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REMOVAL OF METAL IONS BY USING NEW COMPOSITE ION-EXCHANGERS

Ragavan[1] and R.K.Seenivasan[2]
[1]Department of Chemistry, Raja Durai Singam Govt Arts College, Sivagangai-630561
[2]Department of Chemistry, Govt Arts College, Melur-625106

Abstract
Phenol - formaldehyde resin (PFR) was prepared and blended with sulphonated charcoals (SCs) prepared from Crateva Nurvala_Carbon. Composite ion exchange resins (IERs) were prepared by varying the amount of SCs (10-50%w/w) in the blends. All the important physico - chemical properties, effect of initial concentration of metal ion has been done. Composites up to 20% (w/w) blending retain almost all the essential characteristics and Cation Exchange Capacity (CEC) of the original PFR. It is concluded that blending of PFR by SCs will reduce the cost of IERs.
Key Words: *Phenol - formaldehyde Resin - Sulphonated Crateva Nurvala_Carbon-Cation Exchange Capacity - Composite resin - low cost Ion Exchangers.*

Introduction

Industrialised nations of the world are taking active measures to control the environmental pollution caused by the hazardous chemicals especially toxic metal ions. In the wastewater treatment, usually a decreasing level of pollutants is achieved, rather than the selective removal and recovery. Ion exchange is an appropriate technique for removal and recovery, as it is employed in the separation and concentration of ionic materials from liquids[1].

Many ion exchangers owe their origin to petroleum products and there is a continual increase in their cost. Furthermore the difficulty also exists in its procurement due to the scarcity of petroleum resources. Hence, there is an urgent need to find out the new low - cost ion exchange resin (IERs) and reduce the cost of IERs by blending it with sulphonated carbons (SCs) prepared from plant materials containing phenolic groups. Earlier studies show that the cheaper composite ion-exchangers could be prepared by partially blending the macro porous / macro reticular phenol-formaldehyde sulphonic acid resin (PFSAR) matrix by SCs prepared from coal[2], saw dust [3], spent coffee[4], cashew nut husk[5], wheat husk[6], turmeric plant[7], spent tea, gum tree bark[8] *Accacia nilotica*[9] and Egyptian bagasse pith[10].

Attempts have been does made to prepare cheaper cationic resins (CRs) from natural products. Ion-exchange process finds a valuable place in the treatment of waters and waste water discharged from plating and other industrial processes containing metal ions.

The aims and objectives of the present work are to synthesise, characterise the new composite ion exchangers of PhOH - HCHO type/cationic matrices blended with sulphonated Crateva Nurvala Carbon (CNC) and to estimate the column exchange capacity (CEC) for some selective metal ions.

Experimental

Materials

The raw/plant material used was Crateva Nurvala (Botonical name) and in Tamil: (Maavilangam). This is a plant material freely available in Tamil Nadu, India. Phenol and formaldehyde used were of Fischer reagents (India). LR grade of con. sulphuric acid (Sp.gr.= 1.82) was used. The plant material was locally collected, cleaned, dried and then powdered. The other chemicals / reagents used were of chemically pure grade (AnalaR) procured from SD fine chemicals, India.

Methods

Crateva Nurvala Carbon (500g) was carbonised and sulphonated by con. Sulphuric acid washed to remove excess free acid and dried at 70^0C for12 h[6-10]. It was labeled as SCNC.

Pure phenol - formaldehyde resin (PFR) was prepared according to the literature method[3,6-8]. It was then ground, washed with distilled water and finally with double distilled (DD) water to remove free acid, dried, sieved (210 - 300 μm) using Jayant sieves (India) and preserved for characterisation[3,6-8,11]. It was labeled as PFR.

The composites were obtained as per the method reported in literature[3, 6- 8]. The products with 10,20,30,40 and 50% (*w/w*) of SCNC in the blend / composites respectively were labeled as CN1, CN2, CN3, CN4 and CN5. A separate sample of SCNC was also subjected to the characterisation studies.

