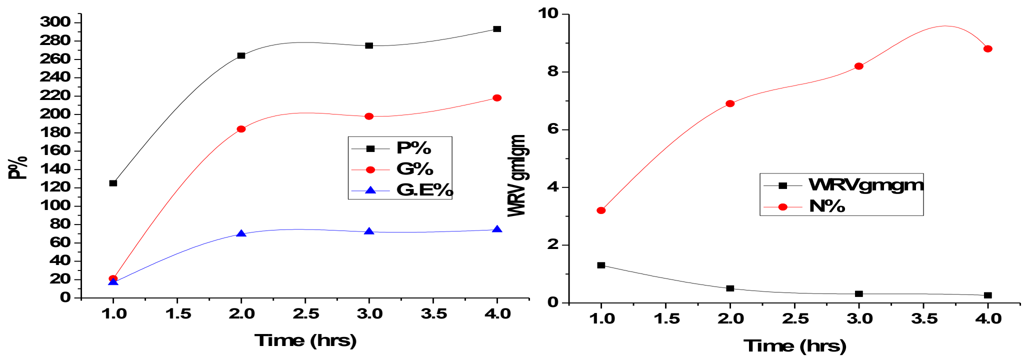
Effect of grafting reaction time on the grafting parameters.

sample	Time (hrs)	P%	G%	G.E%	WRV gm/gm	N_2%
A	1	119	17	14.3	1.4	3.0
	2	237	162	68.5	0.55	6.8
	3	256	182	71.3	0.33	7.8
	4	260	187	72	0.3	8.0
B	1	125	21	16.8	1.3	3.2
	2	264	184	69.7	0.5	6.9
	3	275	198	72.1	0.31	8.2
	4	293	218	74.4	0.26	8.8

Conditions: 1 gm pulp, 1:50 liquor ratio, 3ml monomer, 0.3 gm initiator, at 70^{0}C for different time intervals under vacuum.



Effect of time sample A



Effect of time sample B

Fig. 3. The effect of time on G.E% at the following conditions:(1 gm sample , 1 :50 l.r , 1 sample :3 monomer , 0.3 gm initiator ($K_2S_2O_8$) , at 70^{o}C under vacuum for different time intervals)

3.1.4. Effect of reaction temperature.

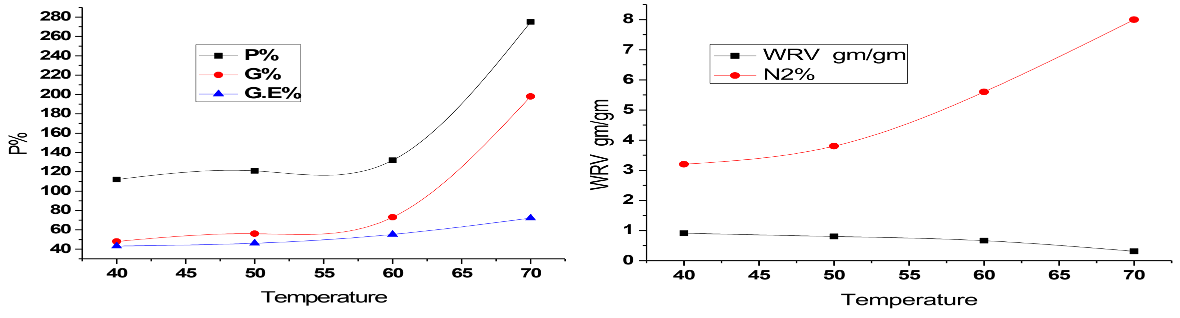
The grafting reaction temperature was changed starting with 40°C to 70°C the effects on grafting parameters were listed in table (5). By increasing reaction temperature the solubility of KPS and monomer diffusion increase so G.E% increases till 70°C. It is undesirable to increase temperature more than 70°C because at high temperature an oxidative degradation of cellulose and decomposition of KPS occurs that give oxygen (a radical scavenger), which reacts with primary free radicals (18, 19) this is shown in Fig.4

