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Synthesis and Characterization of Modified Cellulose and Their Use for Removal of Heavy Metal Ions from Aqueous Solution

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Abstract: In present study an attempt has been made to prepare new polymers depending on Cellulose viscous pulps to study the adsorption activity for removal of heavy metal ions from single aqueous solution. Barley and Corn Straw have been used for the extraction of crude pulps. Grafted viscous pulp has been prepared by using acrylamide as a monomer and benzoyl peroxide as an initiator in different ratios at different conditions of temperature and time. Epichlorohydrin was used as cross linking agent under the optimum conditions of grafting for the preparation of Grafted cross linked viscous pulps. The grafting percentage, grafting efficiency percentage and swelling behavior of new polymers were also studied. The structures of these compounds were established by using FTIR and elemental analysis. For the removal of chromium and nickel ions from an aqueous single metal solution the graft pulp copolymer and grafted crosslink viscous pulps were used as adsorbents. The results of the present study revealed that the ratio of pulp to monomer 1:4g/g, ratio of cellulose to initiator 1: 0.3g/g, grafting time 3 hours and grafting temperature 70 °C showed the optimum conditions of grafting. All the polymers synthesized in the present study showed the activity to remove heavy metal ions from an aqueous solution and the maximum activity have been shown when the cross linking agent was used in the synthesis.

Keywords: straw, pulp, copolymerization, acrylamide**,** hydrolysis, crosslinking, metal ions uptake.

INTRODUCTION

Agriculture produces significant amounts of wastes, which contain high quantities of organic matter. There is an increasing interest in the utilization of agricultural residues as a cheap and eco-friendly material for preparation of ion exchangers for removal of heavy metal ions from waste or industrial water [1, 2]. Many agricultural products and residues are a source of cellulose such as, barley straw, corn straw, olive leaves, cotton rice husk, etc. It has been used as an effective material to absorb heavy metal ions from aqueous solutions, Especially as an adsorbent for bi-valence metals ions [3]. Cellulose is the most renewable biomass material available in nature. It is one of the promising materials for the advanced industry.

Cellulose is a carbohydrate homopolymer consisting of β -D-glucopyranose units joined together by β -1,4-glycosidic linkages (Fig-1) [3, 4].

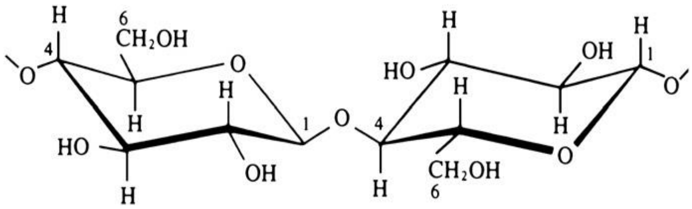

Fig-1: Cellobiose unit: two β-D-glucopyranose unitsjoinedtogetherby β-1, 4-glycosidic linkage

The cellulosic fibre is relatively easy to modify according to presence of three reactive hydroxyl groups on each glucan unit. One method has been studied for the modification of cellulose is graft copolymerization [5]. By grafting of monomer onto Cellulose, the drawbacks can be eliminated. Cellulose graft copolymers are very attractive due to its ability to possess some of the required and important characteristics [6]. Several grafting methods have been developed; however, the method of generating free radicals on cellulose backbone has received considerable attention [5]. The use of benzoyl peroxide as an initiator to generate free radicals that initiate grafting process has been tested by several researchers [7, 8].

Cellulose is a suitable and important substance for the preparation of hydrogels easily by grafting or crosslinking reactions, as its linear shape and structure well provides good reinforcing properties to the network [9]. Cellulose has been selected for fabricating hydrogels according to its safety, hydrophilicity and biodegradability, [10]. Crosslinked polymers Offers a good and exciting range of materials that provide several applications such as waste water treatment [11].

Many possible crosslinking agents can be used to prepare hydrogels such as Epichlorohydrin, aldehydes and aldehydes-based reagents [12, 13].

Epichlorohydrin commonly used as a crosslinking mono-functional agent, effectively stabilizes agricultural residues in order to prepare weak acid cation exchangers and polysaccharide chemistry [14, 15]. Epichlorohydrin was used to form covalent bonds with the carbon atoms on the hydroxyl groups in the cellulose compound [16].

The amount of trapped water by the mesh depends on the structure of the polymer network itself and on the environmental conditions, such as acidity and temperature [17].

Heavy metal ions are the most important toxic components in liquid waste [18]. Adsorption is one of the technically and economically acceptable and suitable methods of treating wastewater containing heavy metal ions and other contaminants such as dyes [19]. Modified cellulosic fibers have been used as adsorbents to remove metal ions from wastewater due to certain properties such as good selectivity, physicochemical stability, adjustable functionality, structural diversity, enhanced surface area and good Porous property [20, 21].

