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RESEARCH ARTICLE

STUDIES ON MACRO RETICULAR ORGANIC RESIN AS LOW COST ION-EXCHANGERS

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ABSTRACT

Sulphonated carbon derived from plant viz., Nelumbo Nucifera has been prepared and blended with Phenol-Formaldehyde Resin (PFR) by varying the percentage of blending (%w/w) and Physico-chemical parameters like, density, gravimetric swelling (%) attritional breaking (%) and Cation Exchange Capacity (CEC) of various metal ions have been determined. For a given metal ion, CEC decreases with the increase in percentage of blending NNSC with PFR. The blending of PFR upto 30% (w/w) of Nelumbo nucifera retains almost all the essential physico-chemical characteristics including CEC, as compared to that of the PFR. It is concluded that the sulphonated Nelumbo nucifera carbon could be used as blending material in the PFR to lower the cost of the ion-exchange resin for water and wastewater treatment, especially for the removal of metal ions.

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INTRODUCTION

Toxic materials are often discharged by a number of industrial processes and this can lead in turn into the contamination of fresh water and marine environment (Low *et al.*, 2000). Heavy metals are major pollutants in marine, ground, industrial and even treated waste waters (Valdman *et al.*, 2001). Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. Due to growing rigorous environmental regulations, limit for heavy metal in drinking water and wastewater becomes more and more strict. Heavy metals in water bodies will accumulate in crops and enter into the food chain ultimately. This influence is not observed in a short term, but it may result in irretrievable loss ten or more years later. The occurrence of the same illness in some regions has a close connection with water pollution. Moreover it will take several decades for the remediation of water bodies and soil polluted by heavy metals.

Many physico-chemical methods have been proposed for their removal from industrial effluents (Iqbal *et al.*, 2002). Adsorption is an effective purification and separation technique used in industry especially in water and waste water treatments (Al-Asheh *et al.*, 2000). Cost is an important parameter for comparing the sorbent materials (Bailey *et al.*, 1999). By products of soyabean and cotton seed hulls, rice straw and sugarcane bagasse were evaluated as metal ion

adsorbents in aqueous solutions (Marshall and Champagne, 1995 and Marshall *et al.*, 1993). Ion exchange process finds a valuable place in the treatment of wastewater containing metal ions discharged from plating and other industries (O. Liebknecht, 1940 and Kunin, 1970). Also, ion exchange is a convenient way to concentrate, remove and recover the ions of valuable metals like copper, zinc and chromium. Special processes using selective IERs are also available in literature for the recovery of precious noble metals like gold, platinum and silver (Pauling, 1927).

The aim and objectives of the present work were to synthesize and characterize low cost ion exchangers of PhOH – HCHO type for the removal of metal ions. Macro-reticular cationic matrices of PFR is blended with various % (w/w) Nelumbo nucifera (lotus waste) to estimate the column / cation exchange capacity (CEC) or ion exchange capacity (IEC) for some selective metal ions. Hence, it is proposed, in this present research work, to mix or blend the sulphonated carbon prepared from Nelumbo nucifera into the macro porous Phenol-formaldehyde resin to get composite cation exchangers with different ratios (w/w) and to study their physico – chemical properties.

MATERIALS AND METHODS

The chemicals used in the present study were either procured commercially or collected locally. LR grade of conc. Sulfuric acid (Specific gravity = 1.82) was used. Formaldehyde (37-40% solution) from SD fine chemicals and phenol

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(Density: 1.057 gm⁻³) of BDH reagent were used. Plant (raw) material used for the preparation of sulphonated charcoal was *Nelumbo nucifera* (lotus waste) and available plenty in Tamilnadu, India. The plant material was collected, cleaned and dried before use. All the other chemicals used were of pure grade procured from SD fine chemicals, India.

Preparation of Activated carbon

The powdered *Nelumbo nucifera* (lotus waste) (about 1 kg) was carbonized and sulphonated by adding concentrated sulphuric acid (about 600ml); kept at room temperature for 24 hours and heated to 90°C in a hot air oven for six hours. It was then cooled, washed with tap water and distilled water for several times, to remove the free acid and finally rinsed with double distilled (DD) water dried at 110°C for twelve hours. It was labeled as *Nelumbo nucifera* sulphonated carbon (NNSC).

