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A Study in Sorption of Cu^{+2} , Fe^{+2} and I_2 onto Graft copolymers of Cellulose with N-Vinyl Pyrrolidone and Butyl Acrylate, and Their Functionalized Derivatives

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Abstract

Cellulose is of special interest due to its abundance in nature and it provides excellent materials for membranes both in native and derivatized forms. Graft copolymers of cellulose when used in separation and enrichment technologies have advantages over the conventional ones, due to chemical resistance, radiation stability and low cost of preparation. Cellulose based graft copolymers and hydrogels offer large hydrophilic area despite being insoluble in water and enrich or separate metal ion by binding, adsorption, chelation and ion exchange processes. Potential of cellulose as sorbent can be improved by radiation and chemical grafting, crosslinking and polymer analogous reactions on some graft copolymers. Grafting of suitable monomers with hydrophobic and hydrophilic/ionic moieties combine high degree of selectivity, permeability and longer stability, and enables complexation with low molecular weight species. Incorporation of functional groups like nitrile, hydrazino, hydroxamic acid and phosphate by derivatization and post polymer reactions enhances metal ion sorption capacity of Cellulosics. In present study an attempt has been made to study the sorption of Fe^{+2}*,* Cu^{+2} *and* I_2 *on select graft copolymers of cellulose with N-Vinylpyrrolidone (1-Vinyl-2-prrolidone, N-VP) and Butyl Acrylate(BuAc) on to cellulose and some of their functionalized derivatives, on the basis of lowest to highest percent grafting (*P_g*). An attempt has also been made to investigate selectivity in metal ion sorption and effects of structural aspects of functionalized graft copolymers to find their end-uses as cost effective and eco-friendly polymeric materials for waste water management technologies.*

Keywords: Graft copolymer, post polymer reaction, sorption, cellulosics.

1.Introduction:

Natural polymers like cellulose are finding increased use in low cost technologies for removal of metal ion from water bodies. These polymers are of renewable origin; environment friendly and offer highly cost effective technologies .Utility of these polymers in membrane processes is however restricted due to lack of selective binding. However, grafting of suitable monomers onto cellulose extracted from pine needles provides high degree of selectivity and offers a wide field to develop reactive graft copolymers for use as sorbents for water technologies. Extracted cellulose is a new backbone polymer. Chauhan and co-workers have used it for the first time to synthesize large variety of functional polymers by grafting as single or from binary monomer mixtures. They have also developed cellulose based hydrogels, and reported these as supports for enzyme immobilization, flocculents and metal ion sorption[1-8].The graft copolymers of cellulose with N-Vinyl pyrrolidone hereafter called Cell-g-poly(N-VP) and those with Butyl Acrylate called as Cell-g-poly(BuAc) synthesized and reported earlier by Chauhan and present author

Suresh[9-12], were used for present study. Cellulose derivatives and their graft copolymers like cellulose phosphate (Cell-PO_4, Cell-PO_4 -g-poly(N-VP), Cell-PO_4-g-poly(BuAc), Deoxyhydrazinocellulose (Cell-$NHNH_2$, Cell-$NHNH_2$-g-poly(N-VP), Cell-$NHNH_2$-g-poly(BuAc) and some of the graft copolymers of cellulose with butyl acrylate functionalized to hydroxamic acid moieties (Cell-g-poly(-CONHOH) were selected and subjected to sorption of Fe^{+2}, Cu^{+2} and I_2. Result were presented and discussed to define end uses of these polymers in water based technologies.

2. Experimental

2.1. Materials

Polymer networks of cellulose and derivatives as synthesized earlier with different monomers and few of their functionalized polymers were selected on the basis of considerable values of percent grafting (P_g). Copper sulphate, Iodine and ferrous sulphate (analytical grade, CDH, Mumbai, India) were used as they received.

2.2 Methods

Sorption studies were carried as reported earlier by Chauhan [4, 5, 6] by immersion of polymer samples for 24hrs in50.00mL solutions of known strength. Filterate of solutions were analysed for concentration of rejected ions on DR20210 Spectrophotometer(HachCo.,Us) by using its standard pillow reagents. Using thismethod maximum limit of ion strength that can be studied is, 5.0, 3.0 mg/L of solution, respectively, ofCu^{+2} andFe^{+2}ions. Thus the residual filtrate was diluted to reach this range. All weights were taken on DenverTR-203 balance having maximum readability of 1.0mg. Different relationships used to express sorption behavior are as follows [6,9-12].

