



Research Article

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Optimization of process parameters for the removal of calcium ions by ion exchange process

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ABSTRACT

Optimisation of process parameters for the removal of calcium ions by phenol-formaldehyde sulphonate resin (PFR) blended with sulphonated carbons (SCs) obtained from various plant materials like AA, EJ and TB was carried out by using Box-Behnken statistics and analysis of variance method. Response surface methodology with three levels of process parameters viz., % (w/w), of SC in condensate (10, 20 and 30), particle size (200, 300 and 400 μm or microns) and initial concentration of calcium ions (0.05, 0.1 and 0.15 mol L⁻¹) were used in the identification of significance of the effects and interactions in ion exchange studies. Response surface methodology requires no assumption and identifies the experimental variables and their interactions which have the greatest effect on ion exchange process. The optimum process parameters for maximum removal of calcium ions were obtained by this procedure. Contour plots were obtained and interpreted.

Key words: Optimisation of process parameters, phenol-formaldehydesulphonate resin, sulphonated carbons, plant materials, Box-Behnken statistics Response surface methodology, Multiple linear regression analysis.

INTRODUCTION

Among various environmental pollution, water pollution is the most significant one. Heavy metals are highly toxic and produce hazardous effect on living things, organisms, plants and animals[1]. Most of the industrial effluents contain a mixture of heavy metals and hence their discharge would demand a great deal of effort and resources. If heavy metals are removed from wastewater, it will safeguard the environment and bring high economic returns to the developing countries like India. The stringent regulations towards the discharge of wastewater, has prompted the researchers to examine new methodologies for treating effluents, especially for the removal of heavy metal ions. Ion exchange resins (IERS) are mostly used for water softening process, especially for the removal of hardness. Hardness arises due to dissolved Ca²⁺ and Mg²⁺ ions and therefore they are to be necessarily removed from water. Ion exchange process with commercial resin (CR) appears to be the best one with least adverse effects with no or lesser sludge formation [2]. CRs are synthesised from petroleum products and hence there is a phenomenal increase in the cost of the ion exchange resins (IERS) and further difficulty in procurement of CRs. Because, of these reasons alternative low-cost IERS have been developed [3,4]. Earlier studies showed that the cheaper composite ionexchangers(IERS) could be used to remove heavy metal ions from solutions and prepared by partiallyblending the macro porous phenol-formaldehyde sulphonate resin (PFR) matrix by blending it withcarbons obtained from coal, saw dust, spent Coffee, cashew nut husk, wheat husk, turmeric plant, spenttea, gum tree bark, *Accacia nilotica* and Egyptian bagasse pith[5-13]. In the past decades, research has been carried out to develop innovative and promising low-cost IERS for water treatment which are obtained by blending SCs derived from plant materials with phenol-formaldehydesulphonate resin (PFR). The ultimate goal of this endeavor is to identify an effective and inexpensive IER for the removal of metal ions causing hardness like metal ions say Ca²⁺ ions from aqueous solution

and to find out the optimum conditions of process parameters for the effective / maximum removal of calcium ions, by ion exchange process.

Sulphonated carbons (SCs) prepared from plant materials containing phenolic groups have been blended in 10, 20 and 30% (w/w) ratio with PFR resin. The resultant condensates were tried as low-cost IERs for the removal of calcium ions. Among the various PFR-SCs, the blends of PFR-SC derived from plants EJ (*Eugenia jambola* Lam.) and TB (*Terminalia bellirica* Roxb.) are found to be the best low-cost material for the removal of metal ions[4] with high and moderate CEC values while the one derived from AA (*Achyranthes aspera* Linn.) has least CEC value. Therefore they are used in the present study. Ion exchange process becomes highly effective, only when the optimum process parameters are employed. This necessitates the study of optimisation of process parameters for the removal of metal ions like calcium ions by ion exchange process with the low-cost IERs obtained by blending 10, 20 and 30% (w/w) of SC derived from AA, TB and EJ with that of PFR. With this aim, and objectives the present study has been carried out.

The effect of several critical factors influencing the ion exchange process of calcium ions, such as the % (w/w) of SC in the condensate, particle size and initial concentration of calcium ions, has been studied. Box-Behnken factorial design[14] with three variables like, % (w/w) of SC in condensate ($x_1 = 10, 20, 30$), particle size ($x_2 = 200, 300$ and $400 \mu\text{m}$) and initial concentration of Ca^{2+} ions ($x_3 = 0.05, 0.10$ and 0.15M) for the removal of calcium ions with IERs at three different levels (-1, 0 and +1) was studied to identify a significant correlation between the cation exchange capacity (CEC) of IERs for the removal of calcium ions ($y = \text{CEC in m mol g}^{-1}$) and the effect of changing these variables (x_1, x_2 and x_3). CEC in m mol g^{-1} (y) values were determined at the experimental conditions employing Box-Behnken design of experiments.

