RASĀYAN J. Chem.
Vol. 6 | No.3 | 212-222| July- September | 2013
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNERGISM MODIFIED ION-EXCHANGE PROCESS OF SELECTIVE METAL IONS AND ITS BINARY MIXTURES BY USING LOW COST ION EXCHANGE RESIN AND ITS BINARY MIXTURE

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ABSTRACT

A few composite ion exchangers were prepared by blending sulphonated carbons (SCs) prepared from plant materials, such as *Phyllanthus emblica,* Linn.(PE), *Eugenia jambolana*, Lam.(EJ), *Terminalia chebula*, Retz. (TC) *Terminalia bellarica*, Roxb. (TB) and *Achyranthes aspere*, Linn.(AA),blended with phenol-formaldehyde resin (PFR) in different weight ratios (from 0 to 50% *w/w*). These, SCs were partially blended into the polymeric matrix of Phenol-Formaldehyde sulphonic acid, which could be used as new cheap/low cost ion exchangers (IERs) for the removal of some selective metal ions.. CEC of selective single metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+}) and binary mixture metal ions such as (Zn^{2+} + Cu^{2+} and Pb^{2+}+ Ca^{2+}) and were determined for using PFR, composite resin with different *%(w/w)* of SCs and 100% SC. Binary mixture of resins(R_1 and R_2) were prepared by mixing of two low cost IERs obtained by blending PFR with 20% SC(prepared from plant materials PE,TB, and AA) which possess high and low CEC value. CEC of selective single and binary metal ions for the binary mixture of resins (R_1 and R_2) was determined. It shows that composites/low cost IERs up to blending PFR with 20% (*w/w*) SC, retains the CEC of the original PFR. CEC values were theoretically calculated using linear or additive (ideal) behaviour and found to be less than that of the observed values of CEC for all the ion exchange systems. This may be due to synergism modified ion exchange process.

Keywords: Cation Exchange Capacity – Composites – Single and Binary mixture of metal ions - Low cost Ion Exchangers – phenol – formaldehyde resin- Binary mixture of resins.

INTRODUCTION

The discovery of ion exchange dates from the middle of the nineteenth century when Thomson and Way noticed that ammonium sulphate was transformed into calcium sulphate after percolation through a tube filled with soil[1, 2]. In 1935, Liebknecht and Smith discovered that certain types of coal could be sulphonated to give a chemically and mechanically stable cation exchanger[3,4]. In addition Adams and Holmes produced the first synthetic cation exchangers by poly condensation of phenol with formaldehyde[5].

Since, the modern commercial ion exchangers owe their origin to the products of petroleum; there is a phenomenal increase in the cost of these ion exchangers. Hence, there is an urgent need of the hour either to find out entirely new resins which are cheaper than the existing ones or to prepare composite ion exchangers by partly replacing the polymeric content of the current ion exchangers to a considerable extent by blending it with the sulphonated carbons (SCs) prepared from plant materials while the important characteristics of the parent resins are being retained. The composite could be very efficient, if the substitute it-self could act as an ion exchange. Earlier studies showed that the cheaper composite ion-exchangers (IERs) could be used to remove heavy metal ions from solutions and prepared by partially blending the macro porous phenol-formaldehyde sulphonic acid resin (PFR) matrix by blending it with carbons obtained from coal, saw dust, spent Coffee, cashew nut husk, wheat husk, turmeric plant, spent tea, gum tree bark, A*ccacia nilotica* and Egyptian bagasse pith[6-14]. Heavy metals are also removed by bamboo activated carbon, natural clinptitolite, titanate nanoflowers and poly(Hydroxy ethyal methacrylate/Malemic acid) hydro gel[15-18]

The present work deals with the synthesis, characterization and CEC values of single metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+}) and binary mixture of metal ions (Cu^{2+}+ $Zn^{2+}$and Pb^{2+}+Ca^{2+}) of new low cost IERs obtained by blending PFR with various % by weight of SCs prepared from plant materials such as *Phyllanthus emblica,* Linn.(PE), *Eugenia jambolana*, Lam.(EJ), *Terminalia chebula*, Retz. (TC),*Terminalia bellarica*, Roxb. (TB) and *Achyranthes aspere*, Linn.(AA). Also binary mixture of resins were prepared by mixing two low cost IERs obtained by blending PFR with 20% SC (prepared from the plant materials PE,TB and AA) which possess high and low CEC values. CEC values of these binary mixtures of resin for single and binary mixture of metal ions were also obtained. Synergism modified ion exchange process is reported in this paper for the low cost IERs and binary mixture of these IERs.