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal taken by the polymer}}{\text{Total amount of metal in the feed}} \times 100$$

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}} \times \frac{\text{Volume of solution (mL)}}{\text{Weight of dry polymer (g)}}$$

$$\text{Retention Capacity } (Q) = \frac{\text{Amount of metal ion in the polymer}}{\text{Weight of dry polymer (g)}}$$

3. Results and Discussions

Interaction of metal ions with polymer occurs by way of binding, adsorption and ion exchange processes.Sorption is a common term used to express the nature of metal ion uptake by adsorption on anchor groups, ion exchange and also in the bulk of polymer hydrogel pores.Metal ions are effectively partitioned between polymer and liquid phase. Retention capacity of a polymer can be effectively enhanced and affected by hydrophilic-hydrophobic balance, nature of monomer and backbone as major factors. Ligand function also dictates reactivity, complexation ability and efficiency of polymer support. Effect of structural aspects of different groups of graft copolymers on metal ions is discussed.

3.1Sorption of Metal ions by Poly(N-VP) BasedCopolymers

In present case N-VP is a good complexing agent. In case of cell-g-poly (N-VP) sorption of Cu^{+2} and Fe^{+2} ions is significant. Metal ions sorption decreases with P_g increase meaning thereby the frequency of grafting may be more but grafted chain length is shorter in case of lower graft copolymer that provides a larger surface area to metal ions for sorption .Graft copolymerization onto cellulose derivatives such as Cell-PO_4,Cell-$NHNH_2$ and CEC results in increase in metal ion sorption (both Cu^{+2} and Fe^{+2}) as compare to native cellulose with maximum P_g as these have extra active groups for attachment of metal ions. Sorption of Fe^{+2} is substantially higher than that of Cu^{+2} (Table 1).

Table.1:Sorption of I_2, Cu^{+2} andFe^{+2} by poly (N-VP) Based Polymers

Polymer	P_g	P_u		
		I_2	Cu^{+2}	Fe^{+2}
Cell-g-poly(N-VP)	67.1	55.7	42	99.9
Cell-g-poly(N-VP)	77.5	46.6	37.4	99.8
Cell-g-poly(N-VP)	124	29.2	32.6	99.2
Cell-g-poly(N-VP)	230	24.7	19.8	90.4
Cell-PO_4	0.0	22.2	2.2	54.2
Cell-$NHNH_2$	0.0	13.9	4.9	70.4
CEC	0.0	24.4	1.85	44.6
Cellulose	0.0	11.1		29.8
Cell-$NHNH_2$-g-poly(N-VP)	183	20	27.8	75.1
CEC-g-poly(N-VP)	177	28.9	8.4	78.5
Cell-PO_4-g-poly(N-VP)	239	33.3	24	73.5

Weight of dry polymer =50mg, Cu^{+2} and Fe^{+2}feed=10mg/L, iodine feed=11.25mg/L

3.2 Sorption of Iodine by Poly (N-VP) Based Copolymers

Poly (N-VP) has been reported to adsorb substantial amounts of iodine, poly iodide anion, sodium do-decyl sulphate, azo dyes and methyl orange.Cell-g-poly (N-VP) also exhibits this property. The biding force between adsorbate and adsorbent is formation of charge transfer complex (CT). Lactum (tertiary cyclic amide) tautomerises to lactim form which is responsible for the formation of CT complex. Adsorption of I_2 is also explained on this basis. Lactim form of poly (N-VP) is unstable and can be converted to lactum by desorption process that means adsorption of I_2 is a reversible process. In present case of cell-g-poly (N-VP) the adsorption decreases with P_g(Table 1). Since lactim form is susceptible to hydrogen bonding as well as hydrolysis, with increase in P_g polymeric association increases and binding sites are blocked. However, during derivatization process the structure of backbone polymer becomes more open and surface area for sorption increases resulting in higher adsorption of iodine by cellulose derivatives such as Cell-PO_4, Cell-$NHNH_2$ and CEC as compare to cellulose.

