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# Graft Copolymers of Acrylonitrile onto Dextrin for Use in Separation Technologies

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The use of polymers in enrichment and separation technologies has attracted a lot of interest in recent times. To develop low-cost and environmentally friendly technologies for the removal of metal ions from water systems, graft copolymers based on dextrin were synthesized by grafting poly(acrylonitrile) onto it. The optimum grafting conditions were evaluated for grafting by varying the nature and amount of solvent, changes in concentration of monomer and initiator, reaction time and temperature. Graft copolymers were further functionalized by partial hydrolysis, and were characterized by water uptake, FTIR, SEM and elemental analysis. Sorption of Fe<sup>2+</sup> and Cr<sup>6+</sup> ions on graft copolymers were investigated as a function of percent grafting, change in metal ion concentration, temperature and pH, to define their end-uses in separation technologies.

**Keywords** FTIR, graft copolymers, sorption studies

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## INTRODUCTION

The problem of nonbiodegradability and the prohibitive cost of synthetic polymers can be reduced and managed by the development of novel materials based on alternate cost-effective and eco-friendly materials based on biopolymers. These alternative materials can be effectively used in management of the environment, like the removal of toxic metal ions or other effluent like phenolics, pesticides and insecticides from water systems, drug delivery devices and packaging materials. Polymer supports based on natural polymers like cellulose, starch, dextrin and guar gum are finding increased use in low-cost technologies for the removal of metal ions from water bodies and in biotechnological applications such as protein adsorption, separation and enrichment of nucleic acids, enzymes and bio-organic molecules. Graft copolymerization is a conventional method to incorporate desired functional groups onto a dextrin backbone. A graft copolymer is formed when growing polymer chains are attached to the polymeric backbone by means of chemical bonds [1].

Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. Dextrins are mixtures of linear  $\alpha$ -(1,4)-linked D-glucose polymers. Because of low viscosity and solution stability at high concentration, dextrin finds uses mainly in the manufacture of adhesives used for envelopes, gummed tapes, postage stamps and bottle labeling [2]. Intermediate and high viscosity dextrins are used in the paper industry for making pigments. Graft copolymers of dextrin with 2-acrylamido-2-methyl-1-propane sulphonic acid were synthesized by free radical initiation using the potassium monopersulphate (PMS)/thiourea pair in an inert atmosphere [3]. Dextrin grafted with poly(AAm), produced by  $Ce^{4+}$  ions initiation method in an aqueous medium [4], were reported as water-based primer coatings. Polyacrylic acid/dextrin adducts were prepared by free radical polymerization of highly concentrated, partially neutralized acrylic acid using the  $Na_2S_2O_8/Na_2S_2O_3$  redox system [5]. Dextrin-*g*-poly(glycidyl methacrylate) hydrogels were prepared by DeSmedt et al. [6] and rheology and swelling behavior [7] of the network structure was studied. The anionic graft polymerization of methyl methacrylate on the potassium alkoxide derivative of dextrin in DMSO was studied [8]. Applicability of cyclodextrins [9] in textile dyeing and washing processes was investigated. The dextrin derivative surfactants [10] are reported to have highly biodegradable properties, which are lacking in traditional surfactants. Polymerization of acrylamide with dextrin was carried out by using potassium permanganate/citric acid. Hydrogen peroxide/ferrous ions redox system [11] and grafting of polyacrylamide on the dextrin produced coating films that were less susceptible to moisture [12]. Chauhan et al. [13] reported hydrogels of dextrin which have been used to extract  $Fe^{2+}$ ,  $Cu^{2+}$  and  $Cr^{6+}$  ions from their aqueous solutions. Hydrogels were obtained by free radical polymerization [14] of dextrin and vinylacrylate (VA), with different

degrees of substitution and monomer concentration, in water. These hydrogels [15] were studied for their potential in the controlled release of protein (bovine serum albumin).

## EXPERIMENTAL

### Materials and Methods

Dextrin (Lucid Colloids, Jodhpur, India), acrylonitrile (AN) (Merck, Germany), potassium persulphate (KPS) (Ranbaxy, SAS Nagar, India), and ferrous ammonium sulphate (FAS) (CDH, New Delhi, India), were used as received. Ferrous sulphate and chromium oxide (analytical grade, BDH, India) buffer tablets (pH 4.0, 7.0 and 9.2) were used as received.

### Graft Copolymerization

Potassium persulphate (KPS) and ferrous ammonium sulphate (FAS), as redox pair initiator, were used to obtain optimum grafting reaction conditions for the grafting of acrylonitrile (AN) onto dextrin. Optimum grafting conditions were obtained by applying the grafting reaction scheme as one condition was varied for a set of reactions, keeping other reaction parameters constant. The effect of the nature and amount of solvent, concentrations of initiator and monomer, reaction time and reaction temperature on grafting were studied (see Table 1). Graft copolymers were characterized by FTIR, SEM, elemental analysis (see Table 2) and by observing swelling behavior in different solvents.