Characterisation of Samples

Samples were ground and sieved into a size of 210 - 300μm using Jayant sieves (India). This was used for further characterisation by using standard procedures[3,7,8] to find out the values of absolute density (Wet and dry in water and toluene, respectively), percentage of gravimetric swelling and percentage of attritional breaking. The solubility of these samples was tested by using various organic solvents and inorganic reagents. The values of cation exchange capacity (CEC) were determined by using standard titration techniques[12], as per the literature method[13]. .

Results And Discussion

Synthesis

The experimental and theoretical compositions of SCNC in the composites (CN1 - CN5) are in good agreement with each other (Table 1). The results are similar to those obtained by Sharma *et al* [2]. This indicates that the preparative methods adopted for the synthesis of PFR and its composites (CN1 - CN5) are more reliable and reproducible. The optimum value of formaldehyde and phenol are found to be 10mL and 11.5 mL, respectively.

Characterisation studies

Physico – chemical properties

The data given in Table 2 show that the values are absolute density (wet and dry in water and toluene respectively) are decreased from PFR to composite with highest %(*w/w*) of SCNC and finally to pure SCNC. The values of absolute density of composite in dry and wet forms depend upon the structure of the resins and its degree of cross linking and ionic form[14]. Generally the absolute density decreased with increase in CN content in the composite.

The high value of absolute density indicates a high degree of cross linking, and hence suitable for making columns for treating polar and non - polar effluent liquids of high density. The values of absolute densities for the different composites in the dehydrated states are higher than the hydrated states. Moreover, the values of wet and dry density are close to each other indicates that the pores of the sample may be macro porous in nature.

The data given in Table 2 indicate that the % of gravimetric swelling decreases from PFR (83.16%) to SCNC (40.41%). The value of average % of gravimetric swelling decreased with increasing CAC content in the composite. The values of % gravimetric swelling are found to be 71.86%, 62.00%, 57.61%, 50.73% and 48.67% respectively, for 10, 20,30,40 and 50% (*w/w*) of mixing of CNC with PFR compared to that of pure PFR. This indicates that up to 20% (*w/w*) CNC could be mixed with the PFR. The rigidity of the resin matrix was thus concluded from the % of gravimetric swelling measurements. Therefore, these composite resins with increasing amount of CNC content in the composites showed lower % of gravimetric swelling which revealed much lower rigid shape, and the rigidity of composites (from CN1 to CN5). It indicates that, pure resin and composites are rigid with non - gel macro porous structure [11]

The values of % of attritional breaking (Table 2) increase with increase in % (*w/w*) of CNC content in the composite, representing the stability of the resin, which decreases from PFR to CNC. Therefore, the mechanical stability is good up to 20 % *(w/w)* substitution of CNC in pure resin. This observation also shows that, the capillaries of the IER may be occupied by the sulphonated carbon (CNC) particles[6-8].

Solubility of Ion Exchangers

The chemical stability of ion exchange resins under the present study are established by testing their solubility in a few selected organic solvents and reagents. The samples tested viz., PFR, SC and (CN1-CN5) are all practically insoluble in almost all the reagents and polar and organic solvents. It was noted that the resins and condensates (except CNC) are partially soluble (6 - 8%) in 20% NaOH solution. This is because these samples have phenolic groups in them and hence could not be used in strongly basic medium owing to its solubility. This indicates a high degree of cross-linking in all the samples (*i.e.*) the basic polymer unit is mostly of higher molecular weight fractions or atleast the absence of very low molecular weight fractions in the resins. Hence, the samples could be used to make cations exchanger column, which could be used acidic neutral and light alkaline medium and treat non-aqueous industrial effluents.

Cation exchange capacity (CEC)

CEC data shown in Table 3 indicate that, the CEC values (for 0.1M solution of metal ions) decrease when the % (*w/w*) of CNC content *(w/w)* in the composite increases.

The relative value of CEC of individual metal ions depends upon the atomic radius or atomic number[15]. At the same time the CEC also depends upon the anionic part of the metal salt. *i.e.,* inter ionic forces of attraction between anions and cations, which plays a vital role in cation exchange capacity of particular metal salt solution [16,17].

From the CEC data given in Table 3, the cation exchange capacity of the samples was found to decrease in the following order.

