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Purification of Heavy Metals from Industrial Waste Water Using Grafted Corn Husks Pulp Ion Exchanger

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Abstract: This study focuses on the development of an ion exchanger based on cellulose extracted from corn husks and grafted with acrylamide followed by base hydrolysis. Corn husk was prehydrolyzed with diluted acid followed by pulping in one or two pulping stages, then bleached by alkaline hydrogen peroxide. Alpha cellulose, lignin, ash and other parameters were measured in the produced pulp. Graft copolymerization of acrylamide onto the pulp was done using Potassium persulfate as initiator followed by sodium hydroxide reflux to convert the amide group to carboxylate group that was used to remove Ni from waste water. Factors affecting grafting such as time, temperature, monomer ratio, and initiator concentration were studied. In addition Factors affecting metal ion removal such as pH, temperature, amount, and time were studied.

Keywords: cellulose, ion exchanger, grafting, pulping, hydrolysis.

1 Introduction

The study of Corn is one of the major crops in the world. In 2002, world corn production was about 640 million tons, associated with corn production was a corresponding about 45 million tons annual production of cornhusk. The cornhusk resource constitutes an alternative to wood as a raw material for making pulp because of its high growth rate and adaptability to various soil types. Recently, a fiber extraction method have been developed to obtain cellulose fibers from cornhusk with mechanical properties similar to that of the common textile fibers [1]. The cornhusk cellulose was used as cellulose source [2]. Moisture regain of cornhusk fibers is about 9 % at standard testing conditions; the moisture regain of the fibers is large due to the higher amorphous regions in the fibers. Cornhusk fibers can be produced using common chemicals and the cost of producing corn fibers would be very competitive to prevail cotton prices [3].

Because cellulose is a linear polymer, the presence of crystalline regions and the strong intermolecular hydrogen bonding decrease its accessibility or reactivity for the grafting reaction. The grafting efficiency can be increased by increasing the ratio of cellulose/monomer either by swelling the cellulose before the reaction or by performing the grafting reaction in a medium in which cellulose swells [4]. Namely, the accessibility or reactivity of cellulose for grafting can be enhanced by decreasing its crystallinity or by increasing the content of amorphous phase since the grafting occurs mainly on the amorphous regions. The change in the physical structure of cellulose can be performed by swelling in concentrated NaOH solution (~20 %) and then by regeneration (mercerization) [5].

Grafting of vinyl monomers onto cellulose is an important tool for the modification of cellulose. Depending on the monomer grafted onto cellulose, it gains new properties. Graft copolymerization of binary mixtures of vinyl monomers has special importance in comparison to simple grafting of individual monomers; the synergistic effect of the co-monomers in grafting mixtures plays an important role in controlling the composition and graft yield onto cellulose [6, 7].

Natural biomasses such as natural fibers are utilized by humans for household or other conventional applications [8]. Natural polymers have found various applications in different fields such as building materials, sports equipment, automobiles, electrolytes, energy storage, aerospace, and as adsorbent for toxic metal ion from different resources [9]. The applications of cellulose graft copolymers change with the structure of polymer grafted on cellulose. For that reason cellulose grafted with hydrophilic monomers could be used as body fluid absorbent in medical applications [10]. The grafting of water-soluble vinyl monomers onto amine-treated cotton fiber gave a graft copolymer with enhanced moisture

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sorption ability that can be used in fabrics, such as underwear and athletic wear [11]. Cellulose-thiocarbamate-g-PAN had high antimicrobial activity. In addition, the cellulose graft copolymers obtained by grafting of acrylonitrile, and 2 acrylamidomethylpropane sulfonic acid have been used in the adsorption of hazardous contaminants such as heavy metal ions or dyes [12] from aqueous solutions [13, 14]. The product of poly (4-vinylpyridine)-grafted cellulose with sodium borohydride has been used as reducing agents for various carbonyl compound such as benzaldehyde, cyclohexanone, crotonaldehyde, acetone and furfural [15].