Table 5

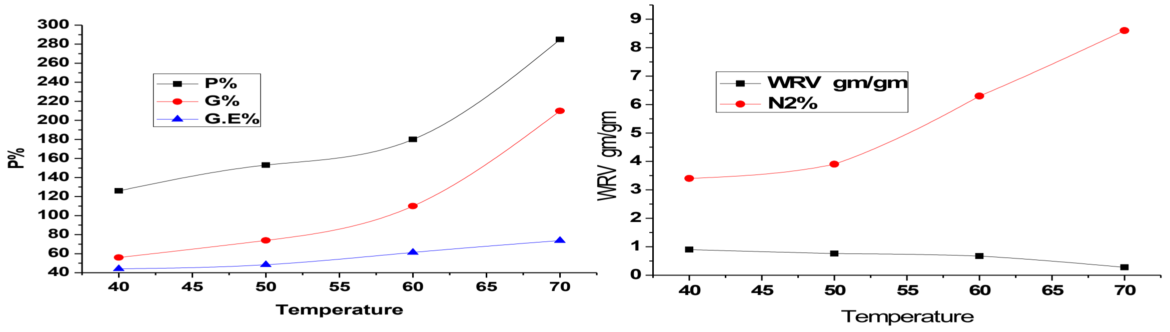
Effect of grafting reaction temperature on the grafting parameters.

sample	Temperature	P%	G%	G.E%	WRV gm/gm	N_2%
A	40	112	48	43.2	0.91	3.2
	50	121	56	46.1	0.80	3.8
	60	132	73	55.2	0.66	5.6
	70	275	198	72.1	0.31	8.0
B	40	126	56	44.1	0.90	3.4
	50	153	74	48.3	0.76	3.9
	60	180	110	61.3	0.67	6.3
	70	285	210	73.8	0.28	8.6

Conditions: 1 gm pulp,1:50 liquor ratio, 0.3 gm KPS, 3ml monomer, at different temperatures and vacuum for 2 hrs.



Effect of temperature sample A



Effect of temperature sample B

Fig. 4. The effect of temperature on G.E% at the following conditions:1 gm sample , 1 :50 l.r , 1 sample :3 monomer , 0.3 gm initiator ($K_2S_2O_8$) , at different temperature for 2 hrs.

. It is clear from the forgiving that in the same conditions for the two types of pulp, the G.E% of the two stages pulp was more than that of the one stage pulp. This causes an increase in the other parameters such as N%. This increase in the G.E% value of pulp B is attributed to the high percent of the amorphous region in it rather than that of pulp A. also Amidoximation of the acrylonitrile grafted cellulose cause high increase in the WRV and approximately 100% increase in the N% this is clear from table (6).

Table 6

WRV and N% of the two pulp samples after grafting and after amidoximation

sample		WRV gm/gm	N%
A	Acrylonitrile grafted pulp (G.E% 72.1)	0.31	8.0
	Amidoximated grafted pulp	6.3	14.4
B	Acrylonitrile grafted pulp (G.E% 73.8)	0.28	8.6
	Amidoximated grafted pulp	7.1	17.0