The determination of optimum experimental conditions for the above mentioned process parameters [% (w/w) SC, initial concentration and particle size] would require large number of experiments with all possible combinations of these parameters. However, it is possible to undertake experiments with a rational design, which reduces the number of experiments and broadens the range of information about the system[15, 16]. The parameters such as % (w/w) of SC in condensate, particle size and initial concentration of Ca^{2+} ions have been considered as the critical variables. Statistical design was used to determine the optimal levels of ion exchange under a given set of experimental conditions.

The usual classical type of optimisation technique involves changing one variable at a time, while keeping the other variables as constants at fixed condition. Being single dimensional, it often does not generate the exact prediction of optimum conditions. Hence, the need of factorial design and the response surface methodology has been understood for the simultaneous optimisation of process parameters and employed in the present study.

MATHEMATICAL MODEL

Response surface methodology is purely an empirical modelisation technique devoted to the evaluation of the relationship of a set of controlled process or experimental factors (x_1, x_2 and x_3) and the observed result (*viz.*, $y = \text{CEC, in m mol}^{-1} \text{g}^{-1}$) for the removal of Ca^{2+} ions by ion exchange process[4]. It requires a prior knowledge of the effect of these process parameters and their impact on CEC.

Basically this optimisation process involves three major steps. They are:

- performing the statistically designed set of experiments
- estimating the co-efficients in a mathematical model and
- predicting the response and checking adequacy of the model

The significant process parameters like % (w/w) of SC in condensate particle size and initial concentration of Ca^{2+} ions were chosen as the critical variables and designated as x_1, x_2 and x_3 , respectively. The low, middle and high levels of each variable were coded as -1, 0 and +1. The actual values of % (w/w) of SC in condensate, particle size and initial concentration of Ca^{2+} ions used in the experiment and the codes are given in Table 1. The actual design of experiments is shown in Table 2. Totally 27 number of ion exchange adsorption experiments were carried out at $30 \pm 1^\circ\text{C}$ as per the conditions of experiments which are given in Table 2.

Table 1 Critical variables of process (experimental) parameters for ion exchange process

S.No.	Variable	x_i	-1	0	+1
1	% (w/w) of SC in condensate	x_1	10	20	30
2	Particle size (μm)	x_2	200	300	400
3	$[\text{Ca}^{2+}]_0$ ions (M)	x_3	0.05	0.10	0.15

Table 2 Experimental condition for the ion exchange studies of calcium ions*

S.No.	x ₁ (% w/w of SC)	x ₂ (Particle Size)	x ₃ ([Ca ²⁺] ₀)
1.	-1	-1	-1
2.	-1	-1	0
3.	-1	-1	+1
4.	-1	0	-1
5.	-1	0	0
6.	-1	0	+1
7.	-1	+1	-1
8.	-1	+1	0
9.	-1	+1	+1
10.	0	-1	-1
11.	0	-1	0
12.	0	-1	+1
13.	0	0	-1
14.	0	0	0
15.	0	0	+1
16.	0	+1	-1
17.	0	+1	0
18.	0	+1	+1
19.	+1	-1	-1
20.	+1	-1	0
21.	+1	-1	+1
22.	+1	0	-1
23.	+1	0	0
24.	+1	0	+1
25.	+1	+1	-1
26.	+1	+1	0
27.	+1	+1	+1

*Code for x₁, x₂ and x₃ as given in Table 1.

The effect of these three variables (x₁, x₂, and x₃) on CEC(y) can be approximated by the quadratic (second degree) polynomial (**Multiple Linear Regression – MLR**) model / equation is :

$$y = C_0 + C_1 x_1 + C_2 x_2 + C_3 x_3 + C_{11} x_1^2 + C_{22} x_2^2 + C_{33} x_3^2 + C_{12} x_1 x_2 + C_{13} x_1 x_3 + C_{23} x_2 x_3$$

$$(R = \text{_____}; 100R^2 = \text{_____}; S = \text{_____}) \quad \dots \quad (i)$$

Where, y is the experimental / predicted response (y = CEC, in m mol g⁻¹), x₁ is the % (w/w) of SC in condensate, x₂ is the particle size, in micron and x₃ is the initial concentration of Ca²⁺ ions in mol L⁻¹ (as their coded data); x₁₂ and x₁₃ are the cross products of parameters, x₁₁ and x₂₂ are square products of parameters; C₁₁ and C₂₂ are coefficients of square terms, C₁₂ are coefficients of the cross terms; C₁, C₂ and C₃ are linear coefficients; C₀ is constant; R is correlation coefficient for MLR model, 100R² is percent variation explained by a set of explanatory variables and 'S' is standard error of the estimate. **MLR model** given in the above equation (Eqn.i), interactions which are higher than the first order have been neglected. The design of experiments is preferred because relatively few experimental combinations of the variables are adequate to estimate potentially complex response function[14]. The set of experiments chosen for this study was based on Box-Behnken statistics[15,16] - a fractional factorial design for three independent variables. It is applicable to the system only when the critical variables have been identified [14].