EXPERIMENTAL SECTION

Materials

The Straw of barley and corn were collected from Janzour, Libya and then cuted into small pieces (1– 2 cm), conc sulphuric acid, sodium hydroxide, hydrogen peroxide (30%), Acetone, Acrylamide, benzoyl peroxide (BPO), Epichlorohydrin, Ammonium hydroxide (NH_4OH), pure salts of nickel chloride ($NiCl_2$), and chromium chloride ($CrCl_3$).

Prehydrolysis

The crude Straw of barley and corn were prehydrolyzed to reduce hemicelluloses that form an envelope around cellulose microfibrile. These hemicelluloses were eliminated by using dilute acid (3% based to the oven dry weight) where the raw materials was refluxed at boiling 100◦C and the liquor ratio was 1: 10 for six hours, then filtered and washes with distilled water until neutrality and dried till constant weight [22].

Pulping

In present study the chemical pulping process has been done by alkaline process, pulping carried out using sodium hydroxide only (one stage pulping). Prehydrolyzed sample (1 g, based on dry weight) was pulped using sodium hydroxide (1 N, 3.50 ml) and the liquor ratio was 1: 10 for 6 h at 100˚C under reflux. The resulting pulps were filtered and washed with distilled water till neutrality and dried in air till constant weight [22].

Bleaching

The crude pulps were bleached using alkaline hydrogen peroxide in water consistency of 20%. The crude pulps kept in solution contain 2% H_2O_2, 3% NaOH, 1% $MgSO_4$, (based on dry sample). In water bath for 1 h at 70˚C with shaking and then the sample was washed with distilled water, filtered , followed by 0.05 % hydrochloric acid (HCl) till neutrality, the procedure was repeated another time at the same condition, then dry in air till constant weight [23].

Moisture content%

A known weight of the samples (W) was taken in oven at 100 C for 3 hours under vacuum till constant weight (WI). The loss in weight was recorded as moisture content of the sample. The moisture content % and the dry matter of the samples was calculated using he following equation.

$$\text{Moisture content (\%)} = \frac{W - W1}{W} \times 100$$

Ash content estimation

A known weight of dry unbleached and bleached samples was taken in a pre-weighed silica crucible W. It was burned in muffle furnace in a porcelain crucible at 450˚C for 30 minutes and then at 800 ˚C for 45 minutes, then estimates ash content by calculates the difference in initial and the final weight (W_1).

α - Cellulose estimation

The **α**-Cellulose % was then estimated gravimetrically by putting known dry of bleached and unbleached samples in alkaline media. 50 ml of (17.5% NaOH) was added in two times, the contents were mixed thoroughly till gets homogeneous after that the contents were mixed thoroughly till gets homogeneous, The beaker were covered and left for 35 minutes at ambient temperature. the contents was filtered using distilled water under suction using sintered glass funnel

(G-2) till neutrality then 100 ml of acetic acid (10%) was added slowly followed by distilled water to complete the neutralization process. The temperature must be kept at 20 °C during the whole experiment. The **α**-Cellulose % was then estimated gravimetrically [24].

Grafting

Acrylamide polymerization was performed using benzoyl peroxide (BPO) as an initiator under vacuum in different condition of grafting such as, monomer concentration, initiator concentration, grafting time and grafting temperature, the grafting process was carried out in a polymerization flask (100 mL), and One gram of cellulose fiber was dissolved in 20 mL water and 4 mL acetone in the polymerization flask. And then the necessary amount of monomer and initiator and monomer were added (The reaction flask was closed and transferred to a thermostat and maintained at desired temperature. After the required grafting time the polymerization flask was removed from the thermostat, the sample was filtered and washed with distilled water and then dried at 60 °C (W1). This dried sample was placed in a soxhlet device for 48 hours to dissolve and dispose of the formed homopolymer. After extraction, The sample was then washed and dried at 60 °C until constant weight (W2) [9]. The optimum condition of grafting was performed by using a ratio of 1:3 between cellulose and monomer and 1: 0.3 between cellulose and initiator in 3 hours at 70°C.