EXPERIMENTAL

Materials

Phenol and formaldehyde used were of Fischer reagents (India). LR grade of con. Sulphuric acid (Sp.gr. = 1.82) was used. Sulphonated carbon (SC) obtained from plant materials *viz.*, *Phyllanthus emblica,* Linn.,(PE), *Eugenia jambolana*, Lam.,(EJ), *Terminalia chebula*, Retz.,(TC), *Terminalia bellarica*, Roxb.,(TB) and *Achyranthes aspere*, Linn.,(AA), which were the locally available plants in southern part of India, especially in Tamil Nadu. These plant materials were cleaned, dried and cut into small pieces of about 0.5cm length.

Preparation of Sulphonated Carbons (SC)

About 500g plant materials were carbonized and sulphonated by con. Sulphuric acid (500mL) and kept at room temperature (30 ± 1^0C) for 24 h and heated at 90^0C in a hot air-oven for 6 hours. It was then cooled, washed with distilled water several times and finally with double distilled (DD) water in order to remove excess free acid and dried at 70^0C for 12 h. They were labeled as SPEC,(Sulphonated *Phyllanthus emblica* Linn., Carbon) SEJC (Sulphonated *Eugenia jambolana* Lam.,Carbon), STCC (Sulphonated *Terminalia chebula* Retz.,Carbon), STBC(Sulphonated *Terminalia bellarica* Roxb.,Carbon) and SAAC (Sulphonated *Achyranthes aspere* Linn.,Carbon), respectively for the SCs prepared from the plant materials PE, EJ, TC, TB and AA.

Preparation of Pure Phenol- Formaldehyde Resin (PFR)

Con. Sulphuric acid (12.5mL) was slowly added to phenol (10mL) in drop wise with constant stirring by placing it in an ice-bath at 0 – 5^0C. The mixture was heated at 70^0C for 3 h in a hot air -oven, then cooled immediately in an ice bath and kept over-night. It was then polymerized with formaldehyde solution (11.5mL) at 80^0C and the product was cured in a hot air-oven for 3 h. A brown colored chunky solid mass was obtained. It was then ground, washed with distilled water and finally with double distilled (DD) water to remove excess free acid, dried, sieved (210µm – 300µm size) using Jayant Sieves (India) and preserved for characterisation[19-22]. It was labeled as PFR.

Preparation of Low- Cost Ion-Exchange Resins (IERs)

A known amount of phenol (10 mL) was sulphonated with con. sulphuric acid (12.5 mL) to produce phenol sulphonic acid. Then, it was blended with various percentage by weight *(w/w)* of sulphonated carbons (SCs) obtained from various plant material (PE, EJ, TC, TB and AA) in the blend as 10, 20, 30, 40 and 50,%(*w/w*) respectively. In order to fix the composition of SC as 10, 20, 30, 40 and 50 % (*w/w*) in the composites the following formula was used [7, 10-12, 19]-

$$\text{Required percentage} = b / (a + b) \qquad (1)$$

Where, a = mass of PFR (in g); b = mass of the SC required (in g)

Each mixture was polymerized with formaldehyde solution (11.5mL) at 80^0C and the product was cured in a hot air –oven for 3 h. A brown chunky solid mass was obtained which was ground, washed, dried and preserved for characterization. The product with 10, 20, 30, 40 and 50% (*w/w*) of SCs (obtained from various plant materials) in the blend / composite, respectively were labeled as A, B, C, D and E for each composite, Physico –chemical parameters of PFR, composites and (100%) SC were determined as per the literature methods[23-26]**.** The percentage of SC in the resin calculated in terms of weight of materials used and their actual percentage in the yields are given in Table-1.