EXPERIMENTAL SECTION

Materials and method

Phenol and formaldehyde used were of Fischer reagents (India). LR grade of con. sulphuric acid (Sp. gr. = 1.82) was used. Sulphonated carbons (SCs) obtained from plant materials viz., *Eugenia jambolana*, Lam. (EJ), *Terminalia bellarica*, Roxb.(TB) and *Achyranthes aspera*, 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 0.5 cm length.

Preparation of sulphonated carbons

About 500 g of plant materials (EJ, TB, and AA) were carbonised and sulphonated by con. sulphuric acid (500 ml) and kept at room temperature(30 ±1°C) for 24 h and heated at 90°C in a hot air-oven for 6 h. 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°C for 12 h. They were labeled as SEJC (Sulphonated *Eugenia jambolana* Lam carbon),

STBC(sulphonated *Terminalia bellarica*, Roxb carbon) and SAAC(sulphonated *Achyranthes aspera*, Linn., carbon), respectively for the SCs prepared from EJ, TB and AA.

Preparation of pure phenol formaldehyde resin

Con. sulphuric acid (12.5 mL) was slowly added to phenol (10 mL) in drop-wise with constant stirring by placing it in an ice-bath at 0 – 5°C. The mixture was heated at 70°C for 3 h in a hot air-oven, then cooled immediately in an ice-bath and kept overnight. It was then polymerised with formaldehyde (11.5 mL) at 80°C and the product was cured in a hot air-oven for 3 h. A brown coloured chunky solid mass was obtained[17]. It was then ground, washed with distilled water and finally with DD water to remove excess free acid, dried, sieved (210 – 300µm size) using Jayant sieves(India) and preserved for further studies. It was labeled as PFR.

Preparation of condensate

A known amount of phenol was sulphonated with con. sulphuric acid by the above method to produce phenolsulphonic acid. Then, it was mixed with various percentage by weight of sulphonated carbons (SCs) obtained from various plant materials (EJ, TB, and AA) in the condensate as 10, 20, and 30, respectively.

Each mixture was polymerised with formaldehyde solution (11.5 mL) at 80°C 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 characterisation for the further studies. The product with 10, 20 and 30 % (w/w) of SCs obtained from various plant materials EJ, TB and AA in the condensate, were respectively labeled as A, B and C for each condensate with SEJC, STBC and SAAC.

Cation exchange capacity

A known weight (2 g) of the samples of condensate/ low - cost IERs 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 AgNO₃ solution). The test column was prepared by using graduated burette with glass-wool plug and the slurry of washed resin sample. Forty mL of 0.1 M solution of calcium ions of known initial concentration (C₀ = 0.05, 0.10 and 0.15 M) was used as influent. The rate of flow of effluent was adjusted to 1 mL min⁻¹. The low - cost IER samples exchanged its H⁺ ions with the Ca²⁺ ions – a hardness producing ions. The total amount of cation exchanged was determined by using the standard titration techniques[18]. The values of cation exchange capacity(CEC) were determined as per the literature method[19]. The error in the values of y = ±0.002 – 0.003 mol⁻¹ g⁻¹. All the multiple linear correlations and contour plots were drawn using computer.

RESULTS AND DISCUSSION

MLR Model

Ion exchange process results in the removal of solutes (metal / calcium ions) from aqueous solution and their concentration at the surface of the solid (condensate) and in solution are in dynamic equilibrium. At this position of equilibrium there is a defined distribution of solute between the liquid and solid phases. The CEC of calcium ions was found to be poorly correlated with any one of these process parameters, x₁, x₂ and x₃ [x₁ = % (w/w) of SC in condensate : r = 0.143 – 0.167 ; x₂ = particle size, in µm : r = 0.003 – 0.096; and x₃ = initial concentration of Ca²⁺ ions in M: r = 0.800 – 0.824]. Multiple Linear Regression (MLR) analysis, involving x₁, x₂ and x₃, simultaneously, resulted in a three parameter equation, of the type: y = c₀ + c₁x₁ + c₂x₂ + c₃x₃, (Where x = process parameter, c₁ = regressor coefficient and c₀ = constant) which were noted to be slightly better than the single parameter equations, as evidenced by their r-values (r-value: 0.815 – 0.842), but these MLR equations are not able to predict the experimentally observed y values (r = 0.82 - 83), with slope values not equal to unity (m = 0.81 – 0.83). Further these MLR equations are having only 80% Confidence Level (CL) and are noted to be statistically significant. Analysis of variance (ANOVA), revealed the significance of the square and cross product terms (Table 3) and hence the nine parameter equations shown by eqn.1 were developed. MLR equation obtained, after the analysis of variance, will give the extent of cation exchange capacity (CEC) as a function of different process parameters. All the terms regardless of their significance are included into the MLR equation [14].