Many physiochemical methods like coagulation, flocculation, ion exchange, membrane separation, photodegradation, electrochemical oxidation have been used for the treatment of contaminated water [16 - 19]. Among these methods, adsorption is known to be efficient, and is widely used in wastewater treatment. Several researches utilizing a number of natural materials like chitosan, pectin, and cellulose extracted from different lignocelluloses as natural fibers for the removal of the dyes and heavy metal ions from water [20, 21]. Also chitin and its derivatives have been studied with respect to their ability to remove heavy metals from aqueous solution [22, 23]. The adsorbed ions can be easily desorbed by treating with HCl solution and the desorption percentage reached above 95% when desorbing with 1N HCl solution for one hour at room temperature [24].

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 (P.A.A) only (namely one stage pulping) or by using sodium hydroxide followed by P.A.A (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 wt [25, 26].

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, and then 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, and then washing with 80% A.A and distilled water till neutrality and dried at 50^oC under vacuum till constant weight [26, 27].

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 [27]. 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 [27].

2.5. Grafting

Graft copolymerization of acrylamide onto cornhusks was carried out with $K_2S_2O_8$ (KPS) as an initiator under vacuum. In a two nicked 250 mL flask, cornhusks (1 g) were soaked in 30 mL of degassed distilled water for 24 hrs. The sample was stirred with magnetic stirrer for 15 mins 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 70^{o}C. $K_2S_2O_8$ solution 10 ml (2gm/100ml) was added. After 15 mins 10 ml acrylamide solution (30gm/100ml) was added and the reaction was continued for 2 hrs with shaking from time to time. After the reaction complete 50 ml methanol was added followed by filteration and drying at 50^{o}C under vacuum till constant weight.

2.6. Base hydrolysis of the grafted copolymer

In order to change amide group to carboxylate, 0.5 gm of the grafted sample was mixed with 50ml of 0.1N NaOH solution and the mixture was refluxed for 1 hr. After hydrolysis the reaction mixture was washed with distilled water then neutralized with 2.0 N HCl and washed again with distilled water till neutralization.

2.7. Metal ion uptake

The two pulp samples were grafted with acrylamide and base hydrolyzed then 0.5 gm of the four samples (two grafted samples and two hydrolyzed grafted samples) were soaked into 50 mL of the buffered metal solutions (1500 ppm concentration), whose pH was adjusted in a range of 2.0– 8.0, 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 grafted cellulose before or after hydrolysis, the metal ion concentrations remaining in the solution were determined by atomic spectrophotometer at 232 nm by standard calibration curve method [28]. Initial concentration of Ni in the waste water was 1.5 gm/L (1500 ppm).

3 Results and discussions

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 presence of NaOH which facilitates the enhancement of peracetic acid between cellulose fibers, so a great amount of lignin was eliminated which decreased the yield and increased the ratio of α-cellulose.

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^{o}C for two hrs.
Pulp B (two stages pulp): 10% NaOH, 1:3 liquor ratio at 90^{o}C for 1.5 hrs **then** 16% peracetic acid with liquor ratio 1:6 at 70^{o}C for two hrs.

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

The grafting efficiency of acrylamide 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 (KPS) concentration:

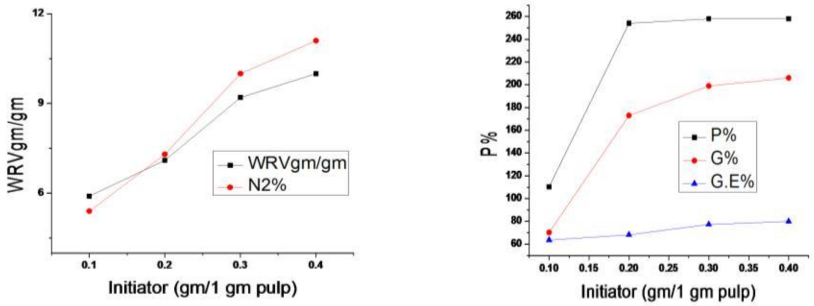
Potassium persulphate $K_2S_2O_8$ was used as an initiator for grafting acrylamide onto corn husks cellulose with concentration from 0.1 to 0.4gm. The effect of increasing the initiator concentration on the grafting factors (polymer loading and grafting efficiency) were illustrated in table (2).