Cation Exchange Capacity of Low-cost IERs

A known weight (2g) of the low cost composite/ IER samples were converted into H^+ form by washing it with 2M HCl acid, and washed with distilled water and finally rinsed with DD water in order to remove excess free acid (tested with $AgNO_3$). The test column was prepared by using graduated burette, glass –wool plug and the slurry of treated resin sample. Forty ml of 0.1M solutions of single metal ions (Cu^{2+} , Zn^{2+} , Pb^{2+} and Ca^{2+}) and binary mixture of metal ions (Cu^{2+} + Zn^{2+} and Pb^{2+} + Ca^{2+}) were used as influents. The rate of flow of effluent was adjusted to 1mL min^{-1}. The low-cost IER samples exchanged its H^+ ion to the corresponding metal ions. The total amount of cation exchanged was determined by using the standard titration techniques[24]. The values of cation exchange capacity (CEC) were determined as per the literature method[25-27]. The CEC value of single metal ions and binary mixture of metal ions for various low-cost IERs / composites resins were shown in Figs. 1-5. The theoretical total cation exchange capacity (CEC) for various low -cost IERs for the binary mixture of metal ions from the CEC value of individual metal ions is calculated as follows:

$$\left.\begin{array}{l}\text{Theoretical total CEC of binary}\\ \text{Mixture of metal ions}\end{array}\right\} = \frac{1}{2}\,[\text{Sum of CEC of individual metal ions}] \qquad (2)$$

Preparation of Binary Mixture of Resin

Based on the results obtained from Figs. 1-5, the CEC value of single metal ion and binary mixture of metal ions by using low-cost IERs was found to be unaffected up to 20% (w/w) blending of SCs obtained from various plant materials with PFR. Therefore in the present study the binary mixture of resins (R_1) were obtained by mixing of the composite resin/IER prepared by blending PFR with 20% (*w/w*) SPEC (X) having high CEC value with the IER obtained by blending PFR with 20% (*w/w*) SAAC (Y) having least CEC value in five different weight proportion ratio (*% w/w*) 100, 75, 50 , 25 and 0 %.These resins were labeled as X, XY1, XY2, XY3 and Y, respectively (Table 2). Similarly, another binary mixture of resins (R_2) were obtained by mixing the composite resin/IER prepared by blending PFR with 20% (*w/w*) STBC (Z) having highest CEC value with the composite resin/IER prepared by blending PFR with 20% (*w/w*) SAAC (Y) having least CEC value in five different weight proportion ratio (*% w/w*) 100, 75, 50 , 25 and 0 % and were labeled as Z, ZY1, ZY2, ZY3 and Y, respectively (Table-2).

CEC of Binary Mixture of Resin

CEC values of various selected single metal ions and binary mixture of metal ions were determined by using these two binary mixture of resins (R_1 andR_2) prepared as given in Table 2.The theoretical CEC value of binary mixture of resins for both single and binary mixture of metal ions is calculated from CEC value of the 100 % pure resin (*i.e.*, Y and Z) as follows:

$$\text{CEC value of binary mixture of Resin} = 1/100\ (C_1 \cdot P_1 + C_2\, P_2) \qquad (3)$$

Where,

C_1 = CEC of (100%) pure low cost IER 'X' or 'Z'

C_2 = CEC of(100%) pure low cost IER 'Y'

P_1 = Percentage by weight of low cost IER 'X' or 'Z' in the binary mixture of resin

P_2 = Percentage by weight of low cost IER 'Y' in the binary mixture of resin

RESULTS AND DISCUSSION

The data given in Table-1 show that, the experimental and theoretical compositions of SC in the composites (A - E) are in good agreement with each other. The results are similar to those obtained by Sharma *et al* [6]. This indicates that the experimental methods adopted for the synthesis of PFR and its composites (A - E) are more reliable and reproducible.

Table-1: Amount of reagents used and yields of the PFR and IERs prepared by blending PFR with SCs obtained from various plant materials[+]

Low cost IERs	% of SC in PFR Theoretical	Amount of Reagents used				Yield* (g)	% of SC in PFR Experimental*
		Phenol (mL)	HCHO (mL)	Con.H_2SO_4 (mL)	SC (g)		
PFR	0	10.0	11.5	12.5	0.00	17.00	0.00
A	10	10.0	11.5	12.5	1.89	18.64 - 18.93	9.98 – 10.13
B	20	10.0	11.5	12.5	4.25	20.68 – 21.63	19.65 – 20.55
C	30	10.0	11.5	12.5	7.29	23.83 – 24.63	29.58 – 30.57
D	40	10.0	11.5	12.5	11.33	27.85 – 28.40	39.91 – 40.69
E	50	10.0	11.5	12.5	17.00	33.64 – 34.28	45.59 – 50.54
SC	100	--	--	--	--	--	100

* Range for various plant materials ([+]PE, EJ, TC, TB and AA)

Physico – Chemical Characteristics

The absolute density (Table-3) values in both hydrated (wet) and dehydrated (dry) states decrease steadily from pure resin to 50% (*w/w*) SC in composite resins and then finally to pure SC(100%). This indicates that PFR and the composites/low cost IERs (A – E) are more closely packed[7 - 14]. It is found that the values of absolute density of 100% SCs prepared from various plants are 41.77 – 61.16% and 47.92 – 63.89% compared to that of density of PFR in hydrated (wet) and dehydrated (dry) states, respectively. This indicates that SCs also have closely packed structure[19, 23].