Table 3 Analysis of variance of process parameters for the removal of Ca²⁺ ions by ion exchange process

S.No.	Variable	Eigen Value *	Percent Variance ⁺		
			AA	EJ	TB
1	y (CEC)	-	18.5	19.0	18.8
2	x ₁ (% (w/w) of SC in condensate)	1.83	15.6	15.4	15.3
3	x ₂ (particle size in micron)	1.36	12.3	12.2	12.2
4	x ₃ ([Ca ²⁺] ₀)	1.26	11.3	11.3	11.3
5	x ₁ ²	1.22	10.4	10.4	10.4
6	x ₂ ²	1.14	10.2	10.1	10.1
7	x ₃ ²	1.12	7.9	7.9	7.9
8	x ₁ x ₂	0.84	7.0	7.1	7.0
9	x ₁ x ₃	0.77	4.5	4.6	4.6
10	x ₂ x ₃	0.46	2.3	2.0	2.2

* percentage variance = 10 × Eigen value, excluding y values.

⁺ Eigen value = percent variance / 11, including y value.

MLR analysis was performed to obtain the coefficients from the experimental results *viz.*, CEC, in m mol⁻¹ g⁻¹ (y values) for the set of statistically designed experiments based on Box-Behnken design of experiments. MLR equations obtained between CEC process parameter of various condensate obtained by blending PFR with various % (w/w) of SCs prepared from various plant materials AA, EJ and TB could be used to predict the response [equations (ii) to (iv)] :

MLR equations:**AA:**

$$y_{AA} = 1.291 - 0.0599x_1 - 0.0405x_2 + 0.346x_3 - 0.0598x_1x_1 - 0.271x_3x_2 - 211x_3x_3 + 0.0668x_1x_2 - 0.0705x_2x_3 - 0.0159x_3x_1$$

(R = 0.988, 100R² = 97.61, S = 0.00449) (ii)

EJ:

$$y_{EJ} = 1.597 - 0.070x_1 + 0.00844x_2 + 0.372x_3 - 0.122x_1x_1 - 0.272x_3x_2 - 0.318x_3x_3 + 0.0363x_1x_2 - 0.0429x_2x_3 - 0.0247x_3x_1$$

(R = 0.984, 100R² = 96.83, S = 0.00722) (iii)

TB:

$$y_{TB} = 1.565 - 0.0739x_1 - 0.00178x_2 + 0.3637x_3 - 0.1132x_1x_1 - 0.2556x_2x_2 - 0.2754x_3x_3 + 0.0305x_1x_2 - 0.0423x_3x_3 - 0.00233x_3x_1$$

(R = 0.986, 100R² = 97.22, S = 0.00573) (iv)

Theoretically calculated value using MLR eqns. (ii) to (iv)

Quadratic regression equations (ii) – (iv) are found to be statistically significant at 95% confidence level (CL) while the MLR equations with these three variables x₁, x₂ and x₃ alone are significant only at 80% CL indicating the combined effect of the % (w/w) of SC in the condensate, particle size and initial concentration (concn.) Ca²⁺ ions (x₁) and their square (x₁₁ or x₂₂) and cross products (x₁₂).

The percent variance obtained from the factor analysis of all the dependent (explanatory) variables, its square term and cross products, including and excluding the independent variable (y = CEC) are presented in Table 3. The percent variance of the variables will give an idea about the significance of each variable and its contribution in explaining the observed experimental results (y values). The predicted/ calculated values of CEC of the condensate from the equations (ii) to (iv) at each set of experimental conditions (y_{cal}) are also summarised in Table 4, along with the experimentally observed values of CEC (y_{obs}).