Preparation of grafted crosslinked barley and corn straw viscous pulp

The crosslinking processes were performed by using epichlorohydrin as cross linking agent in the presence of ammonium hydroxide NH_4OH. The process has been modified [15]. The cross linking reaction was conducted in a flask containing NaOH (4.0 ml, 50% w/w) and 1.0 g of barley and corn straw dissolving pulp, the flask was heated up to 45°C. The mixture was stirred vigorously by magnetic stirrer for 2 hours at 45°C. The desired quantity of EPH (14 ml) and NH_4OH (18ml) was added slowly and, after 3 hours the viscosity of the solution was increased so that it could not be flipped. After several minutes, a solid polymer was obtained, Acetone was added and heating was continued for 30 min. After cooling, the polymer is filtered and washed with distilled water several times. The polymer was dried in drying oven at 50°C for 12 hours and finally granulated to the desired particles. The powders (crosslinking pulp) were grafted with acrylamide in the presence of benzoyl peroxide as initiator under the optimum condition of grafting without crosslinking agent. The adsorbents polymers were established using FTIR and elemental analysis.

Base hydrolysis of the grafted and the crosslinked copolymers

To obtain better absorption specifications, the amide group was changed to caroxylate group, known weight of 0.5 gm of the grafted sample and the grafted crosslinked samples were mixed with 50ml of 0.1N NaOH solution and the mixture was refluxed on a hot plate for 1 hr. After hydrolysis the reaction mixture was washed with distilled water followed by acidic solution (2.0 N HCl) and washed again with distilled water till neutralization [25]. The prepared hydrolyzed pulps were established using FT-IR.

Determination of Metal uptake (Adsorption experiments)

The adsorption process was performed by stirring 0.1 g of grafted and grafted crosslinked viscous pulps as ion exchangers in 20 ml solution containing 25 ppm ions of (Cr^{+3} and Ni^{+2}) at different times (2,4,6,8 hours). After filtration, the remaining metal ions in the filtrate were determined using Atomic Absorption (AA) spectrometer [26].

RESULTS AND DISCUSSION

Specification of the raw materials

The specification of the raw materials used in present study (straw of barley and corn) are listed in table-1.

Table-1: Chemical analysis of the bleached and unbleached of Barley and corn dissolving pulps.

Pulp	Moisture %	α-cellulose %	Ash %
Unbleached (Barley)	5.8	81.46	3.90
Bleached (Barley)	7.3	87.63	1.28
Unbleached (Corn)	6.5	84.29	4.66
Bleached (Corn)	8.1	86.67	1.9

Grafting of acrylamide copolymerization onto barley and corn straw viscous pulp in the presence of crosslinking agent

The grafting of acrylamide onto barley and corn straw dissolving pulp in presence of epichlorohydrin as crosslinker was performed under the optimum condition of grafting of acrylamide onto barley straw dissolving pulp, monomer (3.0 g/g), initiator BPO (0.2 g/g), time (3.0 hours) and temperature (70 °C).

Epichlorohydrin as crosslinker can pentetrate the crystalline region of the pulp and form bands with hydroxyl groups (at C_2 and/or C_3) of the adjacent cellulose chains, this reaction may influences the grafting process of the pulp.

Table-2: Effect of cross-linking agent on grafting parameters (barley straw dissolving pulp.

Sample	G%	G.E%	WRVgm/gm	Na binding capacity m.eqwt/gm	N%
Barley	163	46	625	1285	11.09
barley cross linked	185	64	845	1335	15.82

Grafting condition: pulp =1g, monomer = 3.0 g, reaction time= 3 hr, BPO = 0.2 gr, Temp = 70°C.

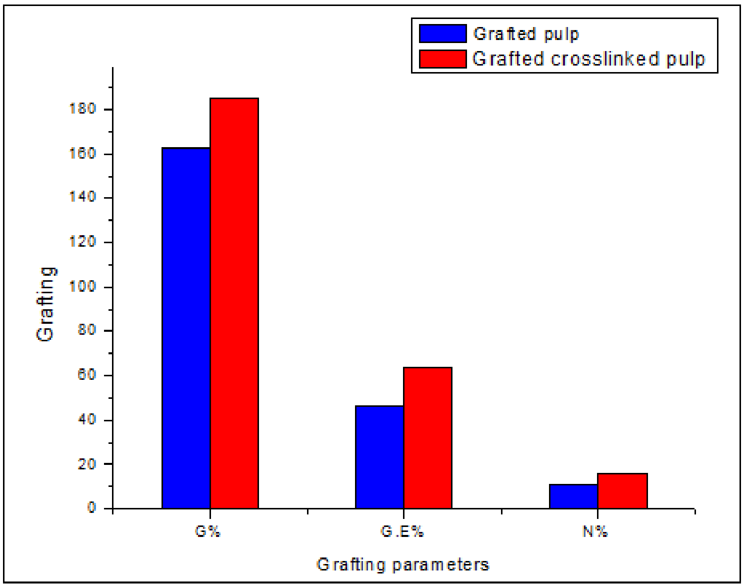

Fig-2: Effect of cross-linking agent on different grafting parameters (G%, G.E %, N_2) of grafted wheat straw viscous pulp.