The value of density of composite resins in dry and wet form depends upon the structure of the resin, its degree of cross linking and ionic form[28-30]. Hence, the high density values are obtained for the low cost IERs /composite resins. Moreover, the wet and dry density values are close to each other, which indicate that the samples may be macro porous in nature[31]. From the data given in Table-3, it is clear that there is no considerable decrease or change in absolute density in both in hydrated (wet) and dehydrated (dry) states up to 20% (*w/w*) blending of PFR with SC in the low-cost IERs compared to that of PFR. This indicates that they also have similar closely packed structures with high degree of cross-linking and hence could become suitable for making ion exchange columns for effluents of high density[23-27].

It is observed that, the % of gravimetric swelling of pure resin (PFR) is higher than that of the other samples (Table-3). Therefore, it indicates that the porosity and polarity are greater in the PFR. The composite resin, in which 50% *(w/w)* blends with SC (sample E) has a gravimetric swelling capacity of 36.35 – 45.06% as compared to that of PFR. This extremely low value of % gravimetric swelling may be due to certain rigidity in their matrix and therefore the pores of the composites are of non-gel type and macro reticular[19]. The decrease in % gravimetric swelling value with % of SC in the blend is attributed due to the loss of polarity and porosity in the composites. Thus, the composites may prove to be highly useful where they are required to withstand a large osmotic shock[23].

The values of % attritional breaking presented in Table 3 also represent the stability of the resin, which decrease from PFR to SC (100%). Therefore, the mechanical stability is good up to 20% *(w/w)* blending of SC with PFR. This observation also shows the possibility of formation of resin in the capillaries of the sulphonated carbon (SC) particles[10-12].

CEC of Single Low-Cost Ion Exchange Resin

The values of Cation exchange capacity (CEC) of 0.1 M solution of single metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+} ions) and binary metal ions (Cu^{2+}+ $Zn^{2+}$and Pb^{2+} + Ca^{2+} ions) were determined by using single low cost IERs are shown in Figs. 1-5. The data indicate that, the CEC value decreases, when the percentage of SC *(w/w)* in PFR increases (*i.e.* from A to E) for various low-cost IERs. CEC of individual metal ions depends upon the atomic radius or atomic number[30-33]. At the same time the CEC value also depends upon the inter ionic forces of attraction between anions and cations of the metal salt solutions, valance of the metal ion and concentration of influent[31,33]. From figures 1 –5, it is observed that the CEC value of Cu^{2+} is higher than Zn^{2+} ions in the binary mixture of solutions of 0.1M metal ions (Copper + Zinc ions) used as influent. Similarly, the CEC value of Pb^{2+} ion is higher than Ca^{2+} ions in the binary mixture of solution of 0.1M metal ions (Lead + Calcium) used as influents. The relative affinities of these cations depend upon their size, mobility, ability to diffuse inside the resin matrix and resin selectivity[34]. Kunnin has found that the CEC value decreases as the ionic size of the cations increases. Kressman, Kitchener and Gregor *et al.* have found that the rate of diffusion of large size ions into and through ion exchange resin precede very slowly[25, 26]. Figs.1–5 also indicate that Cu^{2+} and Pb^{2+} ions are preferentially removed by ion exchange to a greater extent compared to Zn^{2+} and Ca^{2+}ions, respectively from aqueous solution of binary mixture of metal ions.