### Separation of Graft Copolymers

Graft copolymers and homopolymer were separated by solvent extraction method. The reaction mixture was filtered and put into a beaker containing dimethylformamide (DMF) and stirred with an electric stirrer. After some time the reaction mixture was filtered and dried in an oven at 50°C. This process was repeated until the constant weight of the copolymer was obtained. The percent grafting ( $P_g$ ) and percent grafting efficiency (%GE) were calculated and can be expressed as [16]:

$$P_g = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

$$\%GE = \frac{\text{Weight of graft copolymer} - \text{weight of polymer backbone}}{\text{Weight of monomer charged}} \times 100$$

**Table 1:** Grafting parameters of graft copolymerization of AN onto dextrin<sup>a</sup>.

Sr. No.	Solvent	Amount of solvent (ml)	Conc. of monomer (AN) × 10 <sup>-2</sup> mole/L	Initiator concentration × 10 <sup>-2</sup> mole/L			Time in hrs	Temp (°C)	P <sub>g</sub>	%GE
				KPS	FAS	FAS				
1	Dist. H <sub>2</sub> O	10.00	152.51	5.00	4.821	4.821	1.0	60	<b>42.1</b>	<b>52.290</b>
2	Benzene	"	"	"	"	"	"	"	18.6	23.105
3	Dioxane	"	"	"	"	"	"	"	34.2	42.484
4	CCl <sub>4</sub>	"	"	"	"	"	"	"	24.6	30.559
5	Acetone	"	"	"	"	"	"	"	26.4	32.795
6	Dist. H <sub>2</sub> O	5.00	305.0	1.000	9.642	9.642	"	"	20.6	25.590
7	"	10.00	152.51	5.000	4.821	4.821	"	"	<b>42.1</b>	<b>52.290</b>
8	"	15.00	101.6	3.333	3.214	3.214	"	"	45.3	56.273
9	"	20.00	76.25	2.500	2.410	2.410	"	"	46.2	57.391
10	"	25.00	61.01	2.000	1.928	1.928	"	"	<b>54.3</b>	<b>67.453</b>
11	"	"	30.5	"	"	"	"	"	26.1	64.844
12	"	"	91.5	"	"	"	"	"	62.8	52.008
13	"	"	122.0	"	"	"	"	"	79.0	49.068
14	"	"	152.51	"	"	"	"	"	85.0	42.236
15	"	"	"	2.000	"	"	"	"	154.4	38.121
16	"	"	"	4.000	"	"	"	"	<b>155.4</b>	<b>77.217</b>
17	"	"	"	6.000	"	"	"	"	151.5	75.279
18	"	"	"	10.000	"	"	"	"	125.9	62.559
19	"	"	"	6.000	1.928	1.928	"	"	<b>155.4</b>	<b>77.217</b>
20	"	"	"	"	3.857	3.857	"	"	186.7	92.770
21	"	"	"	"	5.785	5.785	"	"	<b>209.3</b>	<b>103.999</b>
22	"	"	"	"	7.714	7.714	"	"	208.1	103.403
23	"	"	"	"	5.785	5.785	1.5	"	153.4	76.223
24	"	"	"	"	"	"	2.0	"	180.3	89.590
25	"	"	"	"	"	"	2.5	"	188.4	93.614
26	"	"	"	"	"	"	3.0	"	162.8	80.894
27	"	"	"	"	"	"	1.0	70	195.5	97.142
28	"	"	"	"	"	"	"	80	182.8	90.832
29	"	"	"	"	"	"	"	90	186.9	92.869
30	"	"	"	"	"	"	"	100	150.1	74.583

<sup>a</sup>Dextrin = 1 g.

**Table 2:** Nitrogen analysis of graft copolymers of AN and dextrin.

Sr. No.	Network	P <sub>g</sub>	Weight of polymer taken (mg)	Percent of nitrogen	Weight of nitrogen (mg)
1	Dex-g-poly(AN)	188.4	1.906	19.18	0.156
2	Dex-g-poly(AN)	209.3	1.789	20.64	0.164

## Characterization of Graft Copolymers

Elemental analysis was conducted using Carlo Erba 1108. FTIR spectra of dextrin and its graft copolymers in KBr pellets were recorded using Thermo Nicolet 6700 spectrometer. Swelling studies (see Tables 3 and 4) were carried out on dextrin graft copolymers in which 100 mg of the copolymer was taken in 20.00 mL of water. Surface water on the swollen polymer was removed by softly pressing between the folds of filter paper and an increase in weight was recorded. Percent swelling (P<sub>s</sub>) was calculated by the following expression [17]:

$$P_s = \frac{\text{Weight of the swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

## Metal Ion Sorption

Graft copolymers of dextrin with polyacrylonitrile were studied for sorption of Fe<sup>+2</sup> and Cr<sup>+6</sup> ions by equilibration method. Various parameters that can affect metal ion sorption were studied, which include ionic strength, temperature and pH. Metal ions sorbed from their aqueous solutions and analyzed for the concentration of rejected ions on a DR 2010 spectrophotometer (Hach, Co., USA) by using standard pillow reagents. The spectrophotometer has high sensitivity with maximum limits of 3.0 and 0.6 mg/L, respectively, of Fe<sup>+2</sup> and Cr<sup>+6</sup> ions. Thus, the residual filtrate was diluted to reach this range. All weights were taken on Denver TR-203 Balance having minimum readability of 1.0 mg. Dextrin and graft copolymers of dextrin with poly(AN) at different P<sub>g</sub> were studied for ion sorption by immersion for 60 minutes in