3.2 IR spectroscopy

Figure (5) shows the IR spectra of ungrafted , acrylonitrile grafted , and amidoximated grafted cellulose samples. In the ungrafted cellulose samples the absorption bands at 3417 and 3414 cm^{-1} for O—H. and at 2917and 2902 cm^{-1} for C—H stretching in A and B respectively. A broad bands at 1647 and 1642 cm^{-1} were attributed to the bending mode of the absorbed water, and a small peak at 1431 cm^{-1} belonged to CH_2 symmetric bending in each type of pulp. Also a small peak at 1373 cm^{-1} showed C—O stretching in each. The C—O—C pyranose ring skeletal vibration gave a strong bands at 1107 and 1030 cm^{-1}. A small sharp peak at 898 cm^{-1} corresponded to the glucosidic C—H deformation with ring vibration contributions and O—H bending. This was characteristic of α- glucosidic linkage between the glucose molecules in cellulose (20). In the acrylonitrile grafted cellulose samples the intensity of the absorption band at 2938 cm^{-1} that corresponds to CH_2 group is much more than that in the ungrafted samples and the appearance of a new band at 2243cm^{-1} that relates to C≡N group. This indicates the success of the grafting process. After amidoximation the C≡N band disappear and a new bands at 1646 cm appear that corresponds to C=N of amidoxime, also the OH band(at 3451cm) become broad and appear at 3398cm^{-1} due to overlap between OH and NH bands and appearance of new OH groups in the amidoxime group. Also bands at 1442cm^{-1} and 1163cm^{-1} are due to N-H and C-N bending respectively. And the bands at 1108cm^{-1} and 940cm^{-1} are due to stretching C-N and C=N respectively. Also the crystallinity index (band intensity at 900/ band intensity at 1430) is 2.33 and 1.73 in pulps A and B respectively This also make the crystallinity% of pulp B lower than pulp A so pulp A is more crystalline than pulp B. The high percent of amorphous portion in pulp B make it more reactive towards grafting reaction so sample B has high G.E% value than sample A at the same conditions.