3.3Sorption of Metal Ions by Poly(BuAc) Based Copolymers

Different graft levels of cell-g-poly (BuAc) and their respective functionalized polymers, cell-g-poly (CONHOH) were selected for metal ion sorption. Results of metal ion uptake are presented in Table 2. In case ofcell-g-poly (BuAc) sorption of Fe^{+2} is less than cellulose and decreases with decrease in P_g but the change is not very much significant. Hydrophobicity of the BuAc may be the major factor to influence the partitioning of ions between polymer and solution phase. It has been observed that Fe^{+2} ions sorption increases significantly in cellulose derivatives as well as functionalized cell-g-poly (CONHOH) as compare to its parent graft polymer. It is on the expected lines as both derivatization and functionalization open up the backbone polymer and exposes the active groups to metal ions. It can also beconcluded that increase in sorption is almost constant and is independent of P_g.Trend in sorption of Fe^{+2} by cellulose and its derivatives follows the order: Cell-$NHNH_2$> Cell-PO_4>CEC> cellulose whereas their graft copolymers follow the order:Cell-PO_4-g-poly(BuAc)>Cell-$NHNH_2$-g-poly(BuAc)>CEC-g-poly(BuAc)>cellulose.The functionalized polymers established the following trend: Cell-$NHNH_2$-g-poly(CONHOH)>Cell-PO_4-g-poly(CONHOH)>CEC-g-poly(CONHOH). AcceptCell-$NHNH_2$-g-poly (CONHOH), the sorption of Fe^{+2} decreases with decrease in P_g implying that sorption is linear function of extent of polymer conversion. In case of Cu^{+2} ions sorption, a reverse trend is observed. Sorption of Cu^{+2} ions by cell-g-poly (BuAc) is higher as compare to cellulose and it decreases with increase in P_g whereas in that of functionalized, cell-g-poly (CONHOH),it is again comparatively less than (almost half) the parent polymers but decreases again with P_g. Thus selectivity is observed in sorption of these two ions. The order of Cu^{+2} ions sorption follows as: Cellulose<Cell-g-poly(BuAc)>Cell-g-poly(CONHOH).Trends in sorption of Cu^{+2} ions in cellulose derivatives are as:Cell-$NHNH_2$>CEC>Cell-PO_4 and in their graft copolymers it follows the order:CEC-g-poly(BuAc)>Cell-PO_4-g-poly(BuAc)>Cell-$NHNH_2$-g-poly(BuAc) without any definite relationship with P_g. Similarly, trend in cell-g-poly (CONHOH) was observed as: Cell-$NHNH_2$-

g-poly (CONHOH)>Cell-PO$_4$-g-poly (CONHOH)>CEC-g-poly (CONHOH) similar to the order followed by Fe ions. Results are presented in Table.2.

Table. 2: Sorption of Cu^{+2} and Fe^{+2} by Poly (BuAc) based Copolymers

Polymer	P_g	P_u	
		Cu^{+2}	Fe^{+2}
Cell-g-poly(BuAc)	70.2	36.55	17.0
Cell-g-poly(BuAc)	108.5	29.14	17.5
Cell-g-poly(BuAc)	158.8	26.00	20.5
Cell-g-poly(BuAc)	188.3	20.00	25
Cell-g-poly(CONHOH)	188.3	6.86	52.0
Cell-g-poly(CONHOH)	158.8	16.28	50.6
Cell-g-poly(CONHOH)	108.5	16.56	43.0
Cell-g-poly(CONHOH)	70.2	18.86	38.4
CEC	0.0	4.92	44.6
Cell-NHNH$_2$	0.0	3.00	70.5
Cell-PO$_4$	0.0	6.8	54.14
Cell-PO4-g-poly(BuAc)	188.4	9.72	22.4
Cell-PO4-g-poly(CONHOH)	188.4	12.00	30.0
CEC-g-poly(BuAc)	185.9	2.86	9.6
CEC-g-poly(CONHOH)	185.9	17.44	24.5
Cell-NHNH$_2$-g-poly(BuAc)	59.1	6.86	19.2
Cell-NHNH$_2$-g-poly(CONHOH)	59.1	12.58	33.5
Cellulose	0.0	1.85	29.8

Weight of dry polymer=50mg, Cu^{+2} and Fe^{+2}feed=10mg/L

Conclusions

Structure of polymer backbone and its modification by grafting and functionalization by post polymer reactions affected the metal ion sorption behaviour appreciably that can be viewed from the percent ion uptake of these polymers. It has been observed that sorption of Fe^{+2} ions is higher as compare to that of Cu^{+2} ions and graft copolymers based on poly(N-VP) are better sorbents than those based on poly(BuAc),and can be successfully used in water technologies.

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