**Table 3:** Swelling study of graft copolymers in water (before hydrolysis).

Sr. No.	Percent grafting (P <sub>g</sub> )	Percent swelling (P <sub>s</sub> )			
		After 2 h	After 4 h	After 6 h	After 24 h
1	54.3	1732	3640	3853	3944
2	85.0	187	185	203	272
3	155.4	167	133	198	276
4	186.7	109	112	105	154
5	209.3	106	98	108	115

Graft copolymer = 100 mg, amount of water = 20 mL, temperature = 25°C.

**Table 4:** Swelling study of graft copolymers in water (after hydrolysis).

Sr. No.	Percent grafting ( $P_g$ )	Percent swelling ( $P_s$ )			
		After 2 h	After 4 h	After 6 h	After 24 h
1	54.3	1884	4098	5923	8214
2	85.0	3596	4977	7734	9788
3	155.4	4983	7142	9971	13495
4	186.7	2615	4759	7267	10559
5	209.3	5532	8501	11793	17809

Graft copolymer = 100 mg, amount of water = 20 mL, temperature = 25°C.

25.00 mL solutions of metal ions of known concentration. Results of analysis are presented in Tables 5 to 12. Different relationships [18] used to express sorption behavior are as follows:

$$\text{Percent Uptake } (P_u) = \frac{\text{amount of metal ions sorbed}}{\text{total amount of metal ions present}} \times 100$$

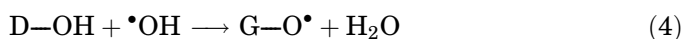
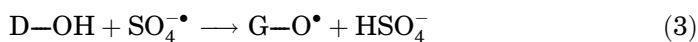
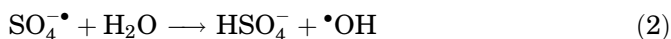
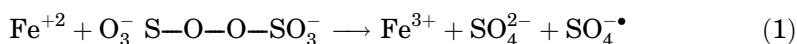
$$\text{Partition Coefficient } (K_d) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of dry polymer (g)}}$$

$$\text{Retention Capacity } (Q_r) = \frac{\text{amount of metal ion in the polymer (mEq)}}{\text{weight of dry polymer (g)}}$$

## RESULTS AND DISCUSSION

For free radical polymerization using potassium persulphate (KPS) and ferrous ammonium sulphate (FAS) as redox pair initiator, the optimum reaction conditions for grafting acrylonitrile onto dextrin were obtained. The mechanism of grafting reactions can be explained by the following equations [19]:

### Initiation



**Table 5:** Sorption studies of  $\text{Cr}^{+6}$  ions on dextrin and its graft copolymers<sup>a</sup> as a function of percent grafting ( $P_g$ ).

Sr. No.	Polymer	$P_g$	Amount of $\text{Cr}^{6+}$ in feed (mg/L)	Amount of $\text{Cr}^{6+}$ sorbed (mg)	Amount of $\text{Cr}^{6+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_r$ ) (meq/g)
1	Dextrin		5.00	0.511	4.489	10.22	113.83	2.358
2	Dex-g-poly(AN)	54.3	"	0.0675	4.932	1.35	13.68	0.311
3	Dex-g-poly(AN)	85.0	"	0.0565	4.943	1.13	11.42	0.261
4	Dex-g-poly(AN)	155.4	"	0.7885	4.211	15.77	187.22	3.639
5	Dex-g-poly(AN)	186.7	"	0.6655	4.334	13.31	153.53	3.071
6	Dex-g-poly(AN)	209.3	"	0.797	4.203	<b>15.94</b>	189.62	3.678

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, temperature = 25°C.



**Table 6:** Sorption studies of  $\text{Fe}^{2+}$  ions on dextrin and its graft copolymers<sup>a</sup> as a function of percent grafting ( $P_g$ ).

Sr. No.	Polymer	$P_g$	Amount of $\text{Fe}^{2+}$ in feed (mg/L)	Amount of $\text{Fe}^{2+}$ sorbed (mg)	Amount of $\text{Fe}^{2+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_r$ ) (meq/g)
1	Dextrin		5.00	0.3715	4.6285	7.43	80.26	0.531
2	Dex-g-poly(AN)	54.3	"	0.1555	4.8445	3.11	32.09	0.222
3	Dex-g-poly(AN)	85.0	"	0.6915	4.3085	13.83	160.49	0.988
4	Dex-g-poly(AN)	155.4	"	0.683	4.317	13.66	158.21	0.976
5	Dex-g-poly(AN)	186.7	"	0.8665	4.1335	17.33	209.63	1.238
6	Dex-g-poly(AN)	209.3	"	1.1425	3.8575	<b>22.85</b>	296.18	1.632

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, temperature = 25°C.