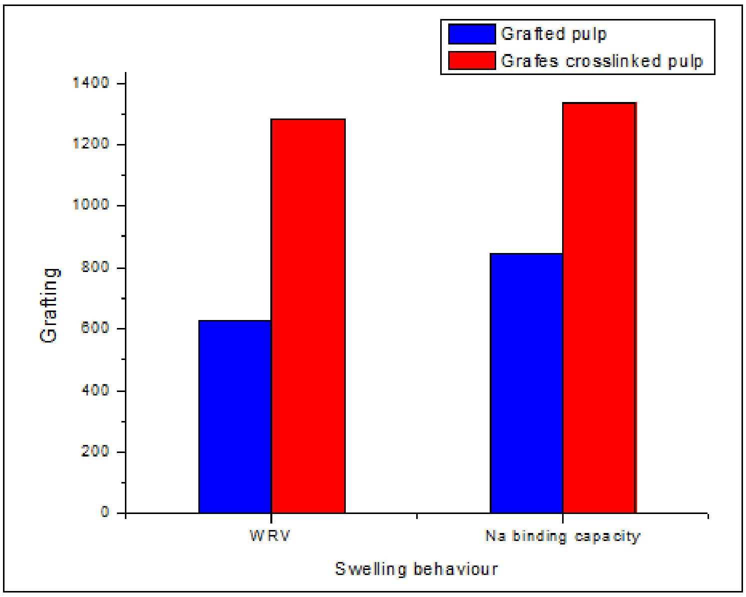

Fig-3: Effect of cross-linking agent on (WRV) and sodium binding capacity of grafted wheat straw viscous pulp.

Table-3: Effect of cross-linking agent on different grafting parameters of corn straw viscous pulp.

sample	G%	G.E%	WRVgm/gm	Na binding capacity m.eqwt/gm	N%
Grafted corn	65	35	585	1328	10.49
Crosslinked grafted corn	155	66	715	1483	14.66

Grafting conditions: pulp (1.0g), monomer (3.5 g), reaction time(3 hr), BPO (0.2 g).

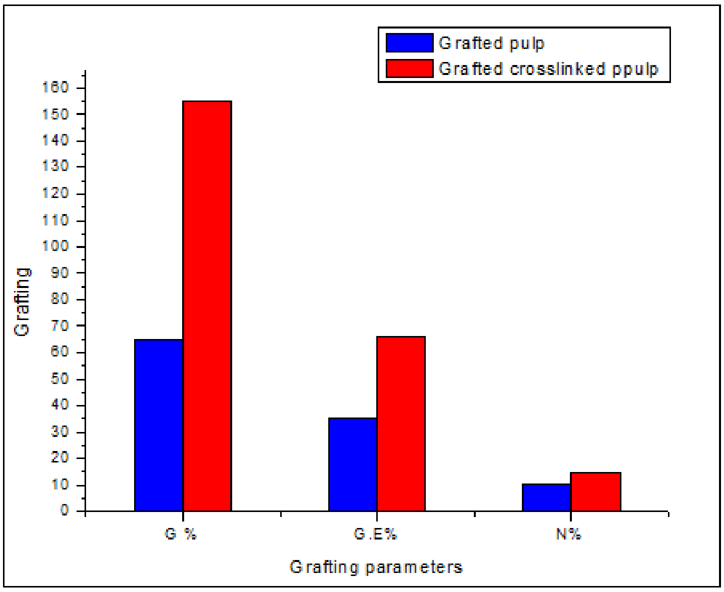

Fig-4: Effect of cross-linking agent on different grafting parameters (G%, G.E %) of corn straw viscous pulp.