Table 2: Effect of initiator concentration on the grafting parameters.

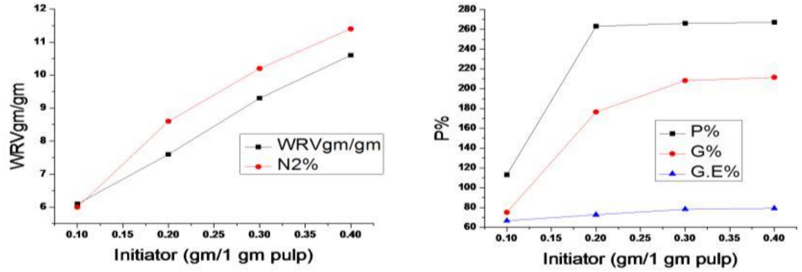
Sample	Initiator (gm/1 gm pulp)	P%	G%	G.E%	WRVgm/gm	N_2%
A	0.1	110	70.2	63.6	5.9	5.4
	0.2	254	173.0	68.2	7.1	7.3
	0.3	258	199.0	77.3	9.2	10.0
	0.4	258	206.1	79.9	10	11.1
B	0.1	113	75.2	66.6	6.1	6.0
	0.2	263	176.5	72.8	7.6	8.6
	0.3	266	208.2	78.3	9.3	10.2
	0.4	267	211.5	79.2	10.6	11.4

Conditions: 1 Sample: 3 monomer, 1:50 l.r with different initiator ($K_2S_2O_8$) concentrations, for 2 hrs at 70^{o}C under vacuum.

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% and G.E%, WRV, 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 consumption of accessible sites on cellulose [29], fig 1.



Effect of initiator concentration sample A



Effect of initiator concentration sample B

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

3.1.2 Effect of monomer concentration:

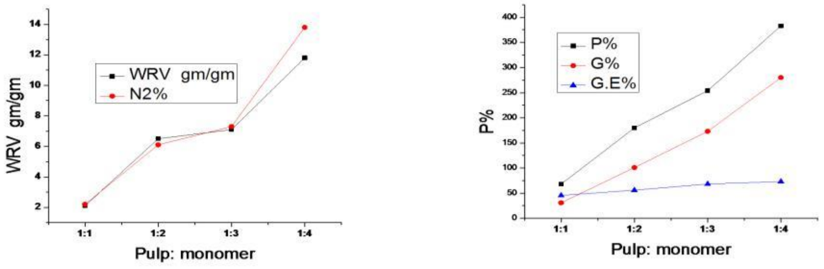
The monomer to substrate ratio was varied from 1:1 up to 1:4 with fixing other conditions and the values of P%, G%, G.E%, WRV and N% were listed in table (3).

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 [30-32] fig.2.

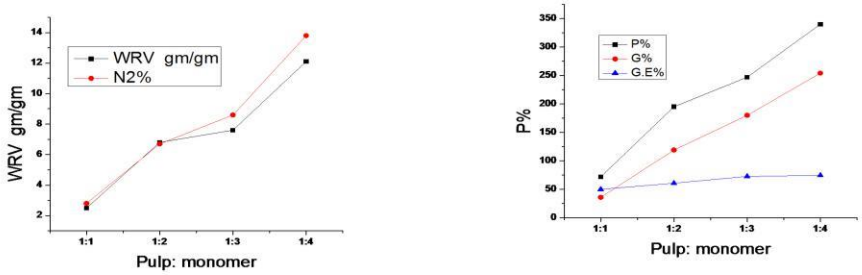
Table 3: Effect of monomer ratio on the grafting parameters.