**Table 7:** Sorption studies of  $\text{Cr}^{+6}$  ions as a function of change in metal ion concentration at optimum graft conditions of dextrin graft copolymer<sup>a</sup>.

Sr. No.	Polymer	P <sub>g</sub>	Amount of $\text{Cr}^{6+}$ in feed (mg/L)	Amount of $\text{Cr}^{6+}$ sorbed (mg)	Amount of $\text{Cr}^{6+}$ rejected (mg)	Percent ion uptake (P <sub>u</sub> )	Partition coefficient (K <sub>d</sub> ) (g/g)	Retention capacity (Q <sub>t</sub> ) (meq/g)
1	Dex-g-poly(AN)	209.3	5.00	0.788	4.212	15.76	187.08	3.637
2	Dex-g-poly(AN)	"	25.00	4.303	20.697	17.21	207.88	19.858
3	Dex-g-poly(AN)	"	50.00	10.065	39.935	20.13	252.03	46.454
4	Dex-g-poly(AN)	"	75.00	16.02	58.98	21.36	271.62	73.939
5	Dex-g-poly(AN)	"	<b>100.00</b>	21.99	78.01	21.99	281.89	101.493

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, temperature = 25°C.

**Table 8:** Sorption studies of  $\text{Fe}^{2+}$  ions as a function of change in metal ion concentration at optimum graft conditions of dextrin graft copolymer<sup>a</sup>.

Sr. No.	Polymer	P <sub>g</sub>	Amount of $\text{Fe}^{2+}$ in feed (mg/L)	Amount of $\text{Fe}^{2+}$ sorbed (mg)	Amount of $\text{Fe}^{2+}$ rejected (mg)	Percent ion uptake (P <sub>i</sub> )	Partition coefficient (K <sub>d</sub> ) (g/g)	Retention capacity (Q <sub>i</sub> ) (meq/g)
1	Dex-g-poly(AN)	209.3	5.00	1.1435	3.8565	22.87	296.51	1.634
2	Dex-g-poly(AN)	"	25.00	6.5275	18.472	26.11	353.36	9.325
3	Dex-g-poly(AN)	"	50.00	14.995	35.005	29.99	428.37	21.421
4	Dex-g-poly(AN)	"	75.00	28.125	46.875	37.50	600.00	40.179
5	Dex-g-poly(AN)	"	<b>100.00</b>	44.33	55.67	44.33	796.29	63.329

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, temperature = 25°C.

**Table 9:** Sorption studies of  $\text{Cr}^{+6}$  ions as a function of change in temperature at optimum graft conditions of dextrin graft copolymer<sup>a</sup>.

Sr. No.	Polymer	Temp (°C)	Amount of $\text{Cr}^{6+}$ in feed (mg/L)	Amount of $\text{Cr}^{6+}$ sorbed (mg)	Amount of $\text{Cr}^{6+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_t$ ) (meq/g)
1	Dex-g-poly(AN)	25	100.00	21.99	78.01	21.99	281.89	101.493
2	Dex-g-poly(AN)	30	100.00	20.33	79.67	20.33	255.18	93.832
3	Dex-g-poly(AN)	35	100.00	11.45	88.55	11.45	129.31	52.847
4	Dex-g-poly(AN)	40	100.00	6.66	93.34	6.66	71.35	30.739
5	Dex-g-poly(AN)	45	100.00	8.87	91.13	8.87	97.33	40.939

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min,  $P_g = 209.3$ .

**Table 10:** Sorption studies of  $\text{Fe}^{2+}$  ions as a function of change in temperature at optimum graft conditions of dextrin graft copolymer<sup>a</sup>.

Sr. No.	Polymer	Temp (°C)	Amount of $\text{Fe}^{2+}$ in feed (mg/L)	Amount of $\text{Fe}^{2+}$ sorbed (mg)	Amount of $\text{Fe}^{2+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_s$ ) (meq/g)
1	Dex-g-poly(AN)	25	100.00	44.33	55.67	44.33	796.29	63.329
2	Dex-g-poly(AN)	30	100.00	45.75	54.25	45.75	843.32	65.357
3	Dex-g-poly(AN)	35	100.00	21.66	78.34	21.66	276.49	30.943
4	Dex-g-poly(AN)	40	100.00	12.25	87.75	12.25	139.60	17.500
5	Dex-g-poly(AN)	45	100.00	13.11	86.89	13.11	150.88	18.729

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min,  $P_0 = 209.3$ .

**Table 11:** Sorption studies of  $\text{Cr}^{+6}$  ions as a function of change in pH at optimum graft conditions of guar gum graft copolymer<sup>a</sup>.

Sr. No.	Polymer	pH	Amount of $\text{Cr}^{6+}$ in feed (mg/L)	Amount of $\text{Cr}^{6+}$ sorbed (mg)	Amount of $\text{Cr}^{6+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_s$ ) (meq/g)
1	Dex-g-poly(AN)	4.0	100.00	11.38	88.62	11.38	128.41	52.523
2	Dex-g-poly(AN)	9.2	100.00	5.56	94.44	5.56	58.87	25.662

<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, Temperature = (30°C),  $P_g$  = 209.3.