Preparation of Composite resin

The Phenol-formaldehyde resin (PFR) was prepared by mixing phenol (10ml) and conc. sulphuric acid (12.5ml) slowly with constant stirring in a ice bath. The mixture was then, heated to 80°C for three hours cooled immediately in ice bath and kept overnight. Then, it was polymerized with formaldehyde solution (12.5ml) then heated at 80°C for three hours and the product was cured at room temperature. A reddish brown colour chunky solid mass was obtained. It was then ground, washed with tap water and distilled water and finally with DD water, to remove the free acid, dried at 70°C for twelve hours. The material was sieved and preserved for further characterization (property) studies and for the preparation of composites. It was labeled as PFR.

To prepare the composites by blending PFR with the sulphonated *Nelumbo nucifera*, calculated quantities of NN were added to the phenol sulphonic acid solution to keep the percentage of blending or mixing of the carbon 10, 20, 30, 40 and 50 weight / weight (w/w) ratio in the composites. These products were labeled as A to E for the percentages 10 – 50.

Characterization of samples

Determination of Physical Properties

The absolute density of the samples was determined in both hydrated and dehydrated states with the aid of a specific gravity bottle in water and toluene media respectively. Swelling measurements were made by allowing the samples to equilibrate in water overnight. The weight of the swollen sample (wet weight) was taken as M_w and the corresponding dry weight M_d was determined after drying the same lot at 70°C for 12 hrs and then Gravimetric swelling percentage was determined using the formula,

$$\text{Percentage of swelling} = \frac{M_w - M_d}{M_d} \times 100$$

To find out the percentage of attritional breaking, a known quantity of the samples (w_1 g) was swollen in water and shaken continuously for 6 hrs. The wet sample was separated by

filtration and dried subsequently, it was sieved on a 210 -300 micron mesh and the amount retained by the sieve was weighed (w_2 g).

$$\text{The percentage of Attritional breaking} = \frac{(w_1 - w_2)}{w_1} \times 100$$

Determination of Column Capacity

A known weight (2g) of the sample under investigation was converted into H⁺ (neutral form with H⁺ as counter ion) and by washing it with Hydrochloric acid (2M) followed by distilled water to remove excess free H⁺ ions. A column was prepared using a burette (50ml) glass wool plug and the water or treated sample containing the metal ion was taken in the form of slurry with distilled water. An aqueous solution of sodium chloride (40ml, 0.1M) was added slowly to the column in several portions. The sample exchanged its H⁺ ions with Na⁺ ions in the solution. The cation exchange capacities (CEC) with metal ions were determined similarly using standardized solution. The CEC of the pure resin PFR and condensates A, B, C, D and E was determined using 0.1 M solution of metal ions like Ca²⁺ and Cu²⁺.

RESULTS AND DISCUSSION

Characterization of IERs

IR spectral studies

The IR spectral data are given in Table I. From the FT-IR spectral data (S=O str) which occur at 1030 cm⁻¹ and -SO₂ sym str which appear at 1160 cm⁻¹, C – S str which occur around 552 cm⁻¹ confirm the presence of sulphonic acid groups in the ion exchangers. The appearance of absorption bands at C – C str 1630 cm⁻¹ confirms the presence of aromatic rings in pure resin (PFR) SC and C. The absorption band which appear at 1467 cm⁻¹ due to –CH₂ confirms the presence of –CH₂ groups in the resin sample.

The appearance of broad absorption band at 3396 – 3409 cm⁻¹ (bonded –OH str.) indicate the presence of phenolic and sulphonic acid –OH group in the IER samples. The appearance of absorption band at 1613 – 1626 cm⁻¹ (C-C str.) confirms the presence of aromatic ring in PFR, condensate with 30% (w/w) blending of NNSC with PFR (A) and pure NNSC (100%). The absorption band at 1458-1471 cm⁻¹ (-CH₂ def.) confirms the presence of –CH₂ group in the IER samples. The weak absorption bands at 791 – 902 cm⁻¹ (-C-H def.) in the IER samples indicate that the phenols are tetra substituted.

