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A NEW COMPOSITE ION EXCHANGERS FOR WASTE WATER TREATMENT

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ABSTRACT

Phenol – formaldehyde resin (PFR) was prepared and blended with sulphonated charcoals (SCs) prepared from a plant material. 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 have been analysed. 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.

1. INTRODUCTION

It is necessary duties of industrialized nations to protect our environment from various pollutants caused by toxic metal ions.Many of the industry reduce their polluted level and not to get valuable metal ions.It is very important to recovery and recollect of various metal ios from solution[1]

Since petroleum based Ion-exchangers (IERs) are very high cost, low cost ion exchange method was adopted. So it is important to prepare low cost IERS from plant materials by mixing their sulphonated carbon form with Phenol-Formaldehyde polymeric matrix. Early study showed that Phenol-Formaldehyde polymeric matrix blended with Sulphonated Carbons (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].

Number of methods has been adopted for preparing low cost IERs which is used to remove metal ions from solution. 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 *Alangium salvifoliium L.*Carbon (SASC) and to estimate the column exchange capacity (CEC) for some selective metal ions.

2. EXPERIMENTAL

2.1 Materials

Alangium salvifoliium L. Carbon (ASC) is enormous source of plant material and easily 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. Plant material was collected, cleaned and cut into small pieces of about 0.5cm length and then dried. All other chemicals / reagents obtained from SD fine chemicals, India.

2.2 Methods

Alangium salvifoliium L. Carbon (500g) was carbonised and sulphonated by con. sulphuric acid. Excess of free acid is washed number of times by doubled distilled water. Then heated at 70^0C for 12 h [6-10] and then dried. The powdered form of sulphonated carbon named as ASC.

PFR was obtained as per literature method [3, 6 – 8]. Solid PFR was grinded.Excess sulphuric acid was removed by double (DD).Then dried and sieved by Jayant sieves (India) to get 210 – 300 µm size. It is preserved for further characterisation [3,6-8,11].

As per literature method all composite IERs were obtained.[3,6– 8]. Composites with 10, 20,30,40 and 50% (*w/w*) of ASC respectively were labeled as AS1,AS2,AS3,AS4 and AS5.

2.3 Characterisation of samples

All IERs converted into a size of 210 – 300µm using Jayant sieves (India). Using slandered methods, the IERs were characterised [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. Solubility of all IERs in organic and inorganic solvents were tested.

As per the literature method [13] and using standard titration techniques [12] the values of cation exchange capacity (CEC) were determined.

3. RESULTS AND DISCUSSION

3.1 Synthesis

The experimental and theoretical compositions of BLC in the composites (AS1 – AS5) 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 (AS1 – AS 5) are more reliable and reproducible. The optimum value of formaldehyde and phenol are found to be 10mL and 11.5 mL, respectively.

3.2 Characterisation studies

3.2.1 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 ASC and finally to pure ASC. 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 ASC 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 (98.25%) to ASC (21.77%). The value of average % of gravimetric swelling decreased with increasing ASC content in the composite. The values of % gravimetric swelling are found to be 77.54%, 72.73% and 68.82% respectively, for 10, 20 and 30% (*w/w*) of mixing of ASC with PFR compared to that of pure PFR. This indicates that up to 20% (*w/w*) ASC 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 ASC content in the composites showed lower % of gravimetric swelling which revealed much lower rigid shape, and the rigidity of composites (AS1 – AS5). 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 ASC content in the composite, representing the stability of the resin, which decreases from PFR to ASC. Therefore, the mechanical stability is good upto 20 - 30% *(w/w)* substitution of ASC in pure resin. This observation also shows that, the capillaries of the IER may be occupied by the sulphonated carbon (ASC) particles [6-8].

3.2.2. 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.

Table 1. AMOUNT OF REAGENT USED AND YIELD OF PFR, CONDENSATES (AS1 – AS5) PREPARED BY BLENDING OF PFR WITH VARIOUS %(*W/W*) OF SASC

Sample	**%of SASC in IERs(cal)**	**Amount of reagents used**					
		PhOH (ml)	**HCHO (ml)**	**Con. H_2SO_4 (ml)**	**SASC (g)**	**Yield (g)**	**% of SASC in IERs (obs)**
PFR	**0**	**10**	**11.5**	**12.5**	**0**	**19.50**	**0**
AS 1	**10**	**10**	**11.5**	**12.5**	**2.17**	**21.81**	**9..95**
AS 2	**20**	**10**	**11.5**	**12.5**	**4.75**	**22.09**	**21.5**
AS 3	**30**	**10**	**11.5**	**12.5**	**8.36**	**27.41**	**30.5**
AS 4	**40**	**10**	**11.5**	**12.5**	**13**	**32.62**	**39.85**
AS 5	**50**	**10**	**11.5**	**12.5**	**19.50**	**39.59**	**49.25**
SASC	**100**	**-**	**-**	**-**	**-**	**-**	**100**