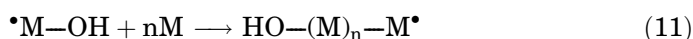
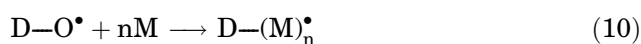
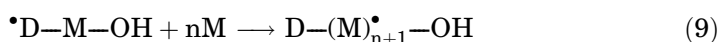
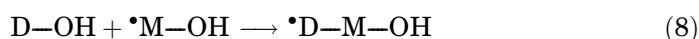
**Table 12:** Sorption studies of  $\text{Fe}^{2+}$  ions as a function of change in pH at optimum graft conditions of guar gum graft copolymer<sup>a</sup>.

Sr. No.	Polymer	pH	Amount of $\text{Fe}^{2+}$ in feed (mg/L)	Amount of $\text{Fe}^{2+}$ sorbed (mg)	Amount of $\text{Fe}^{2+}$ rejected (mg)	Percent ion uptake ( $P_u$ )	Partition coefficient ( $K_d$ ) (g/g)	Retention capacity ( $Q_r$ ) (meq/g)
1	Dex-g-poly(AN)	4.0	100.00	29.23	70.77	29.23	413.03	41.757
2	Dex-g-poly(AN)	9.2	100.00	11.98	88.02	11.98	136.11	17.114

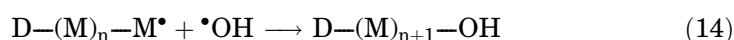
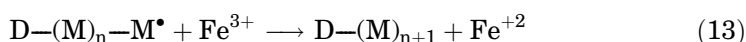
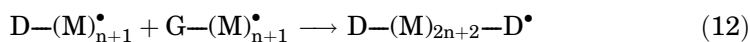
<sup>a</sup>Solution taken = 25 mL, sample taken = 0.025 g, time = 60 min, Temperature = (30°C),  $P_g$  = 209.3.



## Propagation



## Termination



## Effect of Reaction Parameters on Grafting of Acrylonitrile onto Dextrin

The effects of various reaction parameters on percent grafting ( $P_g$ ) and percent grafting efficiency (%GE) of AN onto dextrin have been investigated and the results are discussed below.

### Effect of Nature of Solvent System

Solvents play an important role in determining  $P_g$ . Solvent affects graft yield in many ways. Swelling of the backbone polymer by solvent helps in better diffusion of the monomer to the backbone polymer and also enhances diffusion of growing monomer macroradicals. Viscosity of the medium depends on the nature and amount of solvent and  $P_g$  affects known phenomena like *Tromosdorff Peak* or *gel effect*. Chain transfer reactions of solvent affect not only graft yield but also the size of graft chains and mechanism of grafting. Further, the solvent interacts not only with the backbone polymer but



with the initiator system and monomer, and such interactions are also an important factor that determine graft yield.

In the present study, effects of solvents such as water, benzene, dioxane,  $\text{CCl}_4$  and acetone on  $P_g$  and %GE were studied in 10.00 mL of these solvents, keeping other reaction conditions constant. The order of  $P_g$  in these solvents can be presented as benzene < carbon tetrachloride < acetone < dioxane < water. Similar order was recorded in the case of %GE. Maximum 42.1%  $P_g$  and 52.290 %GE were observed in water (Table 1). The lower  $P_g$  and %GE in organic solvents has been observed despite the fact that KPS/FAS is not soluble in these solvents under the employed reaction conditions. Solubilization requirements of the initiator play an important role in increasing grafting.

### Effect of Amount of Water

The amount of water was varied in the range 5.00 mL to 25.00 mL and appreciable changes in the graft yield have been observed. The optimum value of  $P_g = 54.3$  was observed at 25.00 mL water (Table 1). The same trend was observed for %GE, optimum %GE (67.453) was for 25.00 mL water. This may be because of easy solubilization of the initiator system with increased in solvent content.

### Effect of Monomer Concentration

The concentration of monomer (AN) was varied from  $30.5 \times 10^{-2}$  mole/L to  $152.51 \times 10^{-2}$  mole/L at optimum solvent amount and respective optimum KPS and FAS concentration of  $2.000 \times 10^{-2}$  mole/L and  $1.928 \times 10^{-2}$  mole/L. With the increase in monomer concentration a regular increase in grafting was observed (Table 1). Optimum  $P_g$  of 85.0 was recorded at  $152.51 \times 10^{-2}$  mole/L of AN concentration. But %GE showed a little decrease with AN concentration.

### Effect of Initiator Concentration

#### *Effect of KPS Concentration*

It follows from Table 1 that on the increase of KPS concentration from  $2.000 \times 10^{-2}$  moles/L to  $10.00 \times 10^{-2}$  moles/L, the optimum concentration of KPS has been found to be  $6 \times 10^{-2}$  moles/L. At this concentration 155.4  $P_g$  and 77.217 %GE were recorded.