sample	Pulp: monomer	P%	G%	G.E%	WRVgm/gm	N_2%
A	1:1	68	31	45.5	2.1	2.2
	1:2	180	101	56.0	6.5	6.1
	1:3	254	173	68.2	7.1	7.3
	1:4	383	280	73.1	11.8	13.8
B	1:1	72	36	50.0	2.5	2.8
	1:2	195	119	60.8	6.8	6.7
	1:3	247	180	72.8	7.6	8.6
	1:4	340	254	74.5	12.1	13.8

Conditions: 1gm sample, 1:50 l.r 0.2gm initiator ($K_2S_2O_8$), for 2 hrs at 70^{O}C under vacuum.



Effect of monomer ratio sample A



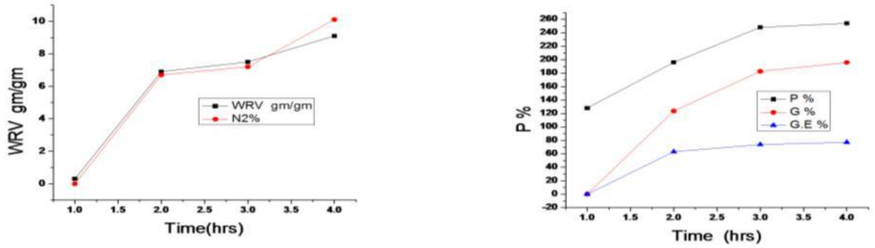
Effect of monomer ratio sample B

Fig.2 shows the effect of monomer conc. on G.E% at the following conditions: (1 gm sample, 1:50 l.r, 0.2 gm initiator ($K_2S_2O_8$), 2 hrs at 70^{O}C).

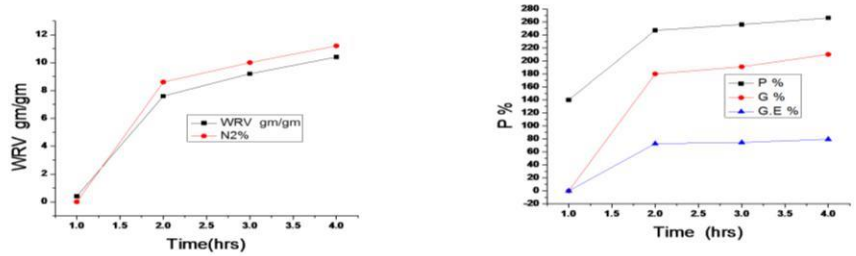
3.1.3 Effect of reaction time:

The grafting reaction time was varied starting with 1 hr to 4 hrs and the effects on grafting parameters were listed in table (4).

From table (4) it is clear that in the first hour no grafting occurs so G.E% is zero. By increasing reaction time G.E% increases till 2 hrs then it starts to increase slowly because the reactant concentration decrease and the medium viscosity increase that retards diffusion.



Effect of reaction time sample A



Effect of reaction time sample B

Fig.3 shows the effect of time on G.E% at the following conditions: (1 gm sample, 1:50 l.r, 1 sample: 3 monomer, 0.2 gm initiator ($K_2S_2O_8$), at 70°C for different time intervals).

Table 4: Effect of grafting reaction time on the grafting parameters.

Sample	Time(hrs)	P%	G%	G.E%	WRVgm/gm	N_2%
A	1	128	0	0	0.3	0.0
	2	196	123.5	63	6.9	6.7
	3	248	182.5	73.6	7.5	7.2
	4	254	195.8	77.1	9.1	10.1
B	1	140	0	0	0.4	0.0
	2	247	180	72.8	7.6	8.6
	3	256	191	74.6	9.2	10
	4	266	210	79.5	10.4	11.2

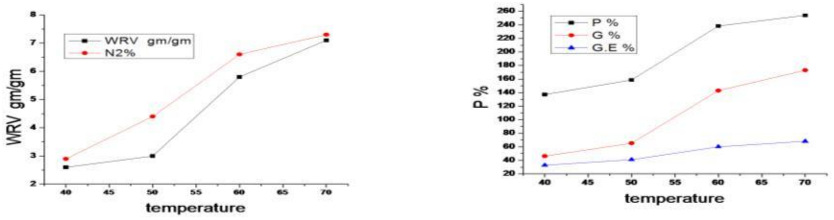
Conditions: 1 gm sample, 1:50 l.r, 1 sample: 3 monomer, 0.2 gm initiator ($K_2S_2O_8$), at 70°C for different time intervals.