Table 2.Physico - chemical properties of PFR, SASCMOC and condensates (AS 1-AS 5)

Sample	% of SASC	Density (gL-1)		Percentage of	
		Wet	Dry	Gravimetric Swelling	Attritional Breaking
PFR	0	1.952	1.910	98.25	7.96
AS 1	10	1.834	1.805	77.54	9.53
AS 2	20	1.822	1.722	72.73	10.76
AS 3	30	1.651	1.553	66.82	11.66
AS 4	40	1.474	1.400	56.20	15.21
AS 5	50	1.276	1.170	53.69	18.05
SASC	100	0.983	1.014	44.28	21.77

The samples tested viz., PFR, SC and AS1 – AS5 are all practically insoluble in almost all the reagents and polar and organic solvents. It was noted that the resins and condensates (except ASC) are partially soluble (5 - 10%) 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.

3.2.2 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 ASC 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]. rom the CEC data given in Table 4, the cation exchange capacity of the samples was found to decrease in the following order.

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

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

TABLE 4 CHEMICAL EFFECT ON CEC OF PFR AND ITS CONDENSATES FOR EXCHANGE WITH 0.1M Zn^{2+} IONS AT 303 K

Reagents	Cation Exchange Capacity(m.mol.g-1)					
	PFR	AS 1	AS 2	AS 3	AS 4	AS 5
CEC(untreated IER)	1.620	1.420	1.350	1.310	1.180	1.100
20%NaOH	1.603	1.394	1.317	1.288	1.157	1.080
Benzene	1.571	1.399	1.323	1.291	1.151	1.070
Boiling water	1.604	1.404	1.334	1.292	1.163	1.084
1M HCl	1.603	1.398	1.322	1.257	1.133	1.056
Thermal Treatment	1.491	1.204	1.129	1.076	0.964	0.910

Table 5. Effect of particle size on CEC of PFR and condensates (AS 3) at 303K

Sample	Particle Size (micron)	Cation Exchange Capacity(m.mol.g^{-1})		
		Cd^{2+}	**Zn^{2+}**	**Mg^{2+}**
PFR	**<210**	**1.39**	**1.49**	**1.61**
	210-300	**1.58**	**1.62**	**1.82**
	300-500	**1.53**	**1.55**	**1.73**
	>500	**1.30**	**1.32**	**1.32**
AS 3	**<210**	**1.15**	**1.21**	**1.26**
	210-300	**1.25**	**1.31**	**1.34**
	300-500	1.17	1.22	1.30
	>500	0.92	1.11	1.18

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. Also, the CEC data given in the Fig.1, conclude that, upto 30% *(w/w)* blending of ASC with PFR retains 86.45 – 93.45% of CEC for all metal ions. Hence, 30% (*w/w*) blending of ASC with PFR to an extent of 30 %(*w/w*) will reduce the cost of the IER.

It is observed that there is a continuous decrease in cation exchange capacity (CEC), as the percentage of ASC content in the blend increases. Hence, any chemical methods requiring ion exchangers of small ion exchange capacity, 30% (*w/w*) blended ASC –PFR resin could be used.ASC can be inexpensively prepared from the plant materials, which is freely available in plenty, in India, especially in Tamil Nadu.

The effects of different reagents on the values of CEC of various cationic resins are shown in Table 4. On treatment with 0.2M NaOH 1.2 – 3.3% reduction in CEC value was noted. A higher decrease was observed for resin containing 50% of SASC. Upon treatment of resins with various organic solvents, the loss in CEC value was 1.0 – 3.9%. All these observations reveal that the composites have high thermal and chemical stability.

CEC data given in Table 5, described that the particle size of <200 μm are fine and > 500μm are coarse compared to a particle size of 200 - 500μm to cause very low ion Exchange capacity.

3.3. Conclusion

It is concluded from the result of the present study that PFR sample could be blended with 30% (*w/w*) of ASC, without affecting its physico-chemical and ion exchange properties. Hence, blending of PFR with 30% (*w/w*) of ASC will definitely lower the cost of IER for the treatment of industrial effluent for the removal of metal ions.

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