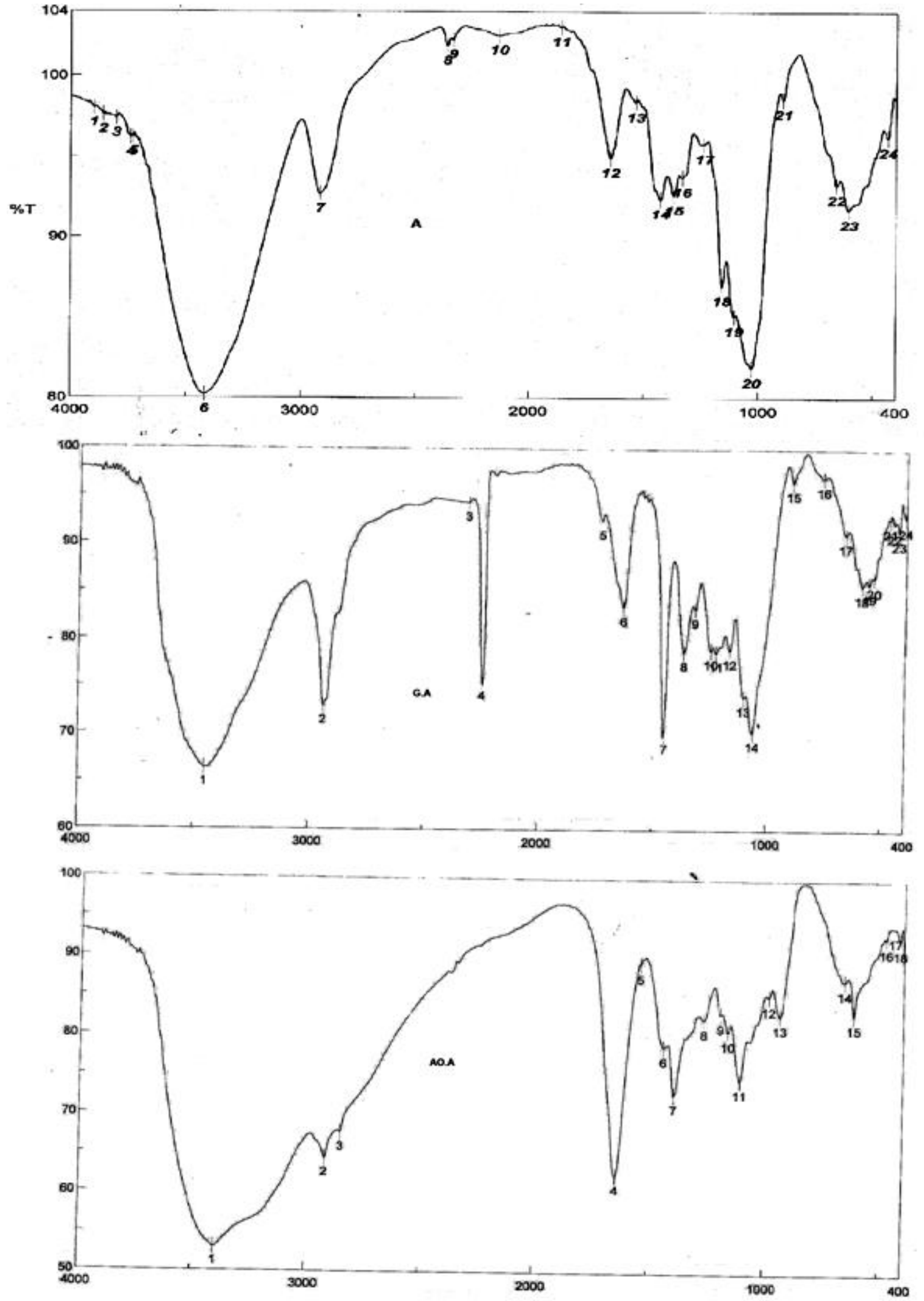


Fig.5a. The IR spectra of ungrafted cellulose sample (A), acrylonitrile grafted cellulose samples (G.A), and amidoximated polyacrylonitrile grafted cellulose samples (AO.A).