The values of correlation coefficient (R) for the MLR equations (ii) to (iv) are found to be in the range of 95% CL and the correlations are statistically significant, which indicate that there should be a close agreement between the experimental (y_{obs}) and theoretical values of CEC (y_{cal}). The simulated values of y_{cal} by the equations (ii) to (iv) are found to be in close agreement with that of the experimental Y_{obs} values (Table 4). The applicability of the model was verified by plotting the calculated values of CEC (y_{cal}) against the experimental (Y_{obs}) values (Fig 1). Values of slope (m, range = 0.972 – 0.975) are computed by correlating the y_{cal} values with y_{obs} and are reported in Table 5, along with the values of intercept (c, range = 0.023 – 0.031) and correlation coefficient (r, range = 0.968 – 0.976) for the ion exchange on Ca²⁺ ions by low-cost IERs obtained from the three different plant materials (EJ, TB and AA). The observed value of slope (m) which is close to unity (m value range = 0.972 – 0.975) reveals that the model is valid and applicable in the case of removal of calcium by these low-cost IERs.

Table 4 Experimentally observed and theoretically calculated values of CEC for the removal of Ca^{2+} ion by IERs obtained by SCs prepared from plant materials

Expt No.	Experimental obs value of CEC			Theoretical calc value of CEC		
	AA	EJ	TB	AA	EJ	TB
1.	0.538	0.590	0.658	0.484	0.542	0.619
2.	1.106	1.280	1.291	1.127	1.300	1.303
3.	1.326	1.442	1.456	1.350	1.422	1.436
4.	0.625	0.783	0.833	0.718	0.830	0.884
5.	1.363	1.597	1.565	1.291	1.545	1.526
6.	1.499	1.621	1.624	1.443	1.624	1.617
7.	0.450	0.593	0.653	0.417	0.573	0.639
8.	0.874	1.182	1.206	0.913	1.245	1.238
9.	0.950	1.273	1.262	0.994	1.281	1.287
10.	0.496	0.644	0.683	0.433	0.583	0.630
11.	0.993	1.237	1.257	0.433	1.316	1.311
12.	1.259	1.437	1.454	1.061	1.413	1.442
13.	0.610	0.768	0.821	1.267	0.906	0.926
14.	1.298	1.565	1.505	0.734	1.597	1.565
15.	1.415	1.613	1.618	1.291	1.651	1.654
16.	0.542	0.709	0.735	1.427	0.685	0.711
17.	1.045	1.528	1.483	0.493	1.333	1.308
18.	1.022	1.326	1.346	0.980	1.343	1.354
19.	0.314	0.418	0.442	0.263	0.379	0.415
20.	0.847	1.006	1.048	0.874	1.088	1.094
21.	1.044	1.149	1.183	1.064	1.160	1.222
22.	0.565	0.744	0.749	0.631	0.739	0.741
23.	1.221	1.517	1.446	1.171	1.405	1.378
24.	1.351	1.523	1.595	1.291	1.434	1.464
25.	0.484	0.544	0.549	0.456	0.554	0.557
26.	0.888	1.092	1.074	0.926	1.177	1.151
27.	0.939	1.108	1.132	0.976	1.164	1.195

Table 5 Statistical results of correlation between the calculated and observed values of CEC for the removal of Ca^{2+} ions by ion exchange process

SC	Slope (m)	Intercept (c)	r-value
AA	0.975	0.0232	0.976
EJ	0.972	0.0307	0.968
TB	0.973	0.0311	0.973

- For the best fit of the model: $m \approx 1.0$, $C \approx 0.0$ and $r \approx 1.0$.

Theoretically calculated value using MLR eqns. (ii) to (iv)

Quadratic regression equations (ii) – (iv) are found to be statistically significant at 95% confidence level (CL) while the MLR equations with these three variables x_1 , x_2 and x_3 alone are significant only at 80% CL indicating the combined effect of the % (w/w) of SC in the condensate, particle size and initial concentration (concn.) Ca^{2+} ions (x_1) and their square (x_{11} or x_{22}) and cross products (x_{12}).

The percent variance obtained from the factor analysis of all the dependent (explanatory) variables, its square term and cross products, including and excluding the independent variable ($y = \text{CEC}$) are presented in Table 3. The percent variance of the variables will give an idea about the significance of each variable and its contribution in explaining the observed experimental results (y values). The predicted/ calculated values of CEC of the condensate from the equations (ii) to (iv) at each set of experimental conditions (y_{cal}) are also summarised in Table 4, along with the experimentally observed values of CEC (y_{obs}).