3.1.4 Effect of reaction temperature:

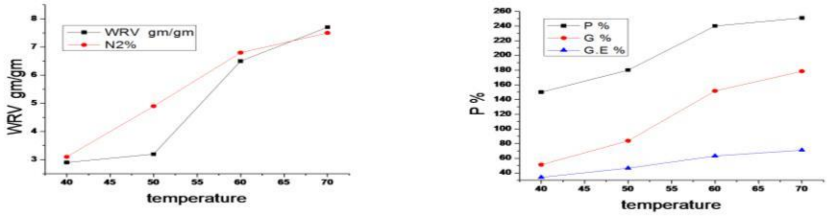
The grafting reaction temperature was changed starting with 40°C to 70°C the effects on grafting parameters were listed in table (5).

By increasing the reaction temperature, the solubility of KPS and monomer diffusion increase so G.E% increases till 60°C. After that G.E% increases slowly because at high temperature oxidative degradation of cellulose and decomposition of KPS occurs to give oxygen (a radical scavenger), which reacts with primary free radicals [33, 34] this is show in Fig.4

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% and WRV. 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 the sodium binding capacity of the two pulp samples A, and B was measured after their grafting and after their grafting hydrolysis and the results were listed in table (6).



Effect of reaction temperature sample A



Effect of reaction temperature sample B

Fig.4 shows the effect of temperature on G.E% at the following conditions: 1 gm sample, 1:50 l.r, 1 sample: 3 monomer, 0.2 gm initiator ($K_2S_2O_8$), at different temperature for 2 hrs.

Table 5: Effect of grafting reaction temperature on the grafting parameters.

sample	temperature	P%	G%	G.E%	WRVgm/gm	N_2%
A	40	137	46.2	32.8	2.6	2.9
	50	158	65.4	41.1	3	4.4
	60	238	143	60	5.8	6.6
	70	254	173	68.2	7.1	7.3
B	40	150	51.3	34.2	2.9	3.1
	50	180	83.8	46.6	3.2	4.9
	60	240	151.6	63.2	6.5	6.8
	70	251	178.4	71.1	7.7	7.5

Conditions:1 gm sample , 1 :50 l.r , 1 sample :3 monomer , 0.2 gm initiator ($K_2S_2O_8$) , at different temperature for 2 hrs and vacuum.

Table 6: sodium binding capacity of the two pulp samples A, and B after their grafting and after their grafting hydrolysis.

Sample		Vol. of 0.01N NaOH	Average	Na binding capacity(m.eqwt/gm)
A	Grafted	38.8	39.53	1209.4
		40.6		
		39.2		
	Hydrolyzed grafted	10.1	9.63	1807.4
		9.6		
		9.2		
B	Grafted	30.2	29.3	1414
		29.1		
		28.6		
	Hydrolyzed grafted	4.1	3.56	1928.6
		3.5		
		3.1		

From table (6) we note that the hydrolysis of the grafted samples cause an increase in their sodium binding capacity value; this is because the carboxyl group is more reactive towards sodium ion than the amide group. Also it is clear that the increase in the G.E% value of pulp B than pulp A cause an increase in its sodium binding capacity values in the grafted and the hydrolyzed grafted forms.