The broad absorption bands which occur at 3400 cm⁻¹ (bonded –OH str) and the bands which appear at 1160 cm⁻¹ due to C – O str or –OH def indicate the presence of phenolic – OH and sulphonic acid –OH groups in the resin samples and condensates.

Thermal studies

TGA curves shown in Figs.2 and 3, reveal that there is a very small (6%) loss in weight for both PFR and condensate resin are prepared by blending PFR with 30% (w/w) by NNSC up to 90°C. This is due to the loss of moisture (water molecule)

absorbed by PFR and the condensate of PFR with 30% (w/w) of NNSC. Between 50 - 90°C, there is 20% weight loss in PFR and 18% loss in weight in condensate with 30% (w/w) NNSC is observed. Upto 450°C, approximately 57% loss in weight in PFR and upto 340°C, approximately 31% weight loss in condensate with 30% (w/w) NNSC is observed. This may be ably due to the decomposition of the materials.

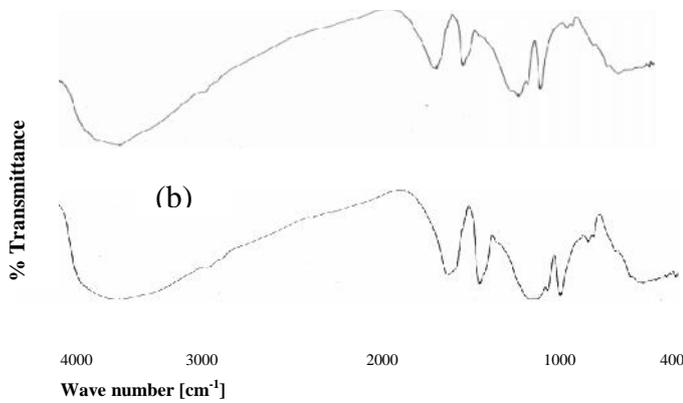


Fig. 1 FT-IR Spectra of PFR, (b) PFR blended with 30 % (w/w) NNSC in composite

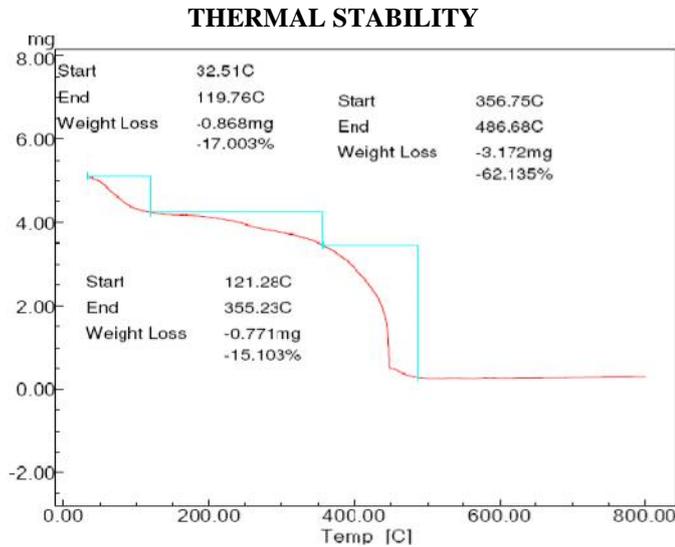


Fig. 2. TGA for pure PFR

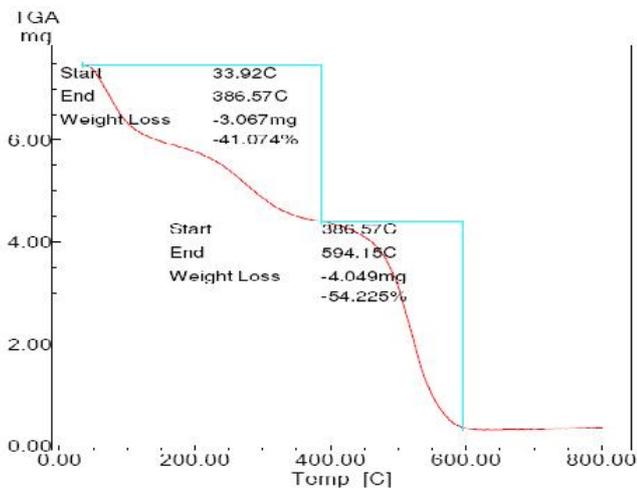


Fig.3.TGA for 30% condensate resin

SEM

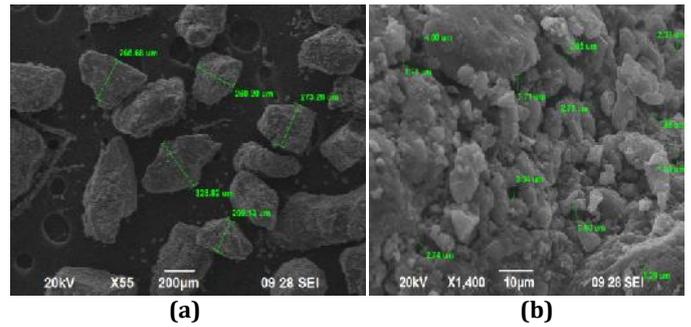


Fig.4 showed the SEMs of before and after metal ion removal. However, the particles of (Fig.4a) had a rough surface with heterogeneous holes and pores that make a large surface area, which indicated that metals can be adsorbed onto its surface. Fig.4b showed micrographs of the NNSC surface after adsorbed metal ions, the surface of NNSC was relatively smoother and less porous because of the formation of a layer over the adsorbent surface after adsorption of metal ions.

Physico-chemical characteristics
Absolute Density

The absolute density in both hydrated (wet) and dehydrated (dry) states of sulphonated phenol-formaldehyde resin (PFR), all the condensates (A, B, C, D and E) and pure sulphonated charcoal (NNSC) are presented in Table II. It is found that the absolute density in both wet (hydrated) and dry (dehydrated) status increases steadily from pure resin PFR (100%) upto 30% of sulphonated Nelumbo nucifera and this indicates that 30% of blended resin is more closely packed than pure resin (PFR). This result is contrary observation with the earlier reports.