Table-2: Weight proportion of Single low-cost IERs (PFR blended with 20 %(*w/w*) SCs) of Binary mixture of resins (R_1 and R_2)

Binary Mixture of Resin R_1	% Weight Ratio		Binary Mixture of Resin R_2	% Weight Ratio	
	X	Y		Z	Y
X	100	0	Z	100	0
XY1	75	25	ZY1	75	25
XY2	50	50	ZY2	50	50
XY3	25	75	ZY3	25	75
Y	0	100	Y	0	100

* SC obtained from plant materials PE (X), AA(Y) and TB (Z)

Table-3: Physico-chemical properties of PFR and IERs prepared by blending PFR with SCs obtained from various plant materials+

Low cost IERs	% of SC in PFR	Density (g mL^{-1})*		% of Gravimetric swelling*	% of attritional breaking*
		Wet	Dry		
PFR	0	2.01	2.066	85.56	8.00
A	10	1.62 – 1.93	1.35 – 1.94	72.16 – 78.11	8.91 – 20.00
B	20	1.21 – 1.90	1.29 – 1.92	63.00 – 72.66	9.00 – 23.53
C	30	1.05 – 1.77	1.20 – 1.83	56.15 – 68.23	11.58 – 27.45
D	40	1.00 – 1.51	1.17 – 1.71	50.24 – 57.45	13.63 – 28.43
E	50	0.98 – 1.37	0.99 – 1.56	40.48 – 52.99	16.83 – 29.00
SC	100	0.84 – 1.23	0.99 – 1.32	36.35 – 45.06	21.78 – 51.49

* Range for various plant materials (+PE, EJ, TC, TB and AA)

Table-4: Observed and Theoretical total cation exchange capacity of Copper and Zinc metal ions for various single low-cost IERs prepared from various SCs

SCs	Total CEC of Binary Mixture of 0.1M metal (Cu^{2+} +Zn^{2+}) ions (m.mol.g^{-1})						
	PFR	A	B	C	D	E	SC
SPEC	1.923 (1.807)*	1.720 (1.611)	1.531 (1.478)	1.462 (1.433)	1.371 (1.355)	1.293 (1.272)	0.768 (0.761)
SEJC	1.923	1.632	1.521	1.398	1.323	1.284	0.721

	(1.807)	(1.550)	(1.486)	(1.369)	(1.304)	(1.257)	(0.600)
STCC	1.923 (1.807)	1.636 (1.570)	1.514 (1.444)	1.412 (1.350)	1.333 (1.277)	1.189 (1.095)	0.779 (0.759)
STBC	1.923 (1.807)	1.712 (1.635)	1.629 (1.559)	1.531 (1.495)	1.318 (1.294)	1.210 (1.107)	0.815 (0.707)
SAAC	1.923 (1.807)	1.532 (1.457)	1.418 (1.343)	1.296 (0.231)	1.185 (1.170)	1.125 (1.116)	0.731 (0.628)

* Values in parentheses are theoretical total CEC obtained by using eqn. 2.

Also the CEC values of single and binary mixture of metal ion solutions (Figs.1-5) by using single low-cost IERs vary by varying the SC prepared from different plant materials. For binary mixture of metal ions, CEC value is high for the low IER prepared from blending of PFR with 20% SC obtained from the plant material *Phyllanthus emblica*, Linn.,(PE) and *Terminalia bellerica.* Roxb.,(TB) compared to other plant materials and CEC value is low for the low-cost IER prepared by blending of PFR with 20% SC obtained from the plant material AA.

Figs.1–5, also indicate that CEC value of the single IER samples (A – E) obtained from various SCs, for single metal ions was found to decrease in the following order-

STBC > SPEC > SEJC > STCC > SAAC

Similarly, for CEC value of binary mixture of metal ions containing Copper and Zinc ions by using single low cost IERs obtained from various SCs, was found to decrease the following order:

SEJC > SPEC > STBC > STCC > SAAC.

CEC value of samples for binary mixture of metal ion containing Lead and Calcium ions by using single IERs obtained from various SCs was found to be decrease in the following order:

STBC > SPEC > SEJC > STCC > SAAC

Many attempts have been made to explain the difference in the ion exchange behavior of the various cations[36, 37]. The order of ion exchange affinities for the various cations is not unique in ion exchange systems [29.]

Synergistic Effect in Single Low-Cost IER

Table-4 and 5 show that, the observed total cation exchange capacity (total CEC) of both binary mixture of metal ions (Cu^{2+}+ $Zn^{2+}$and Pb^{2+} + Ca^{2+}) in a single low cost IER are always, greater than that of the theoretically calculated values (using equation 2). The total CEC for all the IERs prepared from blending of PFR with various SCs such as SPEC, SEJC, STCC, STBC and SAAC.