3.2 IR Spectroscopy

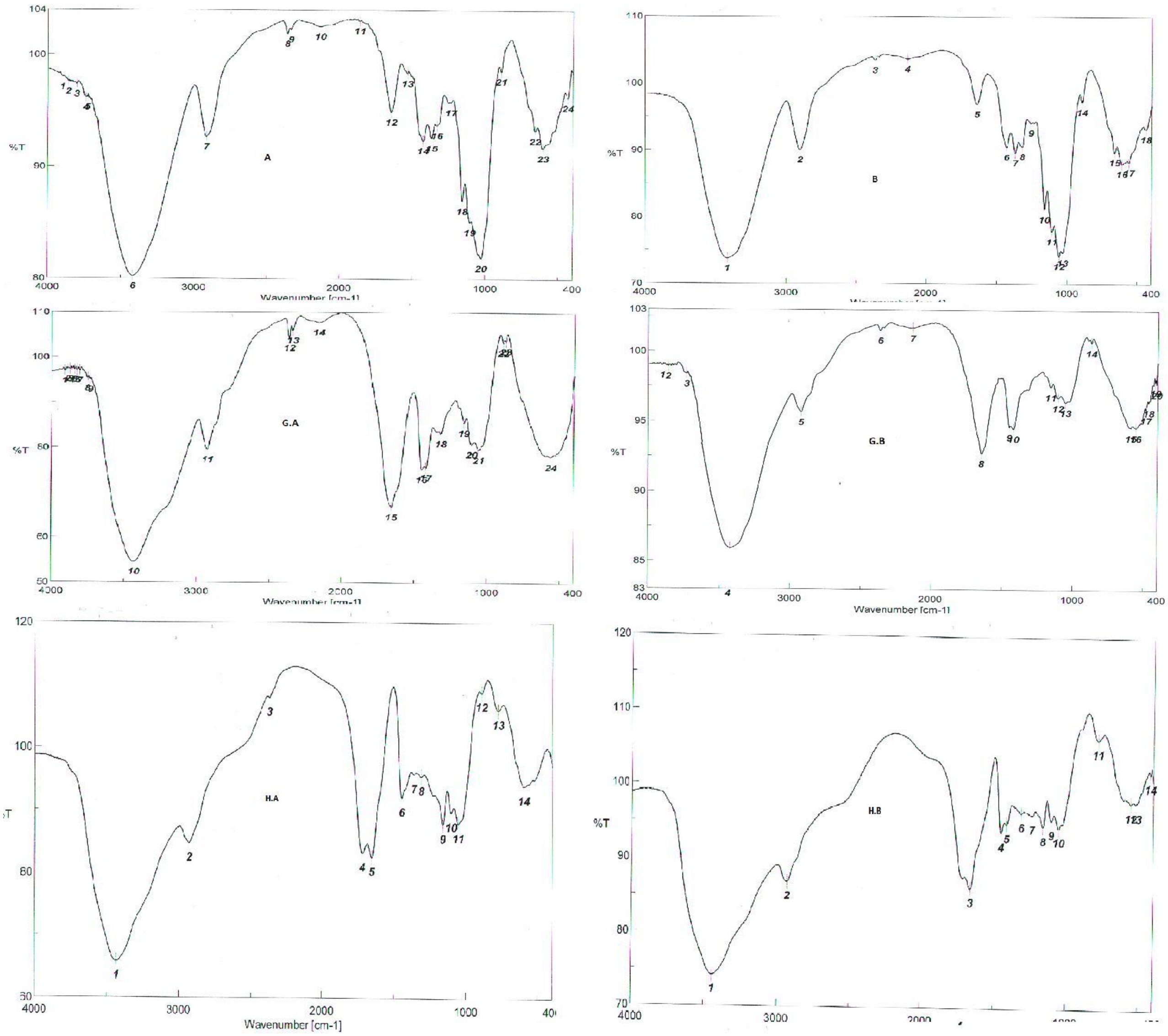


Fig. 5 I.R Spectra of:

Left – one stage pulping sample [A]: A- ungrafted cellulose. G.A- acrylamide grafted cellulose, H.A- acrylamide grafted cellulose after base hydrolysis.