Gravimetric swelling

A close look at the data given in Table III indicates a regular increase in gravimetric swelling percentage of the condensates with the increase in percentage (w/w) composition of NNSC upto 30% in the condensates. In addition, it is seen that the values are not very high because the samples are macro reticular having non-gel pores. GSC has a swelling capacity of only 98.52 % as compared to that of pure resin (PFR). The blending of pure resin even with 50% of NNSC greatly reduces the swelling capacity of the sample. Therefore, PFR could be blended upto 30% w/w of NNSC without affecting its characteristics.

Attritional Breaking

From the data given in the table IV, It is seen that 30% of condensates resin has the lowest percentage of attritional breaking than pure resin (PFR) and the values increase with the increase in (w/w) percentage composition of NNSC in the condensates. It is established that the resin and the composites are mechanically stable and the stability is good up to 30% (w/w) substitution. This indicates that the parent resin (PFR) could be blended upto 30% (w/w) substitution without affecting the characteristics of parent resin.

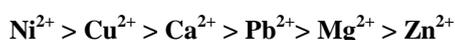
Solubility

The samples PFR, A, B, C, D, E and NNSC are all practically insoluble in almost all the reagents and organic solvents. It

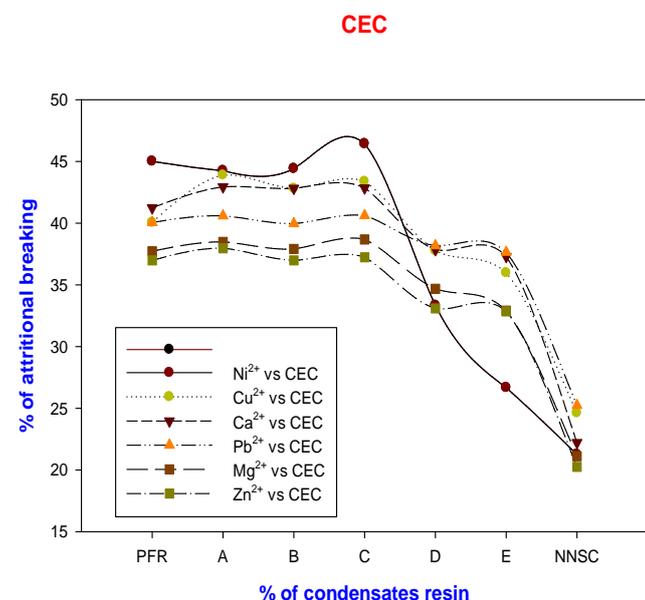
was noted that the resins and condensates (except NNSC) are partially soluble (5 - 10%) in 30% NaOH solution. This is because these samples have phenolic groups in them and hence could not be used in strongly basic medium owing to its solubility. This indicates a high degree of cross-linking in all the 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 cation exchanger columns, which could be used acidic neutral and light alkaline medium and to treat non-aqueous industrial effluents. However, these resins could not be used in highly alkaline medium owing to its partial solubility.