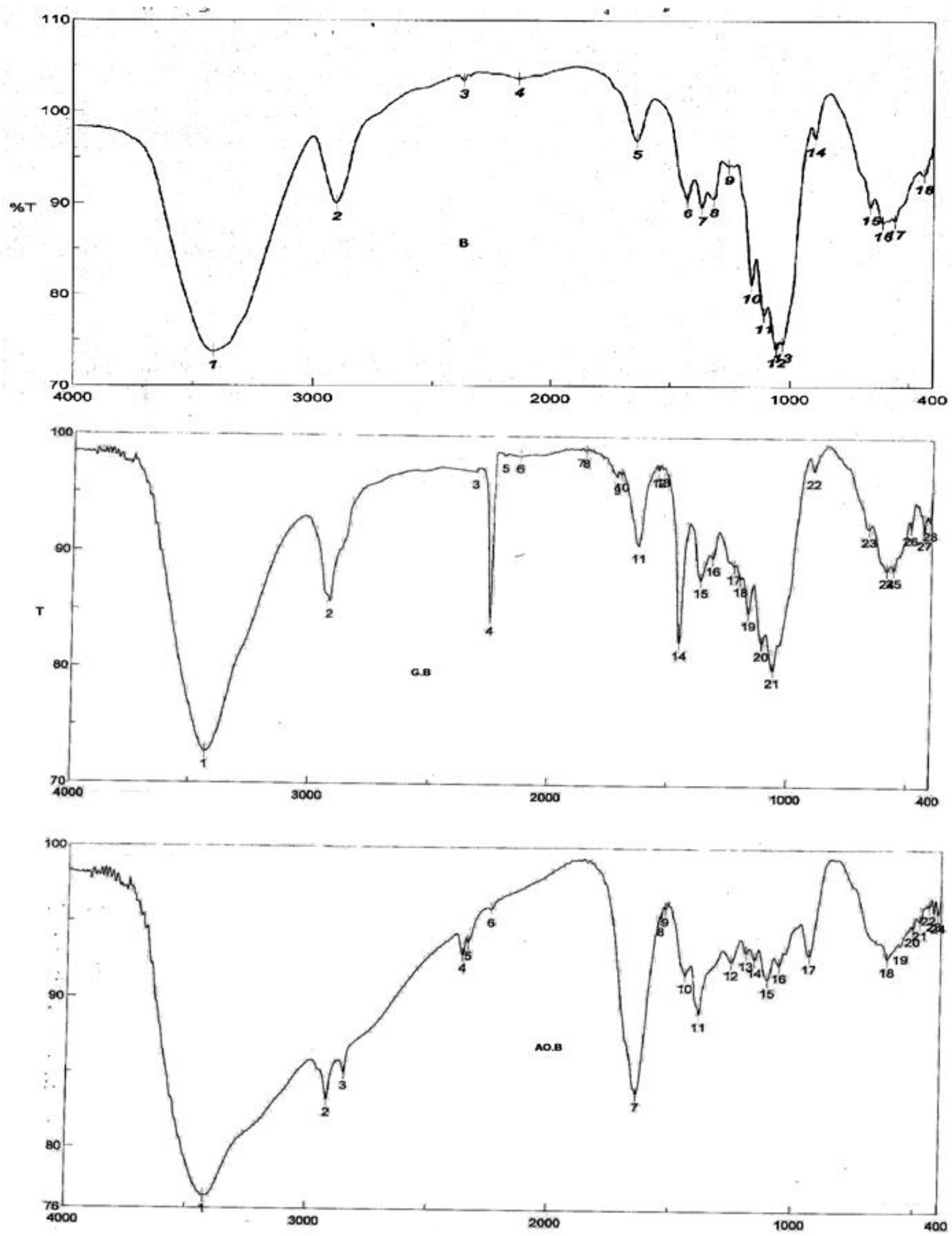


Fig.5b. The IR spectra of ungrafted cellulose sample (B), acrylonitrile grafted cellulose samples (G.B), and amidoximated polyacrylonitrile grafted cellulose samples (AO.B).

3.3 Factors affecting metal ion sorption.

Grafting of acrylonitrile onto cellulose decreases its WRV due to the incorporation of the hydrophobic nitrile group, so increasing the G.E% value decreases the WRV of the sample. But after Amidoximation the nitrile group is converted to amidoxime group that is hydrophilic group this is clear in the WRV of the amidoximated samples. The hydrophilicity of the amidoximated samples will enhance the metal ion sorption. This is besides the chemical structure of the amidoxime group, where it is clear that it is bi dentate (14):

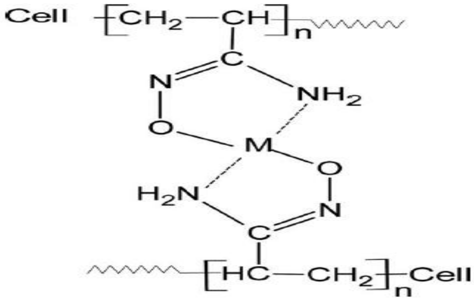


Figure6. Chemical structure of amidoxime group chelation with the metal ion

In this work we will study the effects of pH of the adsorption medium, adsorption time, dose of the adsorbent, and adsorption medium temperature on the metal adsorption.

3.3.1 Effect of pH of the adsorption medium.

The metal ion sorption by the adsorbent is pH dependent because the pH value not only affects the surface charge of the adsorbent, but also affects the ionization degree of the adsorbate. From table (7) and figure (7) we note that increasing the pH value from 3 to 7 increase Ni adsorption that reach the highest value at pH 7 this is because in acidic medium protonation of the two ligands of the amidoxime (=N-OH and $-NH_2$) occur that prevent chelation with Ni ions, also in basic medium precipitation of Ni as hydroxide occur, and the ion exchanger is more compact in alkaline medium(21).