The predicted / theoretical value (by using eqn.2)of the CEC of the single and binary mixture of metal ions by single low-cost IERs by varying the percentage by weight of SC in the composite are also given in parenthesis (Tables 4 and 5).The actually observed total values of CEC for both single and binary mixture of metal ions for the single low-cost IERs (PFR, A,B,C,D,E and SC) for various percentage by weight of SC in the composite are found to be greater than that of the CEC values predicted/theoretical value by the linear equation (eqn.2). This indicate that this may be due to the synergistic effect[38,-40]. Since $CEC_{obs} > CEC_{cal}$ the process of metal ions exchange may be due to Synergism modified ion exchange.

CEC of Binary Mixtures of Resin

Table-6 show that the CEC values of binary mixture of resins for all the metal ions in single and binary mixture decrease from the pure resin sample X[PFR blended with 20% (*w/w*) SPEC] to pure Y [PFR blended with 20% (*w/w)* SAAC]. It is observed that by mixing of these two single low-cost IERs - X and

Y (resin R_1) in equal proportions (sample XY2) retains approximately 95.8 – 99.2% of CEC values for the metal ions *viz.*, Cu^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+} ions and approximately 94.9 – 97.7% of CEC value for the binary mixture of metal ions Cu^{2+} +$Zn^{2+}$and Pb^{2+} + Ca^{2+} compared to that of the pure resin X (100%). Hence, for the removal of metal ions from the single and binary mixture of metal ions in aqueous solution, binary mixture of resin X and Y in equal weight proportion (50:50%)– sample: XY2 could be used as a low- cost ion exchange material.

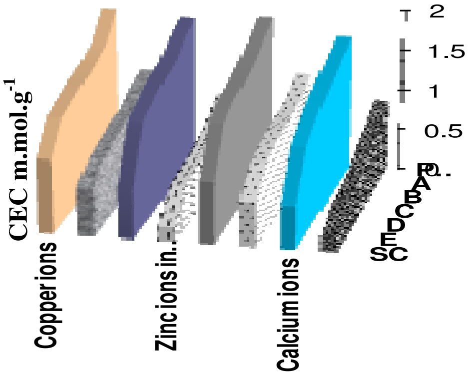

Fig.-1: CEC values of various IERs obtained from *Phyllanthus emblica*, Linn. Carbon for single and binary mixture of metal ions.

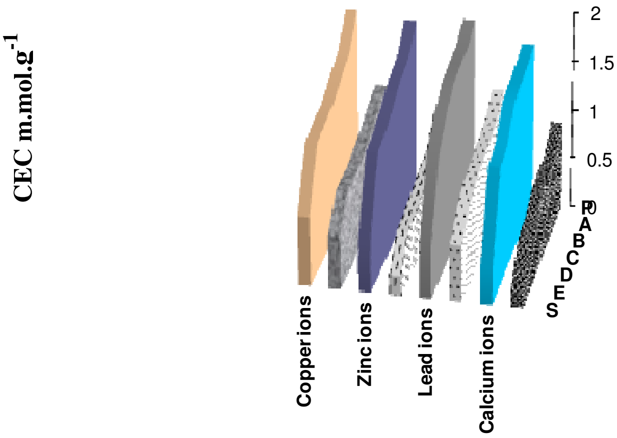

Fig.-2: CEC values of various IERs obtained from *Eugenia jambolana,* Lam. Carbon for single metal ions and its binary mixture of metal ions.

Table-5: Observed and Theoretical total cation exchange capacity of Lead and Calcium metal ions for various single low-cost IERs prepared from various SCs

SCs	Total CEC of Binary Mixture of 0.1M metal (Pb^{2+} +Ca^{2+}) ions (m.mol.g^{-1})						
	PFR	A	B	C	D	E	SC
SPEC	2.024 (1.742)*	1.759 (1.642)	1.446 (1.435)	1.446 (1.435)	1.352 (1.344)	1.267 (1.207)	0.773 (0.652)
SEJC	2.024 (1.742)	1.678 (1.657)	1.642 (1.632)	1.600 (1.592)	1.432 (1.385)	1.314 (1.235)	0.714 (0.464)
STCC	2.024 (1.742	1.703 (1.625)	1.619 (1.574)	1.512 (1.411)	1.428 (1.339)	1.366 (1.312)	0.929 (0.681)

STBC	2.024 (1.742	1.844 (1.646)	1.785 (1.592)	1.595 (1.523)	1.547 (1.420)	1.404 (1.277)	0.868 (0.584)
SAAC	2.024 (1.742)	1.547 (1.512)	1.495 (1.352)	1.321 (1.280)	1.202 (1.116)	1.077 (0.993)	0.762 (0.623)

* Values in parentheses are theoretical total CEC obtained by using eqn. 2.