Pb^{2+}>Zn^{2+}> Mg^{2+}> Cu^{2+} > Ca^{2+} > Na^{+} > K^{+}

The selectivity order of metal ions *i.e.*, orders of CEC values also depends upon the ionic potential and the hydrated atomic radius of the metal ions in solution [17]. The order of exchange affinities of various metal ions is not unique to ion exchange system. Only under dilute conditions Hofmeister or lyotropic series [14] is obeyed. But, under high concentration it is different[14]. It is equally important to note that the relative behaviour of these ions for other ionic phenomena deviates the affinity order under the same conditions[18]. The observed order in the present study is different from that of the Hofmeister or lyotropic series[14]. This may be due to the concentration of the influent metal ion solutions, which is relatively high and also due to the selectivity of the metal ions [19]. Also, the CEC data given in the Fig.1, conclude that, up to 20% *(w/w)* blending of CNC with PFR retains 62.55-59.04 of CEC for all metal ions. Hence, 20% (*w/w*) blending of CNC with PFR to an extent of 20 %(*w/w*) will reduce the cost of the IER.

Effect of initial concentration of Mg^{2+} ion on CEC

Cation exchange capacity (CEC) increases with increase in the initial concentration of Mg^{2+} ions from 0.05M to 0.20 M (Fig.2). It is in accordance with le Chatlier - Braun principle. For PFR, condensates and SCNC, the value of IEC increases with increase in initial concentration of Mg^{2+} ions from 0.05 to 0.20 M. Beyond, 0.10M there is a leveling effect of the value of CEC (*i.e.,* a constant CEC value). This is noticed for various metal ions at high concentrations above 0.15M, similar to Mg^{2+} ions. Hence with solution of metal ions up to 0.10M concentration the condensate resins could be applied since they act as good ion exchangers.

Table 1 Amounts of reagents used and yield of PFR condensates (CN1-CN5) prepared by blending PFR with various % (w/w) of SCNC

Sample	% of SCNC in IER	Amount of reagents used			SCNC (g)	Yield (g)	% of SCNC in IER(Obs)
		Phenol (g)	Formaldehyde (mL)	Con.H_2SO_4 (mL)			
PFR	0	10.0	11.5	12.5	0	16.5	0
CN-1	10	10.0	11.5	12.5	1.83	17.40	10.51
CN-2	20	10.0	11.5	12.5	4.12	20.31	20.28
CN-3	30	10.0	11.5	12.5	7.07	22.81	30.99
CN-4	40	10.0	11.5	12.5	11.00	26.98	40.77
CN-5	50	10.0	11.5	12.5	16.50	32.01	51.54
SCNC	100	-	-	-	-	-	100

Table 2 Physico -Chemical properties of PFR, SCNC and condensates (CN1 -- CN5)

Sample	% of SCNC in IER	Density (g/mL)		Percentage	
		Wet	Dry	Gravimetric swelling	Attritional breaking
PFR	0	2.45	2.24	83.16	8.50
CN1	10	1.64	1.70	71.86	17.00
CN2	20	1.51	1.43	62.00	20.58
CN3	30	1.47	1.33	57.61	25.43
CN4	40	1.36	1.30	50.73	30.51
CN5	50	1.21	1.01	48.67	42.40
SCNC	100	1.15	0.98	40.41	51.00

Table 3 CEC of 0.1M solution of selective metal ions for PFR, SCNC and condensates and SCNC (H^+ form) for at 303K

Sample	% of SCNC	Cation exchange capacity m mol/g						
		Ca^{2+}	Zn^{2+}	Mg^{2+}	Cu^{2+}	Pb^{2+}	Na^+	K^+
PFR	0	1.3109	1.7408	1.7702	1.5107	1.7254	1.2904	1.2108
CN1	10	1.223	1.674	1.610	1.310	1.692	1.115	0.850
CN2	20	1.190	1.523	1.515	1.225	1.568	1.102	0.715
CN3	30	1.175	1.416	1.431	1.100	1.430	1.085	0.614
CN4	40	1.115	1.373	1.326	1.025	1.320	1.010	0.528
CN5	50	1.098	1.286	1.218	0.950	1.225	0.950	0.431
SCNC	100	1.050	1.163	1.119	0.857	1.101	0.771	0.313