Table 7

Effect of pH of the adsorption medium

Sample	pH	Remaining ppm.	Removed ppm.	Activity %	Ni uptake mg/g
A	3	900	600	40.0	60
	4	680	820	54.7	82
	5	440	1060	70.7	106
	6	200	1300	86.7	130
	7	120	1380	92.0	138
	8	380	1120	74.6	112
B	3	820	680	45.3	68
	4	630	870	58.0	87
	5	400	1100	73.3	110
	6	180	1320	88.0	132
	7	80	1420	94.7	142
	8	360	1140	76.0	114

0.5 gm polymer, 50 ml of 1500ppm solution (contain 75mgm) buffered with sodium acetate at different pH values, for I hour, at 30^oC.

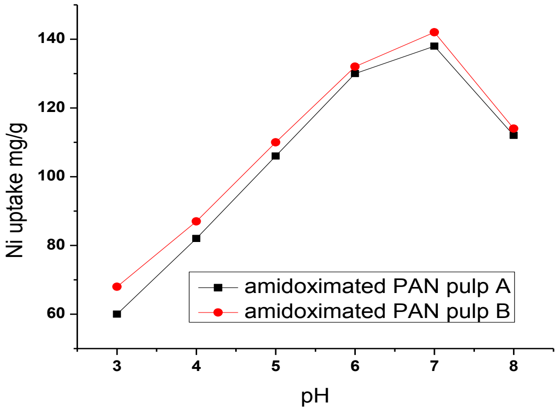


Figure7. Effect of pH of the adsorption medium

3.3.2. Effect of adsorption time on Ni uptake

From table 8 we note that by increasing time of adsorption of Ni on the ion exchanger the amount of Ni uptake increase till about 60 minutes where Ni uptake increase slowly, this is because of the consumption of the active sites on the adsorbent and decreasing the concentration of the adsorbate.

Table 8

Effect of adsorption time

Sample	Time(min.)	Remaining ppm.	Removed ppm.	Activity %	Ni uptake mg/g
A	20	1100	400	26.7	40
	40	600	900	60.0	90
	60	120	1380	92.0	138
	80	60	1440	96.0	144
	100	15	1485	99.0	148
B	20	1010	490	32.7	49
	40	560	940	62.7	94
	60	80	1420	94.6	142
	80	40	1460	97.3	146
	100	5	1495	99.6	149

0.5 gm polymer, 50 ml of 1500ppm solution (contain 75mgm) buffered with sodium acetate at pH 7, at 30°C.

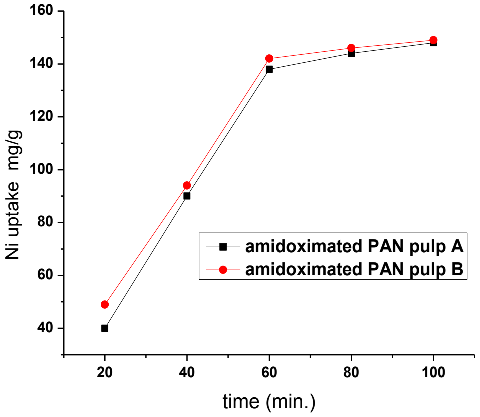


Figure8. Effect of adsorption time on Ni uptake

3.3.3. Effect of adsorbent amount on Ni uptake

From table 9 we can note that increasing the amount of the adsorbent the number of active amidoxime group increase, so the activity% of the adsorption of Ni from waste water increase where 1.6 gm can purify 100ml of 1500 ppm solution that contain about 150 mgm/gm, this is clear in figure 9 as follow(22):

Table 9
Effect of adsorbent amount.

Sample	Amount (gm)	Remaining ppm.	Removed ppm.	Activity %	Ni uptake mg/g
A	0.2	910	590	39.3	59
	0.4	420	1080	72.0	108
	0.6	100	1400	93.3	140
	0.8	0.0	1500	100.0	150
B	0.2	880	620	41.3	62
	0.4	390	1110	74.0	111
	0.6	60	1440	96.0	144
	0.8	0.0	1500	100.0	150

Different weights of polymer, 50 ml of 1500ppm solution (contain 75mgm) buffered with sodium acetate at pH 7, for I hour, at 30^o.