The values of correlation coefficient (R) for the MLR equations (ii) to (iv) are found to be in the range of 95% CL and the correlations are statistically significant, which indicate that there should be a close agreement between the experimental (y_{obs}) and theoretical values of CEC (y_{cal}). The simulated values of y_{cal} by the equations (ii) to (iv) are found to be in close agreement with that of the experimental Y_{obs} values (Table 4). The applicability of the model was verified by plotting the calculated values of CEC (y_{cal}) against the experimental (Y_{obs}) values (Fig 1). Values of slope (m, range = 0.972 – 0.975) are computed by correlating the y_{cal} values with y_{obs} and are reported in Table 5, along with the values of intercept (c, range = 0.023 – 0.031) and correlation coefficient (r, range = 0.968 – 0.976) for the ion exchange on Ca^{2+} ions by low-cost IERs obtained from the three different plant materials (EJ, TB and AA). The observed value of slope (m) which is close to unity (m value range = 0.972 – 0.975) reveals that the model is valid and applicable in the case of removal of calcium by these low-cost IERs.

Optimisation of Process Parameters

Contour plots were drawn using **Mathematica** software, representing the CEC versus % (w/w) of SC in condensate (x axis) and particle size in μm (y axis) at a constant initial concentration of Ca^{2+} ions say 0.10M (Fig. 2, segments A, B and C for AA, EJ and TB respectively). The CEC of calcium ion exchanged (y-value) increases and then decreases with increase in particle size and decreases with the increase in % (w/w) of SC in condensate. The maximum value of CEC for a given set of experimental conditions of % (w/w) of SC in condensate and particle size and also the optimum values of process parameters for maximum value of CEC could be obtained from contour plots. At 0.10M initial concentration of Ca^{2+} ions, the optimum values of process parameters are 18% (w/w) of SAAC with 250 μm particle size; 20% (w/w) of SEJC with 275 μm particle size; and 20% (w/w) of STBC with 50 μm particle size of the IERs.

Contour plots of CEC versus initial concentration of Ca^{2+} ions and particle (μm) size of IER (y axis) and initial concentration of Ca^{2+} ions (C_0 , x axis) at constant amount of SC *viz.*, 20% (w/w) of SCs in the condensate (Fig. 3, segments A, B and C, respectively for AA, EJ, and TB) reveal that CEC value increases with increase in particle size and then decreases and the CEC value increases with increase in $[\text{Ca}^{2+}]_0$ up to 0.15 mol L^{-1} . The extent of variation of CEC with these parameters could be obtained from these contour plots. The maximum value of CEC with 20% (w/w) of SC in the condensate occurs at the following optimum conditions: 0.08 M $[\text{Ca}^{2+}]_0$ with 375 μm particle size of resin prepared from SAAC, 0.10M $[\text{Ca}^{2+}]_0$ with 360 μm particle size of resin prepared from SEJC and 0.10M $[\text{Ca}^{2+}]_0$ with 360 μm particle size of resin prepared from STBC.

Contour plots (drawn using **Mathematica** software) representing the CEC versus % (w/w) of SC in condensate (in y axis) and initial concentration of Ca^{2+} ions (C_0 , in x axis) at constant particle size of 300 micron

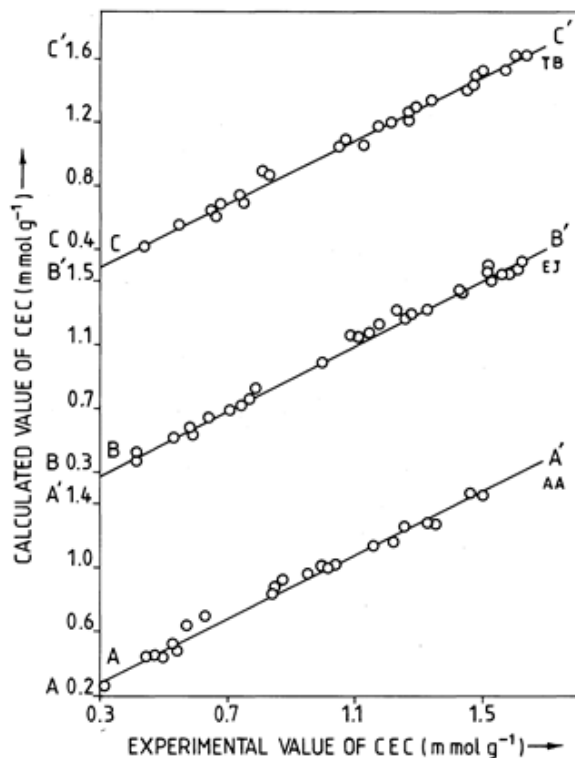


Fig 1 Plots between the experimental and calculated values of CEC of various low cost IERs by blending SCs prepared from various plant materials (AA, EJ and TB)