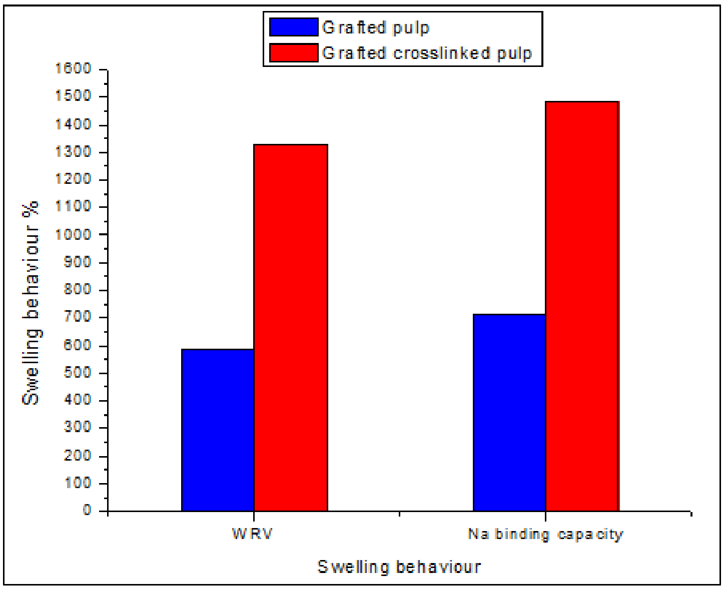

Fig-5: Effect of cross-linking agent on WRV and sodium binding capacity

Tables-2, 3 and figures-2, 3, 4, 5 explains the comparison between the barley and corn grafted straw viscous pulp and grafted crosslinked barley viscous pulp in Grafting (G %), grafting efficiency (G.E %), water retention value (WRV), sodium binding capacity and nitrogen %. The results of the present study reveals that the grafting parameters, water retention value (WRV) and the sodium binding capacity had a positive relationship while using the cross linking agent in the grafting process. This is due to the increasing amorphous in the pulp backbone, resulting in improve the swelling properties of the produced crosslinked grafted pulp.

Metal ions uptake

Metal ions uptake of grafted barley and grafted crosslinked straw viscous pulp.

Metal ions uptake of chromium (Cr^{+3})

Table-4: Effect of time on chromium ions (Cr^{+3}) sorption by using grafted barley straw dissolving pulp and grafted crosslinked pulp.

Time (hour)	Activity %	
	Grafted pulp	Grafted Crosslinked pulp
2	77.68	94.77
4	82.5	95.9
6	86.5	97.3
8	93.5	98.2

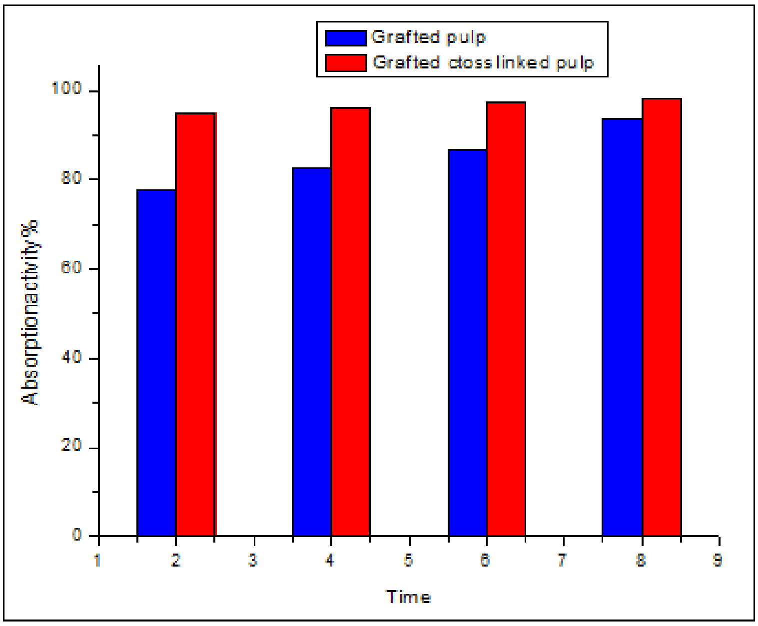

Fig 6: Effect of time on Cr^{+3} ions sorption by using grafted and grafted crosslinked barley straw viscous pulp.

Metal ions uptake of nickel (Ni^{+2})

Table-5: Effect of time on Nickel ions (Ni^{+2}) sorption by using grafted and grafted crosslinked barley straw viscous pulp.

Time (hour)	Activity %	
	Grafted pulp	Grafted Crosslinked pulp
2	74.3	91.0
4	80.5	92.8
6	86.4	96.8
8	94.6	97.5