#### *Effect of FAS Concentration*

It follows from Table 1 that on the increase of FAS concentration from  $1.928 \times 10^{-2}$  moles/L to  $7.714 \times 10^{-2}$  moles/L, the optimum concentration of

FAS has been found to be  $5.785 \times 10^{-2}$  moles/L at which maximum  $P_g = 209.3$  and 103.999 %GE were observed. At higher initiator concentrations, a fall in the graft yields is observed because growing polymeric chains enhance the chances of mutual termination leading to more homopolymer formation.

### Effect of Reaction Time

Reaction time was varied from 1.0 h to 3.0 h at constant conditions of temperature (60°C), initiator concentration (KPS,  $6 \times 10^{-2}$  moles/L) and FAS ( $5.785 \times 10^{-2}$  moles/L), and monomer concentration ( $152.51 \times 10^{-2}$  mole/L). Maximum  $P_g = 209.3$  and maximum %GE 103.999 were reported at 1.0 h reaction time (Table 1). Propagation rate is adversely affected by reaction time, as an increase in the rates of initiation leading to chain termination reactions.

### Effect of Temperature

Temperature was varied from 60° to 100°C at the evaluated optimum reaction parameters discussed above. Grafting rates at different temperatures were observed to follow the order  $60^\circ > 70^\circ > 80^\circ < 90^\circ > 100^\circ$ . Thus, there exists an optimum temperature to afford maximum graft yield; below this temperature decomposition of initiator and diffusion processes are not adequate to yield high graft levels. Optimum  $P_g = 209.3$  and %GE = 103.999 were observed at 60°C (Table 1).

### Characterization of Dextrin and Its Graft Copolymers

Dextrin and its graft copolymers were characterized by various chemical and physical methods. Elemental analysis, FTIR spectroscopy, scanning electron microscopy (SEM) and swelling behavior of graft copolymers have been studied and the results were compared with those of dextrin. Characterization of polymers not only provides positive evidence of grafting, but an insight into the mechanism of grafting processes can be obtained from various physical and chemical means. Important information on morphology, quantitative and qualitative attributes of grafted polymers and structural differences between backbone and graft copolymers can be applied to determine the end uses of graft copolymers.

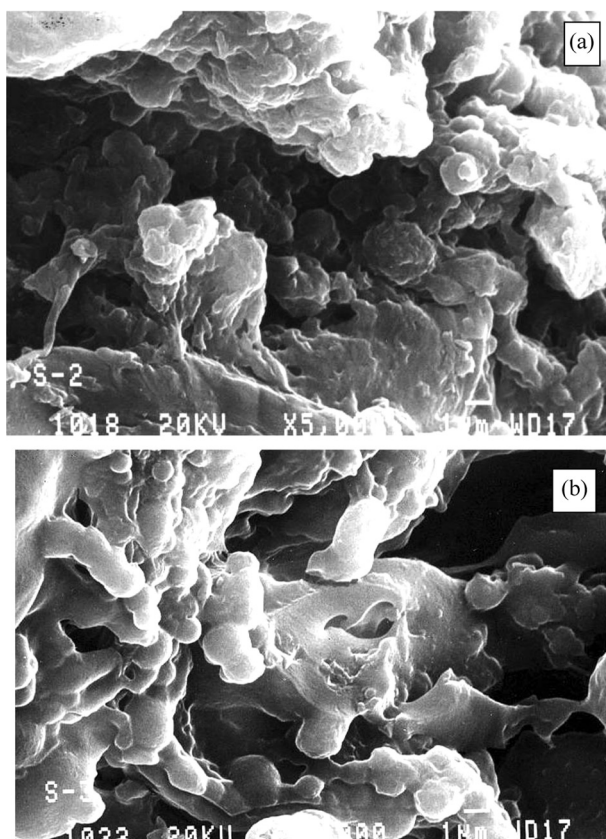
#### *Elemental Analysis of Dextrin and Its Graft Copolymers*

Elemental analysis of two samples of graft copolymers of dextrin was performed and considerable amount of nitrogen has been found in these networks. The two samples had different  $P_g$ . Higher amounts of nitrogen with

an increase in  $P_g$  is a manifestation of a higher incorporation of the monomer onto dextrin. The results presented in Table 2 confirm the incorporation of N-containing monomers onto dextrin.

#### *Scanning Electron Microscopy of Cellulose and Its Graft Copolymers*

Scanning electron micrographs (SEM) of dextrin and graft copolymers are presented in Figures 1a–1b. Grafting of acrylonitrile on the backbone considerably opens up its matrix. SEM of the grafted sample reveals that grafting is uniform in the dextrin as deposits of the graft copolymers are seen both in the amorphous and crystalline regions. It appears that grafting of acrylonitrile leads to physical and chemical crosslinking, as well-defined pores are visible in these micrographs.