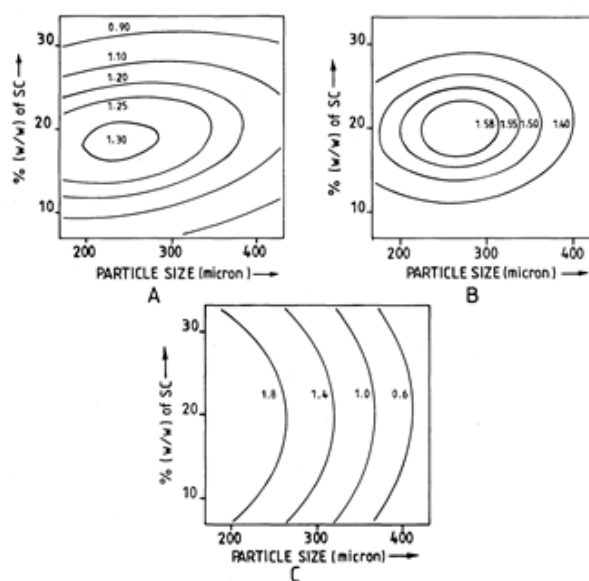


Fig.2 Contour plots representing CEC of 0.1M $[\text{Ca}^{2+}]_0$ solution as a function of % (w/w) of SC versus particle size (micron); A=AA, B = EJ and C = TB

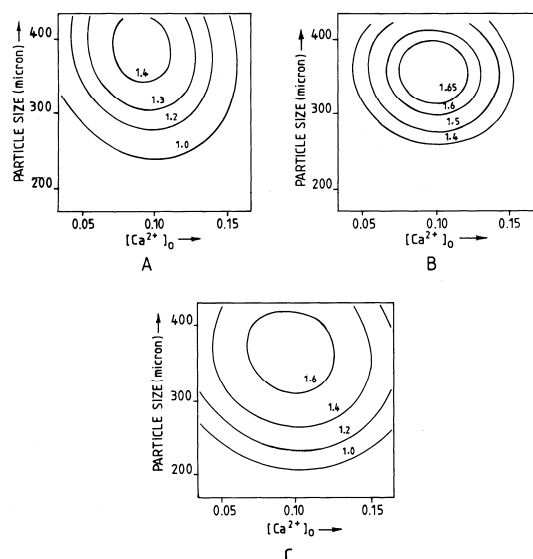


Fig. 3 Contour plots representing CEC of composite prepared with 20%(w/w) of SC as a function of particle size (micron) versus $[Ca^{2+}]_0$; A = AA, B = EJ and C = TB

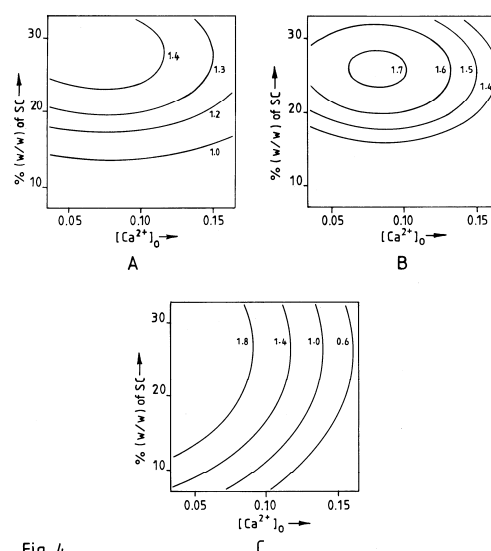


Fig. 4

Fig. 4 Contour Plots representing CEC of composite with 300 micron particle size as a function of % (w/w) of SC versus $[Ca^{2+}]_0$; A = AA, B = EJ and C = TB

(Fig. 4, segments A, B and C respectively for AA, EJ and TB) indicate that the CEC increases with decrease in % (w/w) of SCs in the condensate and increases with increase in initial concentration of Ca^{2+} ions ($[Ca^{2+}]_0$) up to 0.15 mol L^{-1} . The contour plots give an idea about the variation in CEC values with the simultaneous changes in these process parameters. The maximum value of y (CEC) reached with 300 μm particle size of resin which occur at the following optimum conditions of process parameters;

SAAC : 27.5 % (w/w) of SC in blend and 0.075M of $[Ca^{2+}]_0$
 SEJC : 25 % (w/w) of SC in blend and 0.08M of $[Ca^{2+}]_0$ and
 STBC : 27.5 % (w/w) of SC in blend and 0.01 M of $[Ca^{2+}]_0$

Hence in general the optimum conditions of process parameters are 20% (w/w) of SC in the condensate, 200-300 micron particle size of condensate and 0.08M initial concentration of Ca^{2+} ions. Among the low-cost IERs, the IER obtained by blending SC prepared from TB, posses the maximum CEC value and hence it could be used as low-cost IER as an alternative to CR. These IERs could be used as low-cost materials for the removal of calcium ions, for water softening under the experimental conditions.