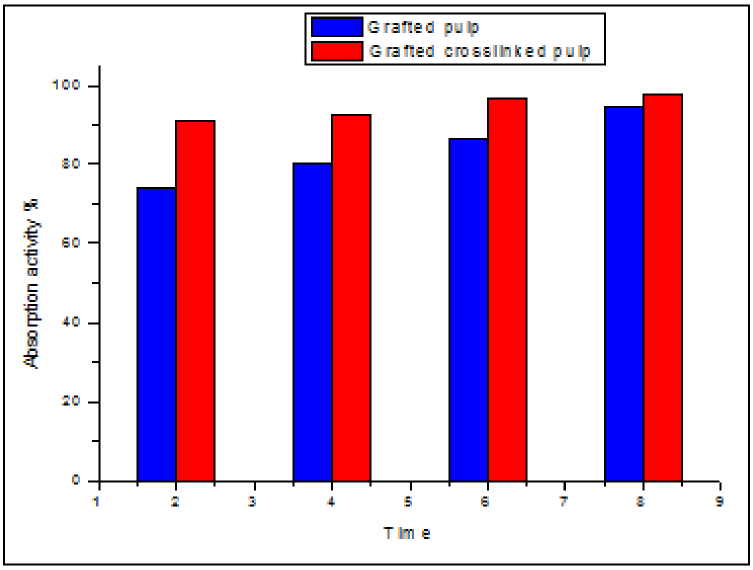

Fig-7: Effect of time on Ni^{+2} ions sorption by grafted and crosslinked barley straw viscous pulp.

Tables-4, 5 and figure-6, 7 shows the comparison of agitation time effect on the adsorption capacity of Cr^{+3} and Ni^{+2} ions by using grafted and grafted crosslinked barley straw viscous pulp as adsorbents. Results shows that the percent Cr^{+3} and Ni^{+2} removal. The activity of sorption in case of grafted crosslinked viscous pulp was higher than in case of grafted viscous pulp. The sorption of these species should have a direct relationship to the capacity of the graft copolymers to swell in water. The prepared hydrogels were challenged with Cr^{+3} and Ni^{+2} metal ions. It was noticed that the metal ions uptake percentage of Cr^{+3} ions was higher. This can be attributed to Cr^{+3} ions has smaller ionic radius which increases its access to function groups in the interior matrix of the polymer [20].

Metal ions uptake of chromium (Cr^{+3}) and nickel (Ni^{+2}) ions by using hydrolyzed grafted barley straw in presence of epichlorohydrin

Table-6: Effect of base hydrolysis of grafted barley and grafted crosslinked viscous pulp on chromium and nickel ions (Cr^{+3}, Ni^{+2}) sorption

Time (hour)	Sample	Activity %	
		Cr^{+3}	Ni^{+2}
4	Grafted pulp	82.5	83.8
4	Grafted pulp after hydrolysis	89.6	92.8
4	Grafted Crosslinked	95.9	92.8
4	Grafted Crosslinked pulp after hydrolysis	98.5	98.4

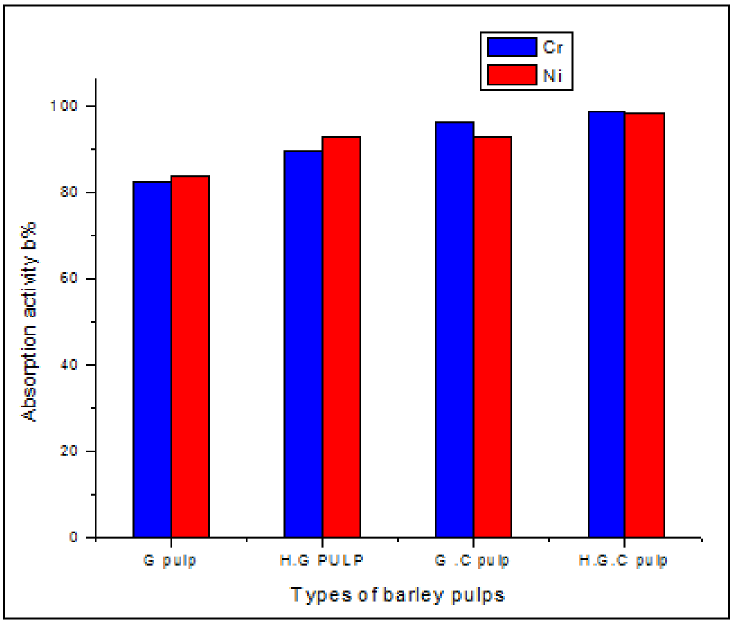

Fig-8: Effect of hydrolysis of grafted and grafted crosslinked barley straw viscous pulp on sorption of (Cr^{+3}, Ni^{+2}) ions.

Where G barley is barley straw grafted pulp, H.G barley is grafted pulp after hydrolysis, G. cross is grafted crosslinked pulp and H.G cross is grafted crosslinked pulp after hydrolysis.

Table-6 and figure-8 explains the comparison in the activity of metal ions (Cr^{+3}, Ni^{+2}) sorption between the copolymers before and after hydrolysis. It can be noted that, the metal sorption increases by hydrolysis the copolymers because the carboxyl groups are more hydrophilic than amide groups. Partial hydrolysis of amide groups increased water uptake of hydrogel and increased the tendency of functionalized hydrogel, leading to enhanced metal ions sorption [22].