**Figure 1:** Scanning electron micrograph of (a) Dextrin; (b) Dex-g-poly(AN).

*FTIR Study of Dextrin and Its Graft Copolymers*

FTIR of dextrin showed broad peaks at  $3392.1\text{ cm}^{-1}$  (O–H stretching). This broad band indicates association due to –OH groups (Figure 2a). Other important peaks were observed at  $2930.5\text{ cm}^{-1}$  (C–H stretching) and  $1017.1\text{ cm}^{-1}$  (C–O–C stretching). On grafting of acrylonitrile, IR bands due to characteristic functional groups incorporated onto dextrin have appeared in addition to the above listed bands. FTIR of graft copolymer showed a prominent peak at  $2243.8$  (C≡N stretching) (Figure 2b), which is characteristic of the nitrile functionality. FTIR of hydrolyzed graft copolymer (Figure 2c) shows weak peak at  $2243.0$  and the appearance of new peaks at  $3567.4$  (N–H stretching) and at  $1647.5$  (C–O stretching) which confirm the conversion of –C≡N group to –CONH<sub>2</sub> and –COOH groups by the hydrolysis process.

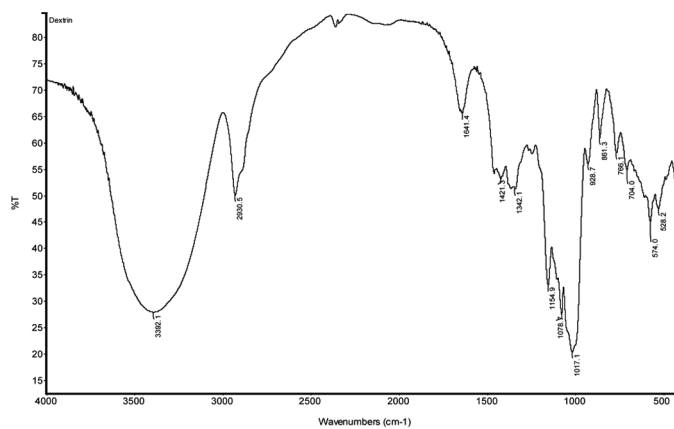
*Swelling Study*

Swelling studies of dex-*g*-poly(AN) were carried out in water at room temperature (Table 3). Swelling behavior of graft copolymers was also studied after hydrolyzing in 0.5 N NaOH for 48 h at 50°C (Table 4). The swelling study was carried out with dex-*g*-poly(AN) synthesized under different reaction conditions, having P<sub>g</sub> of 54.3, 85.0, 155.4, 186.7 and 209.3. Percent swelling (P<sub>s</sub>) of graft copolymers before hydrolysis was not appreciable except for the graft copolymer with minimum P<sub>g</sub> that (54.3) that showed maximum percent swelling (1732) in 2 h, which increased to 3640 in 4 h and 3853 in 6 h. But after 24 h little increase in percent swelling (3944) was observed (Table 3).

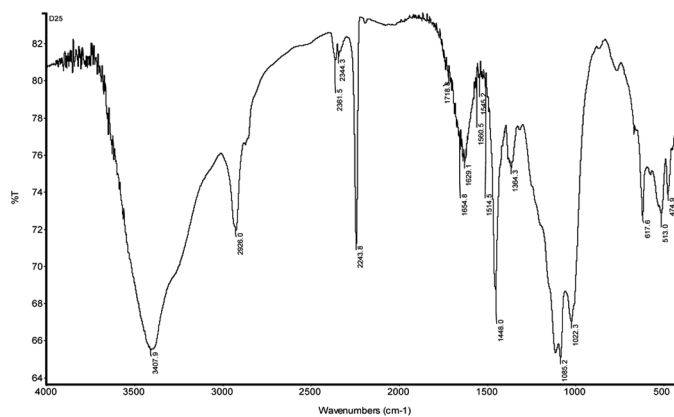
Graft copolymers of dextrin with poly(AN), when subjected to hydrolysis, show remarkable increase in percent swelling. Percent swelling (P<sub>s</sub>) of graft copolymers are very high within 2 h. Graft copolymers with maximum P<sub>g</sub> (209.3) showed maximum percent swelling (Table 4). In 2 h 5532, in 4 h 8501, in 6 h 11793 and after 24 h maximum percent swelling 17809 was observed. This may be because of the conversion of hydrophobic –C≡N group to hydrophilic –CONH<sub>2</sub> or –COOH groups by the hydrolysis process.

**Metal Ion Sorption**

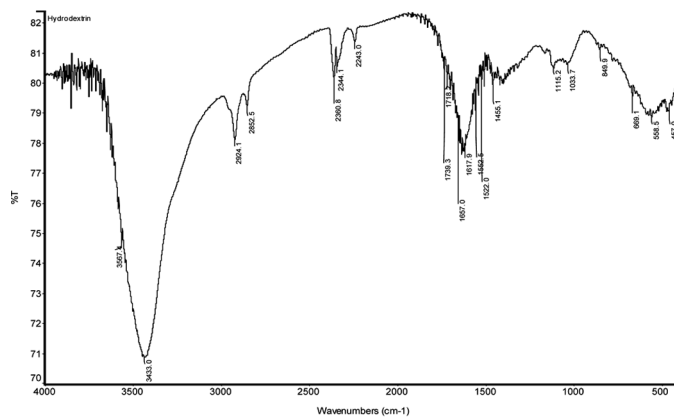
Polymers having active glycolic functionalities can engage in metal ion complexation. The linkage is mainly of coordinate type. Depending on the structure of the supports, sorption is a combination of ion exchange and simple adsorption processes. The results from the sorption of Fe<sup>2+</sup> and Cr<sup>6+</sup> ions are discussed. However, the nature of particular functional groups and their ability to interact with metal ions may play an important role in determining the selectivity and quantity of metal ion uptake.