CONCLUSION

The following conclusions have been arrived at from the results of the present study:

- The mathematical modeling has been useful for theoretically predicting the CEC values under various experimental conditions. The balanced nature of a statistical design leads it-self to an organised method of experimentation and to a straight forward approximation to data analysis. Graphical presentation is facilitated with such results from designed experiments.
- The variables such as % (w/w) of SC in condensate, particle size and initial concentration of Ca^{2+} ions were proved to be the most significant(critical) parameters for the maximum CEC of calcium ions as evidenced from the MLR equation and contour plots.
- The results obtained could be used for better designing of cost-effective IERs for effluent / water treatment plant, for the economic removal of metal ions in general and calcium ion in particular by ion exchange process..

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Notations

C_0 = Constant
 C_1 = linear coefficient for x_1

C_2	=	linear coefficient for x_2
C_3	=	linear coefficient for x_3
C_{11}	=	Coefficient of square term x_1^2
C_{22}	=	Coefficient of square term x_2^2
C_{33}	=	Coefficient of square term x_3^2
C_{12}	=	Coefficient of the cross product term x_1x_2
C_{13}	=	Coefficient of the cross product term x_1x_3
C_{23}	=	Coefficient of the cross product term x_2x_3
CEC (y)	=	Cation exchange capacity, in $\text{m mol}^{-1} \text{g}^{-1}$
r, R	=	correlation coefficient
$100R^2$	=	percent of variation explained / coefficient of determination
S	=	standard error of the estimate
X_1	=	% (w/w) of SC in condensate
x_2	=	particle size (in μm)
x_3	=	initial concentration Ca^{2+} ions (in M or mol L^{-1}).
X_{11}, X_{22}	=	square term of the process parameters
X_{12}	=	cross product of the process parameters
y	=	experimental / predicted response (CEC)

REFERENCES

- [1] A.M., Wachinski and J.E.Etzel *Environmental ion exchange*, Lewis, New York, **1997**.
- [2] J.W. Patterson, *Wastewater treatment technology*. Ann Arbor Sci. Publ., Ann Arbor, Michigan **1975**.
- [3] R.Kunin, *Ion exchange resin*. 2nd Edn., Wiley, Newyork ; Cn.15, pp. 320 – 325. **1958**.
- [4] N.Kannan, and R.K. Seenivasan *J.Appl. polym. Sci.*, 101, 4104 **2006**.
- [5] N.L.N.Sharma, Joseph Mary and Padma Vasudevan, *Res. Ind.*, **21**, 173 **1976**.
- [6] Padma Vasudevan and N.L.N. Sarma, *J.Appl. Poly.Sci.*, **23**, 1443 **1979**.
- [7] G.J.Mohan Rao and S.C. Pillai, *J. Indian Inst.Sci.* , **36A**, 70 **1954**.
- [8] Shahha and S.L.Batna, *J.Appl. Chem. Lond.*, **8**, 335 **1953**.
- [9] T.Dheiveesan and S.Krishnamoorthy, *J. Indian Chem.Soc.*, **65**, 731 **1988**.
- [10] D.Kathiresapandian and S.Krishnamoorthy, *Indian. J. Technol.*, **29**, 487 **1991**.
- [11] A.Mariamichel and S.Krishnamoorthy, *Asian J. Chem.*, **9(1)**, 136 **1997**.
- [12] N.Kannan, R.K.Seenivasan and R.Mayilmurugan, *Indian J. Chem. Technol.*, **10**, 623 **2003**.
- [13] M.S.Metwally, N.E.Metwally and T.M. Samy, *J. Appl. Poly. Sci.*, **52**, 61 **1994**.
- [14] N.Kannan, and G.Rengasamy, *Env. Technol.*, **25** : 513 –522 **2004**.
- [15] G E P Box., and J S. Hunter, *Ann. Math. Statist.* **28**, 195 – 200 **1957**.
- [16] G E P Box., and K B. Wilson On the experimental attainment of optimum conditions *J. Roy. Statist. Soc. B13*, 1 – 6 **1957**.
- [17] S.Ramachandran, and S.Krishnamoorthy, *Indian J.Tech.*, **22** : 355 – 356 **1984**
- [18] G.H.Jeffery, J.Bassett, J. Mendhan. and R.C Denney. *Voget's Text book of quantitative chemical analysis*. 5th edn., ELBS, Longman, London, 689 **1991**.
- [19] A.Mariamichel and S.Krishnamoorthy , *Asian J. Chem.*, **9** (1) : 136 – 148 (1997); *J. Sci. Ind Res.*, **56** : 680 – 685 **1997**