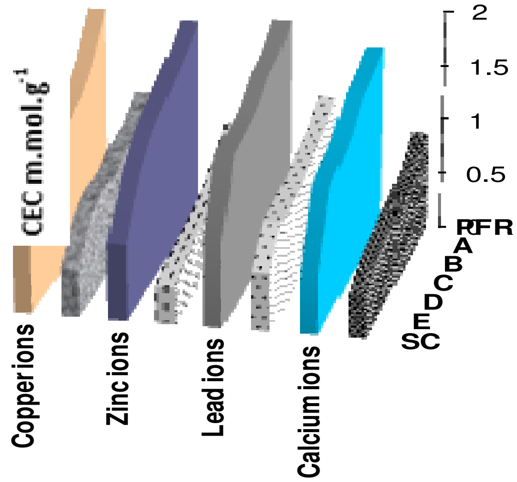

Fig.-3: CEC values of various IERs obtained from *Terminalia chebula*, Retz. Carbon for single and binary mixture of metal ions

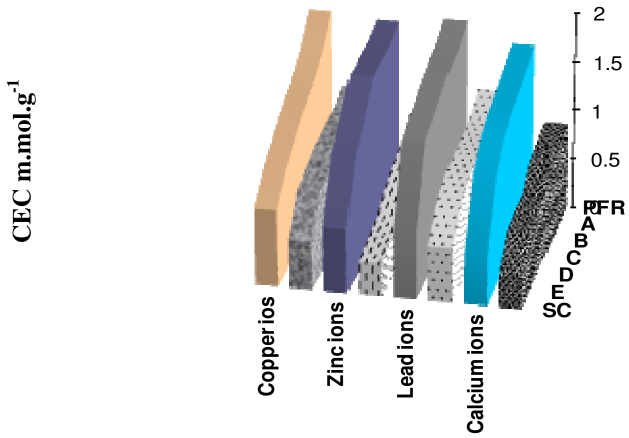

Fig.-4: CEC values of various IERs obtained from *Terminalia bellerica*, Roxb. Carbon for single and binary mixture of metal ions

Table-6: CEC of single and binary mixture of metal ions for binary mixture of resin, R_1

R_1	Cation Exchange Capacity (m.mol g^{-1})							
	Single Metal Ions				Binary Metal Ions Solution			
					0.1M [Cu^{2+} + Zn^{2+}]		0.1M [Pb^{2+} + Ca^{2+}]	
	Cu^{2+}	Zn^{2+}	Pb^{2+}	Ca^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Ca^{2+}

X	1.445	1.511	1.583	1.458	0.832	0.691	0.993	0.623
XY1	1.441 (1.429)*	1.483 (1.459)	1.551 (1.539)	1.442 (1.418)	0.826 (0.818)	0.678 (0.673)	0.965 (0.956)	0.615 (0.608)
XY2	1.434 (1.413)	1.447 (1.408)	1.536 (1.494)	1.405 (1.378)	0.813 (0.804)	0.667 (0.654)	0.942 (0.919)	0.608 (0.594)
XY3	1.401 (1.397)	1.414 (1.356)	1.491 (1.450)	1.366 (1.338)	0.802 (0.79)	0.644 (0.636)	0.922 (0.881)	0.595 (0.579)
Y	1.382	1.304	1.405	1.298	0.776	0.617	0.843	0.564

* Values in parentheses are theoretical total CEC obtained by using eqn. 3.

Table-7 show that the CEC values of binary mixture of resins for all the metal ions in single and binary mixture decrease from the pure resin sample Z [PFR blended with 20% (*w/w*) STBC] to pure Y [PFR blended with 20% (*w/w)* SAAC]. It is observed that by mixing of these two single low-cost IERs - Z and Y (resin R_2) in equal proportions (sample : ZY2) retains approximately 93.0–99.65% of CEC values for the metal ions *viz.*, Cu^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+} ions and approximately 90.8 – 96.1% of CEC value for the binary mixture of metal ions Cu^{2+} +$Zn^{2+}$and Pb^{2+} + Ca^{2+} compared to that of the pure resin Z (100%).Therefore, for the removal of metal ions from the single and binary mixture of metal ions in aqueous solution, mixture of resin Z and resin Y in equal weight proportion (50:50%) – sample : ZY2 could be used as a low-cost ion exchange material.