Metal ions uptake of grafted corn and grafted crosslinked straw viscous pulp

Metal ions uptake of chromium (Cr^{+3})

Table-7: Effect of time on chromium ions (Cr^{+3}) sorption by using grafted and grafted crosslinked corn straw viscous pulp

Time (hour)	Activity %	
	Grafted pulp	Grafted Crosslinked pulp
2	87.4	92.07
4	88.6	94.9
6	90.7	95.8
8	92.5	97.3

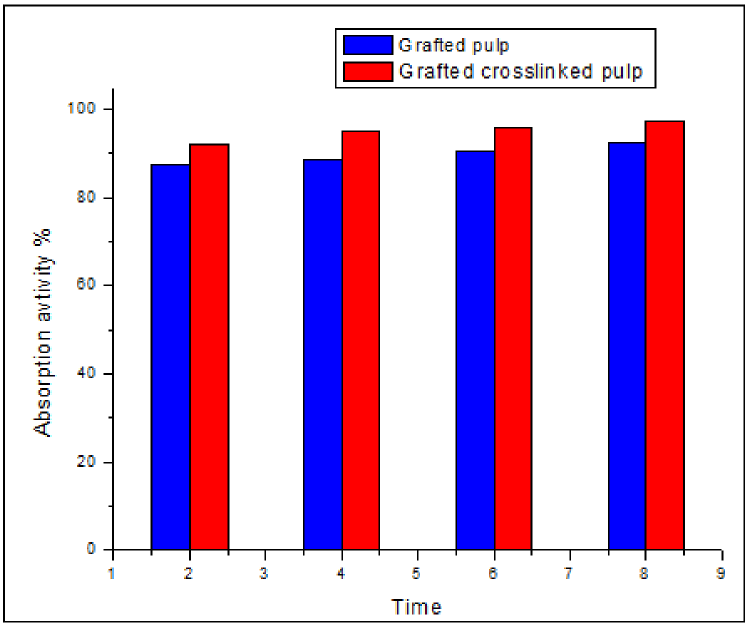

Fig-9: Effect of time on Cr^{+3} ions sorption by using grafted and crosslinking corn viscous pulp.

Metal ions uptake of chromium (Ni^{+2})

Table-8: Effect of time on nickel ions (Ni^{+2}) sorption by using grafted and grafted crosslinked corn straw dissolving pulp.

Time (hour)	Activity %	
	Grafted pulp	Grafted Crosslinked pulp
2	80.3	91.6
4	82.1	93.1
6	84.8	95
8	86.6	97

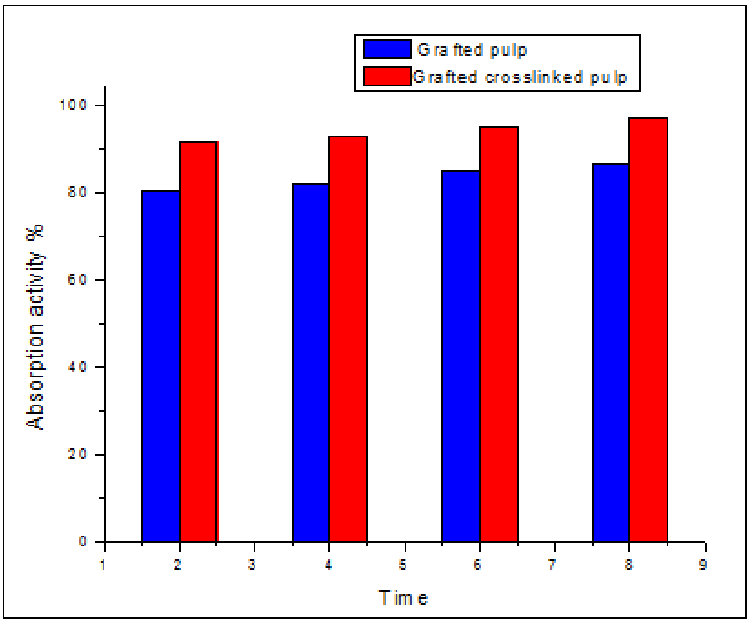

Fig-10: Effect of time on Ni^{+2} ions sorption by grafted and grafted crosslinked corn straw viscous pulp.

Table-7, 8 and figure-9, 10 shows the sorption of Cr^{+3} and Ni^{+2} ions by using grafted corn straw pulp and grafted crosslinked corn straw pulp. The activity of chromium sorption ion by using grafted crosslinked corn straw viscous pulp as adsorbent more than the activity percent in case of grafted barley straw viscous pulp without crosslinker. These results according to the hydrogel have more ability to swell in water.