(a)



(b)



(c)

**Figure 2:** FTIR of (a) Dexrin; (b) Dex-g-poly(AN); (c) Hydrolyzed Dex-g-poly(AN).

## Sorption Behavior of $\text{Cr}^{6+}$ Ions

Dextrin and graft copolymers of dextrin with poly(AN) with different  $P_g$  were studied for ion sorption studies by immersion of 0.025 g sample for 60 min in 25.00 mL solutions of  $\text{Cr}^{6+}$  ions of 5.00 mg/L concentration at 25°C (Table 5). The nature of polymeric backbone and percent grafting of graft copolymer has no significant effect on ion uptake. In the present study, sorption of  $\text{Cr}^{6+}$  ions was not significant by any graft copolymer. Maximum percent ion uptake ( $P_u$ ) of 15.94% was observed in sample with maximum percent grafting ( $P_g = 209.3$ ) (Table 5).

## Sorption Behavior of $\text{Fe}^{2+}$ Ions

0.025 g sample of dextrin and graft copolymers of dextrin with poly(AN) with different  $P_g$  were studied for ion sorption studies by immersion for 60 min in 25.00 mL solutions of  $\text{Fe}^{2+}$  ions of 5.00 mg/L concentration at 25°C. Percent grafting of graft copolymer has significant effect on ion-uptake as compared with the sorption behavior of  $\text{Cr}^{6+}$  ions. Results of sorption of  $\text{Fe}^{2+}$  ions onto dextrin and graft copolymers of dextrin are presented in Table 6. In the present study, sorption of  $\text{Fe}^{2+}$  ions is not significant by pure dextrin, but it was observed that percent ion uptake increased with percent grafting. Maximum percent ion uptake ( $P_u = 22.85\%$ ) was observed in the sample with maximum percent grafting (209.3) (Table 6).

## Metal Ion Sorption Efficiency Under Variable Parameters

### *Effect of Change in Ion Strength*

Ion sorption of graft copolymers with maximum  $P_g$  was studied by the immersion of 0.025 g sample for 60 min in 25.00 mL solutions of 5 mg/L, 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L concentration of the  $\text{Fe}^{2+}$  and  $\text{Cr}^{6+}$  ions at 25°C. As the concentration of the  $\text{Cr}^{6+}$  ions increases in the solution, the percent uptake increases but the increase in metal ion uptake is not significant. Maximum ion uptake of 21.99% was observed in the solution with 100 mg/L concentration of  $\text{Cr}^{6+}$  ions (Table 7). But a remarkable increase in the percent ion uptake (44.33%) and partition coefficient (796.29) was observed in the case of solution with 100 mg/L concentration of  $\text{Fe}^{2+}$  ions (Table 8). Sorption of  $\text{Fe}^{2+}$  ions is appreciable as compare to sorption of  $\text{Cr}^{6+}$  ions.

### *Effect of Change in Temperature*

Graft copolymers with maximum  $P_g$  were immersed in 100 mg/L concentrated solution of  $\text{Fe}^{2+}$  and  $\text{Cr}^{6+}$  ions at five different temperatures 25°C, 30°C, 35°C, 40°C and 45°C. The graft copolymers showed continuous decrease

in  $\text{Cr}^{6+}$  ion uptake with an increase in temperature (Table 9). A slight increase in the percent ion uptake (45.75%) when temperature was increased from 25°C to 30°C was observed in a solution containing  $\text{Fe}^{2+}$  ions (Table 10). But with further increase in temperature the percent ion uptake decreases. This is because of desorption at higher temperature.

### *Effect of Change in pH*

Graft copolymers with maximum  $P_g$  were studied for ion sorption studies by the immersion of 0.025 g sample for 60 min in 25.00 mL solutions of  $\text{Cr}^{6+}$  and  $\text{Fe}^{2+}$  ions of 100.00 mg/L concentration at 30°C at two different pH. The pH of the two solutions was adjusted at 4 and 9.2. Decrease in percent ion uptake was observed in both  $\text{Cr}^{6+}$  and  $\text{Fe}^{2+}$  ion-containing solutions with a change in pH from 4 to 9.2 (Tables 11 and 12).

## CONCLUSIONS

It has been observed from the above discussion that the sorption of  $\text{Fe}^{+2}$  ions is appreciable.  $\text{Cr}^{+6}$  ions are not well sorbed and this may be due to their oxidizing nature. Thus, an order can be formulated as:  $\text{Fe}^{+2} \gg \text{Cr}^{+6}$  ions. Thus, as expected for the sorption process the results for all types of hydrogels may follow the order  $\text{Fe}^{+2} > \text{Cr}^{+6}$  ions. With an increase in temperature and change in pH, desorption processes cause a decrease in percent ion uptake ( $P_u$ ) for both  $\text{Fe}^{+2}$  and  $\text{Cr}^{+6}$  ions.

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