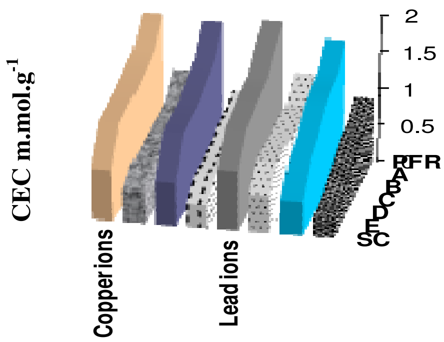

Fig.-5: CEC values of various IERs obtained from *Achyranthes aspera*, Linn. Carbon for single and binary mixture of metal ions

Synergim modified ion exchange process

The experimentally observed values of CEC are also given in Tables 6 and 7 along with the theoretically calculated values of CEC (using eqn.3). The predicted/ theoretical values of CEC of binary mixture resins (R_1 and R_2)for both single metal ions (Cu^{2+} , Zn^{2+}, Pb^{2+} and Ca^{2+} ions) and binary mixture of metal ions (Cu^{2+} + Zn^{2+}; and Pb^{2+} + Ca^{2+} ions) were calculated by using the linear equation (eqn.3). The observed values of CEC (Table. 6) of the single and binary mixture of metal ions by using the binary mixture of resins are found to be greater than that of the theoretically calculated values obtained by using eqn.3. If calculated and observed CEC values are equal, then it indicates that the linear or additive (ideal) behaviour of ion exchange process exists. The observation.$CEC_{obs.}> CEC_{cal}$ indicate that the linear or additive(ideal) behaviour(eqn.3) of ion exchange process is not applicable for mixed resin (binary mixture of resin *viz.,* R_1 and R_2).A similar behaviour on adsorption capacity of mixed adsorbents was noticed and reported earlier in literature[38,41]. The high observed value of CEC, than that of the theoretical value, may be due to the non-ideal (non – linear) and non – additive cation exchange process of the mixed resins (binary mixture of resins R_1 and R_2). This may be probably due to synergistic effect of the mixture of (mixed) resins. The phenomenon may be termed as 'synergism – modified ion exchange processes.

CONCLUSION

From the present study, it is concluded that, the single low-cost IERs prepared by blending PFR with 20% (*w/w*) SC prepared from various plant materials(PE, EJ,TC,TB,and AA) almost retain the CEC value of PFR. Also, these single low-cost IERs are found to be suitable for the removal of metal ions, particularly Copper, Zinc, Lead and Calcium ions for single and binary mixtures from water and wastewater. Hence, these IERs could be used as low-cost IERs, compared to the available commercial IER. It is also concluded that, the mixing of these low-cost IERs to form binary mixture of resins($R_1$and R_2) shows greater CEC value compared to that of the theoretically calculated value based on the linear or additive (ideal) property. This may be due to synergism modified ion – exchange process.

Table-7: CEC of single and binary mixture of metal ions for binary mixture of resin R_2

R_2	Cation Exchange Capacity (m.mol g^{-1})							
	Single Metal Ions				Binary Metal Ions Solution			
					0.1M [Cu^{2+} + Zn^{2+}]		0.1M [Pb^{2+} + Ca^{2+}]	
	Cu^{2+}	Zn^{2+}	Pb^{2+}	Ca^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Ca^{2+}
Z	1.415	1.702	1.678	1.505	0.900	0.703	0.946	0.682
ZY1	1.412 (1.407)*	1.684 (1.603)	1.638 (1.610)	1.475 (1.453)	0.893 (0.866)	0.694 (0.676)	0.926 (0.919)	0.666 (0.645)
ZY2	1.410 (1.399)	1.583 (1.503)	1.587 (1.542)	1.439 (1.402)	0.846 (0.833)	0.668 (0.650)	0.909 (0.892)	0.619 (0.609)
ZY3	1.406 (1.390)	1.463 (1.404)	1.501 (1.473)	1.410 (1.350)	0.808 (0.797)	0.654 (0.623)	0.891 (0.865)	0.593 (0.572)
Y	1.382	1.304	1.405	1.298	0.765	0.596	0.838	0.535

* Values in parentheses are theoretical total CEC obtained by using eqn. 3.

ACKNOWLEDGEMENTS

The authors thank the management and principal of their colleges for providing research facilities and encouragement, respectively.

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[RJC-1062/2013]