Metal ions uptake of chromium (Cr^{+3}) and nickel (Ni^{+2}) ions using hydrolyzed grafted corn straw in presence of epichlorohydrin.

Table-9: Effect of base hydrolysis of grafted and grafted crosslinked corn straw viscous pulp on chromium and nickel ions (Cr^{+3}, Ni^{+2}) sorption

Time (hour)	Sample	Activity %	
		Cr^{+3}	Ni^{+2}
4	Grafted pulp	88.6	82.1
4	Grafted pulp after hydrolysis	97.2	95.8
4	Grafted Crosslinked	94.9	93.1
4	Grafted Crosslinked pulp after hydrolysis	97.2	96.1

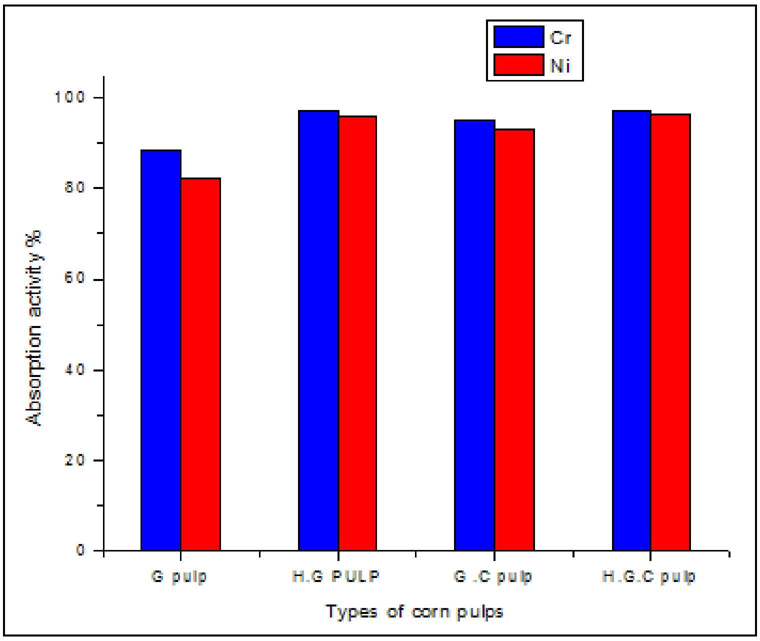

Fig-11: Effect of hydrolysis on grafted and grafted crosslinked corn straw viscous pulp for sorption of (Cr^{+3}, Ni^{+2}) ions.

Where G corn is corn straw grafted pulp, H.G corn is grafted pulp after hydrolysis, G. cross corn is grafted crosslinked pulp and H.G cross corn is grafted crosslinked pulp after hydrolysis.

Table-9 and figure-11 the results reveal the comparison in the activity percent for removal metal ions between the copolymers before and after hydrolysis. The metal sorption increases by hydrolysis the grafted copolymers because the carboxyl groups are more hydrophilic than amide groups. Hydrolysis of the hydrogel affected the metal ions uptake percentage and retention capacity by activation of functional groups of grafting chains by opening up the hydrogel network and activating amide groups into more active groups, such as carboxyl groups, which have a stronger tendency to chelate and exchange ions [22]. From Table 8 it is seen that the metal ions uptake percentage and retention capacity of hydrolyzed grafted straw pulp viscous pulps was higher than the grafted viscous straw pulp before hydrolysis.

SUMMARY AND CONCLUSION

Summary

In the present study water insoluble cellulose (Cellulose based hydro gels) possessing properties such as hydrophilicity, biodegrability, biocompatibility, transparency, low cost and non toxicity were synthesized. For the synthesis of cellulose based hydro gels barley and corn straw viscous pulps were grafted in the presence of epichlorohydrin as cross linking agent. The grafting of barley and corn straw pulps was carried out under the optimum conditions (without cross linking agent).

The ratio of pulp to monomer pulp 1:4g/g, and cellulose to initiator 1:0.3g/g, grafting time 3 hours and grafting temperature was taken as 70°C. Produced copolymers were hydrolyzed to create more hydrophilic function groups. The structure of the synthesized copolymers was established by using FTIR spectroscopy.

The results of the present study reveals that the grafting (G %), grafting efficiency (G.E %), water retention value (WRV) and the sodium binding capacity had a positive relationship while using the cross linking agent in the grafting process. The grafted copolymer synthesized in present study was used as adsorbent for different heavy metals such as chromium and nickel. The sorption capacity of grafted cross linked copolymers to remove chromium and nickel ions from the water was higher than the grafted copolymers.

CONCLUSION

In present study grafted cross-linked copolymers showed better activities like biocompatibility and removal of heavy metals like chromium and nickel from water than the grafted copolymers.

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