Column Exchange Capacity

A critical analysis of the data presented in table V reveal that the column capacity steadily decreases with the increase in the percentage weight of NNSC in phenol formaldehyde composite resins obtained by blending (A – E). Among the divalent metal ions the column capacity (CEC) is found to decrease in the following order:



The important factor in concentrated solutions for the above said trend being size of the metal ions or ionic radius (Mg^{2+} - 0.65 Å, Zn^{2+} - 0.74 Å, Cu^{2+} - 0.93 Å, and Ca^{2+} - 0.99 Å) data provided by L.Pauling¹¹. Since ion exchange in a column is mainly diffusion controlled; smaller size ions can diffuse more readily and easily through the solution, than the pores and the channels of the resin and the composite particles of bigger size ions. In addition, the $-\text{SO}_3\text{H}^+$ group, due to its electrostatic attraction, prefers smaller counter ions.



The order of CEC of the resins and condensates for the exchange of divalent metal ions is of the order: $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Ca}^{2+} > \text{Pb}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+}$. This may be due to the selectivity of the metal ions for ion exchanger process. From the results given in table V (Fig. 4), it is noted that condensates upto 30%

of SC retain nearly 92% of the column capacity, while 40% of SC retain nearly 85% of the column capacity. Hence, it is concluded that the Phenol- Formaldehyde resin could be blended with NNSC obtained from **Nelumbo nucifera** (NN) charcoal upto 30% (w/w) and the condensates obtained would be a new and cheaper cation exchanger. This could be used for the treatment of water and industrial effluent or the removal of metal ions. **Nelumbo nucifera** (NN) charcoal has only 95% column capacity to exchange its H^+ ions with divalent metal ions as compared to that of pure resin. The 30% of condensates resin is somewhat higher replacement capacity than the pure phenol- formaldehyde resin. This observation is contrary report with the already reported one.

Effect of particle size on CEC

From Table VI it was observed that the particle size of $< 200 \mu\text{m}$ are fine and $> 500 \mu\text{m}$ are coarse compared to a particle size of $210 - 300 \mu\text{m}$. Hence, for the effective removal of metal ions, the bed size and particle size are to be maintained and the recommended particle size of IERs is **210 – 300- μm** .

Regeneration capacity of IERS

Table VII describes that, the regeneration data with 40 ml of 0.2M NaCl solution (brine) reveal that it effectively regenerates PFR, all the condensate resins and NNSC. Most of the commercial IERs are in Na^+ form and hence 40ml of 0.1M NaCl was used as a regenerate for every 2g of the resin.

4.Conclusion

The results of the present study conclude that Phenol-formaldehyde ion exchange resin could be partly blended by sulphonated charcoal obtained from *Nelumbo nucifera* (NN) charcoal upto 30% (w/w) without affecting its physical, chemical, thermal, spectral and column capacity. The Composite containing *Nelumbo nucifera* (NN) charcoal of 30% is found to have high density values than the pure PFR, which is contrary effect with the already reported resins. It has good swelling behaviour, comparable attritional resistance, efficient column and absolute capacities, sufficient thermal stability, and is particularly macro-porous and cheap. It may form a cheaper substitute for the costlier sulphonated phenol-formaldehyde resin. Such blended macro reticular composite ion exchange resins could be employed as low-cost materials in the water softening process, wastewater treatment process, especially for the removal of metal ions.

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