Right- two stage pulping sample [B]: A- ungrafted cellulose. G.B- acrylamide grafted cellulose, H.B- acrylamide grafted cellulose after base hydrolysis.

The IR spectrum of ungrafted corn husks cellulose (figures A and B) showed 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. 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 [35]. Figures G.A and G.B showed the IR spectrum of the acrylamide grafted cellulose exhibited the new absorption bands at 1658 and1649cm^{-1} which were attributed to the C=O of the amide group. Also the O-H band and C-O-C band intensities at 3428 and 1109 cm^{-1} decrease after grafting and after hydrolysis this is because of the degradation of the glucose units. In figures H.A and H.B it was shown that a new band appears at 1720cm^{-1} that corresponding to the carbonyl group of COOH which proofs the base hydrolysis of the amide group giving the carboxyl group. The ratio of band intensity at 1430 to the band intensity at 900 cm^{-1} express the crystallinity index of the sample, this is reported in table (7) [36, 37].

Table 7: crystallinity indexes of the two types of ungrafted, grafted and hydrolysed grafted pulp.

Sample		Band I at 1430	Band I at 900	Crystal. index
Cellulose	A	1.4	0.6	2.33
	B	1.3	0.75	1.73
Grafted cellulose	A	0.6	0.4	1.5
	B	0.36	0.25	1.44
Hyd. Grafted cellulose	A	0.2	0.25	0.8
	B	0.2	0.27	0.74

From this table we note that the crystallinity index decreases by grafting and decreases again after the hydrolysis of the grafted sample. This may be related to the penetration of the hydrophilic monomer molecules in the fibers. This was also noted from the values of WRV that increase by grafting and hydrolysis. Also from the table, we noted that the crystallinity index of the one stage pulp (PAA only) is higher than that of the two stages pulp (NaOH/PAA), this is because the treatment of the fibers first with NaOH decreases the crystalline region and lignin that is clear from the chemical measurements of the crystallinity %. Because the amorphous region of the two stages pulp is higher than that of the one stage pulp; we also note that the G.E% at the same conditions in the two stages pulp is higher than that of the one stage pulp. This has appeared in the N% and the WRV. Increase of the G.E% increases the number of active sites that absorbs Ni ions from its solution.

3.3 Factors affecting metal ion sorption.

We note that with increasing G.E%, the WRV and WAV were increased due to the incorporation of the hydrophilic amide group. Also the base hydrolysis of the grafted samples converts most of the amide groups to the carboxyl groups that also is more hydrophilic than amide groups. Increasing the swelling properties and the negative charge of the fibers makes them more efficient in metal ion sorption. Here we study some factors that affect the adsorption of Ni ions on the surface of acrylamide grafted corn husks cellulose and hydrolyzed grafted corn husks cellulose.

3.3.1 Effect of pH.

pH is one of the most important factors that affects the adsorption of Ni on the ion exchanger. It not only affects the surface charge of the adsorbent, but also affects the ionization degree of the adsorbate. We note that by raising pH value; the adsorption increases till neutral medium. After pH 7, adsorption starts to decrease. This is because at low values of pH a competition between Ni ions and H ions occurs that retards Ni ions from adsorption [37] while raising the pH gradually decreases the H^+ ion concentration which gives a chance to Ni ions to be adsorbed. But at high pH values (alkaline medium) the fibers are more compact and Ni ions are precipitated as $Ni(OH)_2$. Because the hydrolyzed grafted sample contains acidic COOH group instead of $CONH_2$ group and the carboxyl group is more sensitive to the alkaline medium, the activity% begins to decrease after pH 4[38].