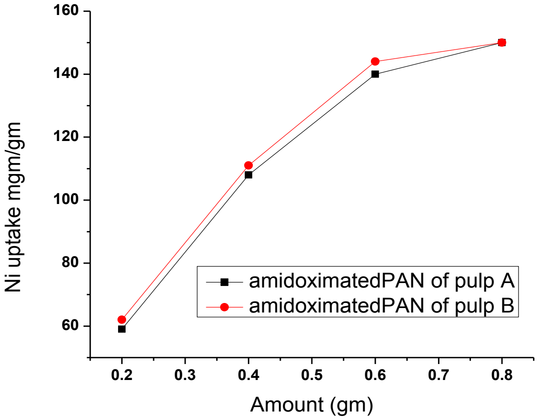


Figure 9. Effect of adsorbent amount on Ni uptake

3.3.4. Effect of adsorption medium temperature on Ni uptake

Increasing the temperature of the adsorption medium activate the adsorption of Ni ions on the surface of the adsorbent. So we note that the uptake of Ni on the ion exchanger increase by increasing temperature from 20 up to 40^{o}C. But after that desorption occur by raising temperature so the amount of Ni uptake decrease. This is shown in table 10 and illustrated in figure 10 also.

Table 10
Effect of adsorption medium temperature on Ni uptake

Sample	Temperature	Remaining ppm.	Removed ppm.	Activity %	Ni uptake mg/g
A	20	830	670	44.6	67
	30	320	1180	78.6	118

	40	100	1400	93.3	140
	50	290	1210	80.6	121
	60	450	1050	70.0	105
B	20	800	700	46.6	70
	30	300	1200	80.0	120
	40	20	1480	98.6	148
	50	250	1250	83.3	125
	60	400	1100	73.3	110

0.5 gm of polymer, 50 ml of 1500ppm solution (contain 75mgm) buffered with sodium acetate at pH 7, for I hour, at different temperature.

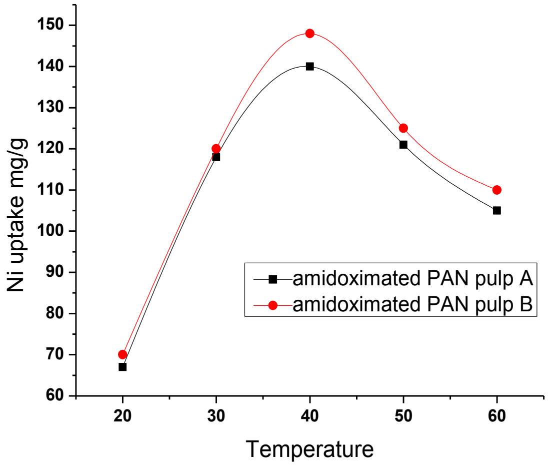


Figure 10
Effect of adsorption medium temperature on Ni uptake

4. Conclusion

A polyamidoximated chelating ligand was successfully synthesized by amidoximation of polyacrylonitrile grafted corn husks pulp, a waste material. The optimum conditions were pulping in two stages by NaOH followed by peracetic acid, and grafting at 1:50 liquor ratio, 1 gm cellulose: 3ml Monomer: 0.3gm potassium persulfate, for 2 hrs at 70^0C. After that the grafted pulp was amidoximated by reaction with hydroxyl amine to convert the nitrile group to amidoxime. The polymeric ligand give good adsorption capacity toward Ni, and this was found to be pH-dependent. The low-cost production of the corn husks cellulose-based polyamidoximated ligand could be considered a promising way for waste water treatment because 142mgm can be adsorbed from aqueous media by soaking 1 gm of the ion exchanger in 100 ml of the waste water containing 1500ppm Ni for 1 hr at 40^0 C and 7 P^H. The reusability of the polymeric ligand can be performed by dilute solution of hydrochloric acid.

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