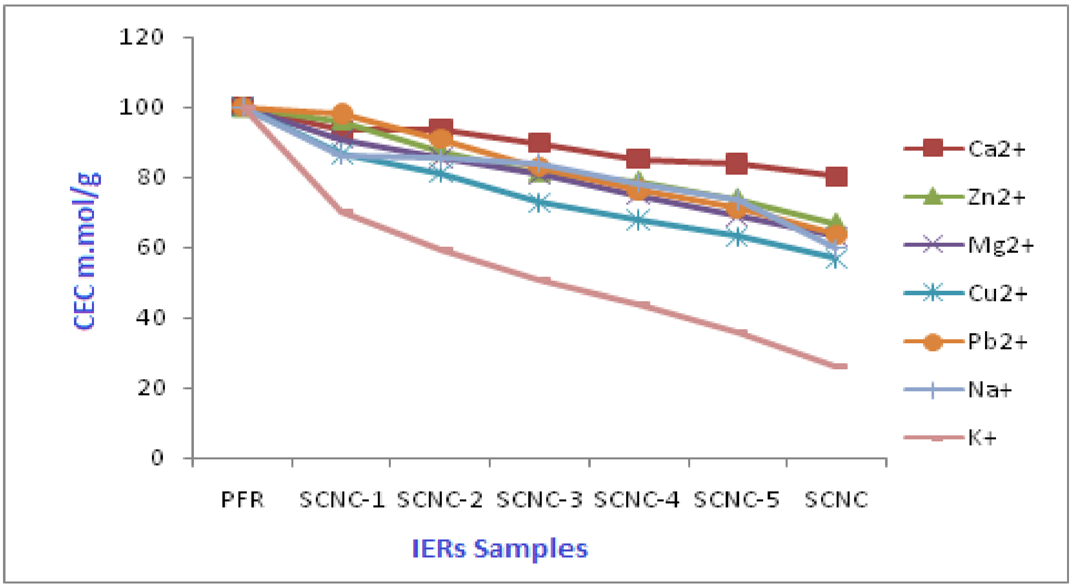

Fig.1. CEC of 0.1M solution of selective metal ions for PFR, SCNC and condensates and SCNC (H^+ form) for at 303K

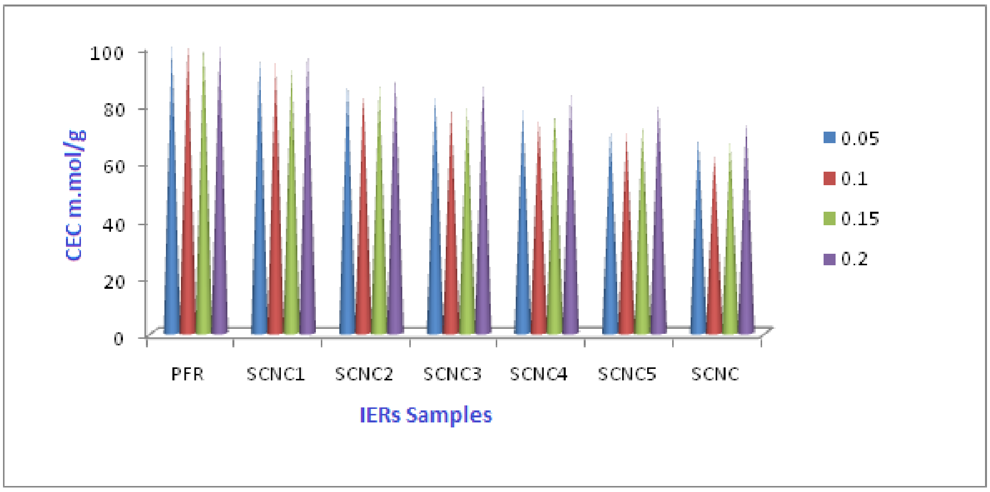

Fig.2. Effect of initial concentration of Mg^{2+} ion on CEC by various IERs

Conclusion

It is concluded from the result of the present study that PFR sample could be blended with 20% (*w/w*) of SCAC, without affecting its physico-chemical and ion exchange properties. Hence, blending of PFR with 20% (*w/w*) of CAC will definitely lower the cost of IER for the treatment of industrial effluent for the removal of metal ions.

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