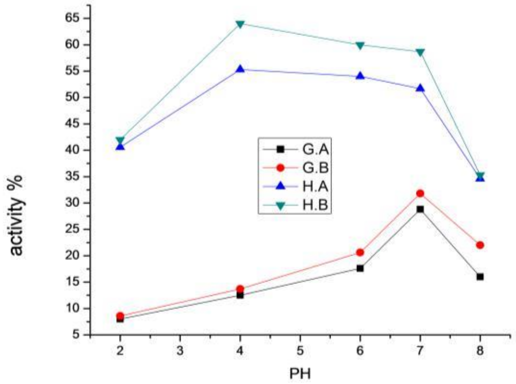


Fig.6 Effect of P^H of the medium on the metal ion sorption

3.3.2 Effect of amount of the ion exchanger.

By increasing the amount of the ion exchanger, the amount of removed Ni increases. This may be attributed to increasing the active sites available for adsorption process [39].

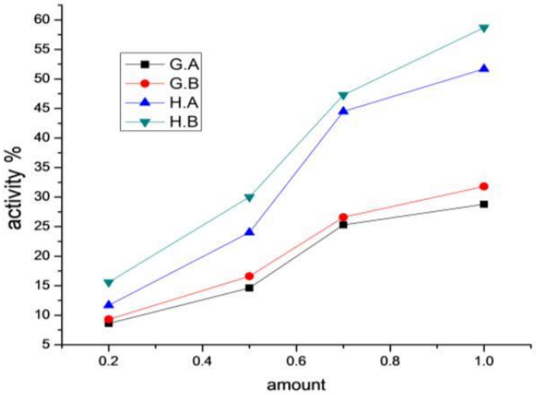


Fig.7 Effect ion exchanger amount on the metal ion sorption

3.3.3 Effect of adsorption time.

By increasing the time of adsorption process the amount of removed Ni increases till 1 hour the activity% increase slowly afterwards. This may be attributed to decreasing the active sites available for adsorption process after formation of a layer of Ni ions on the surface of the adsorbent.

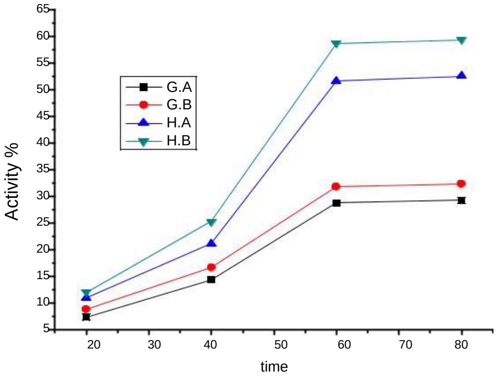


Fig.8 Effect time on the metal ion sorption

3.3.4 Effect of adsorption temperature

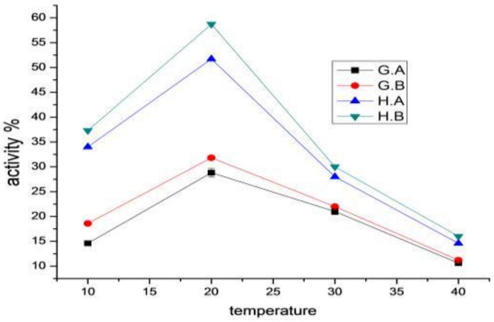


Fig.9 Effect medium temperature on the metal ion sorption

The activity% of the ion exchanger reaches its maximum value at 20^{o} C while after that it decreases by increasing temperature may because of liberation of Ni ions from the ion exchanger surface.

4 Conclusions

A polycarboxylate chelating ligand was successfully synthesized by base hydrolysis of polyacrylamide grafted corn husks cellulose, 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: 3gm Monomer: 0.2gm potassium persulfate, for 2 hrs at 70^{0}C.The polymeric ligand gives good adsorption capacity toward Ni, and this was found to be pH-dependent. The low-cost production of the corn husks cellulose-based polycarboxylate ligand could be considered a promising candidate for waste water treatment because the activity %was up to 58.7%from aqueous media by soaking 1 gm of the ion exchanger in 30 ml of the waste water containing 1500ppm Ni for 1 hr at 20^0 C and 7 P^H. The reusability of the polymeric ligand can be performed by dilute solution of hydrochloric acid.

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