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Optimization Studies on the Removal of Metal Ions Using Modified Cation Exchange Resin

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ABSTRACT: Heavy metal pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from wastewater have been extensively studied. This paper reviews the current methods that have been used to treat heavy metal wastewater and evaluates these techniques. These technologies include ion-exchange, adsorption methods. The present ion exchanges are mainly based on petroleum compounds and it is very high cost in order to reduce the cost of commercial ion exchangers by substituting sulphonated carbon present in plant waste material. This work was first done by Dima et al in 1960. It is evident from the literature survey articles that ion-exchange, adsorption and membrane filtration are the most frequently studied for the treatment of heavy metal wastewater. Also, ion exchanges is convenient way to concentrate, remove and recover the valuable metals like Cu, Zn, and Cr.

I. INTRODUCTION

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro et al., 2007). Copper does essential work in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Paulino et al., 2006). Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). And it is known that nickel is human carcinogen. Mercury is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function, chest pain and dyspnoea (Namasivayam and Kadirvelu, 1999). The classic example of mercury poisoning is Minamata Bay. Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Cadmium exposes human health to severe risks. Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death. Lead can cause central nervous system damage. Lead can also damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001). Chromium exists in the aquatic environment mainly in two states: Cr(III) and Cr(VI). In general, Cr(VI) is more toxic than Cr(III). Cr(VI) affects human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma (Khezami and Capart, 2005). Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the waste water to protect the people and the environment. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption,

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membrane filtration, electrochemical treatment technologies, etc. The present review article deals with the current techniques for the removal of heavy metal ions from wastewater. Their advantages and limitations in application are also evaluated. * Corresponding author. E-mail address: ufenglian2006@163.com (F. Fu). Contents lists available at ScienceDirect Journal of Environmental Management journal homepage: www.elsevier.com/locate/jenvman 0301-4797/\$ e see front matter _ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/

II. ION EXCHANGE

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kanget al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli, 2009). The most common cation exchangers are strongly acidic resins with sulfonic acid groups (eSO₃H) and weakly acid resins with carboxylic acid groups (eCOOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Gode and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process. The influence of ionic charge on the removal of Ce⁴⁺, Fe³⁺ and Pb²⁺ from aqueous systems by cation-exchange resin purolite C100 was tested by Abo-Farha et al. (2009). They found that the metal ions adsorption sequence can be given as Ce⁴⁺ > Fe³⁺ > Pb²⁺. Similar results for Co²⁺, Ni²⁺ and Cr³⁺ on an Amberlite IRN-77 cationexchange resin were previously obtained by Kang et al. (2004). Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions (Motsi et al., 2009; Ostroski et al., 2009; Taffarel and Rubio, 2009). Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. Table 2 shows the efficiency of clinoptilolite for removing heavy metal ions. Recently, some researchers reported that the surface of clinoptilolite loaded with amorphous Fe-oxide species would significantly improve the exchange capacity of clinoptilolite (Doula and Dimirkou, 2008; Doula, 2009). Doula (2009) employed clinoptilolite/Fe system to simultaneously remove Cu, Mn and Zn from drinking water. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins. And the application of zeolites is on the laboratory experiments scale. More work is needed for the application of zeolites at an industrial scale.

III. EXPERIMENTAL

MATERIALS

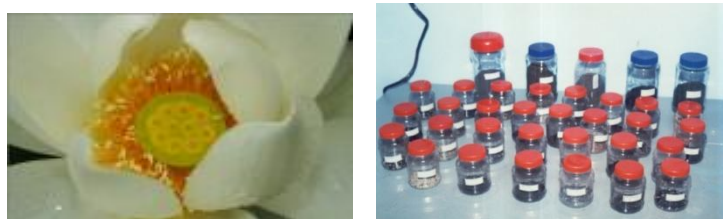
- The chemicals used in the present study are either procured commercially or collected locally.
- Resorcinol (Density: 1.057 gm⁻¹, BDH reagent)
- Formaldehyde (37 – 40% solution, SD Fine reagent)
- Concentrated Sulphuric acid (Specific gravity = 1.82)
- Plant (raw) material used for the preparation of sulphonated charcoal viz, *Hybanthus enneaspermus* (L.) F. v. Muell (NILAPPIRANTAI STEM)

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IV. METHODOLOGY & MATERIALS



1. Formaldehyde (37 – 40% solution, SD Fine reagent)
2. resorcinol (Density: 1.057 gm⁻¹, BDH reagent)
3. Concentrated sulphuric acid (Specific gravity = 1.82)

Plant (raw) material used for the preparation of sulphonated charcoal *viz* Hybanthus enneaspermus (L.) F. v. Muell (NILAPPIRANTAI STEM)

V. EXPERIMENTAL

Preparation of Phenol – HCHO resin:

* Resorcinol + Con.H₂SO₄ → Resorcinol sulphuric acid (RSA) → Resorcinol-HCHO (RFR)

Preparation of condensate resins:

RFR + * SC (calc. amount 10,20,etc) → RFR mixture
Condensate resin

10%, 20%, 30%, 40% and 50% Required percentage = $\frac{x}{y}$

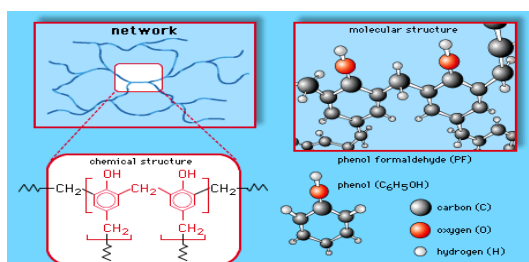
Where, 'y' is the mass in grams of pure resin (PFR) and 'x' is the mass in grams of the sulphonated Hybanthus enneaspermus (L.) F. v. Muell (NILAPPIRANTAI STEM) required to achieve the required percentage (w/w) of SC in the composite. SC blended with RFR in order to obtain 10,20,30,40 and 50% (w/w) condensate resins (samples A,B,C,D, & E) by using the formula

Required Percentage = [b / (a + b)]

Where,

a = mass of RFR (in g)

b = mass of the SC required (in g) for blending

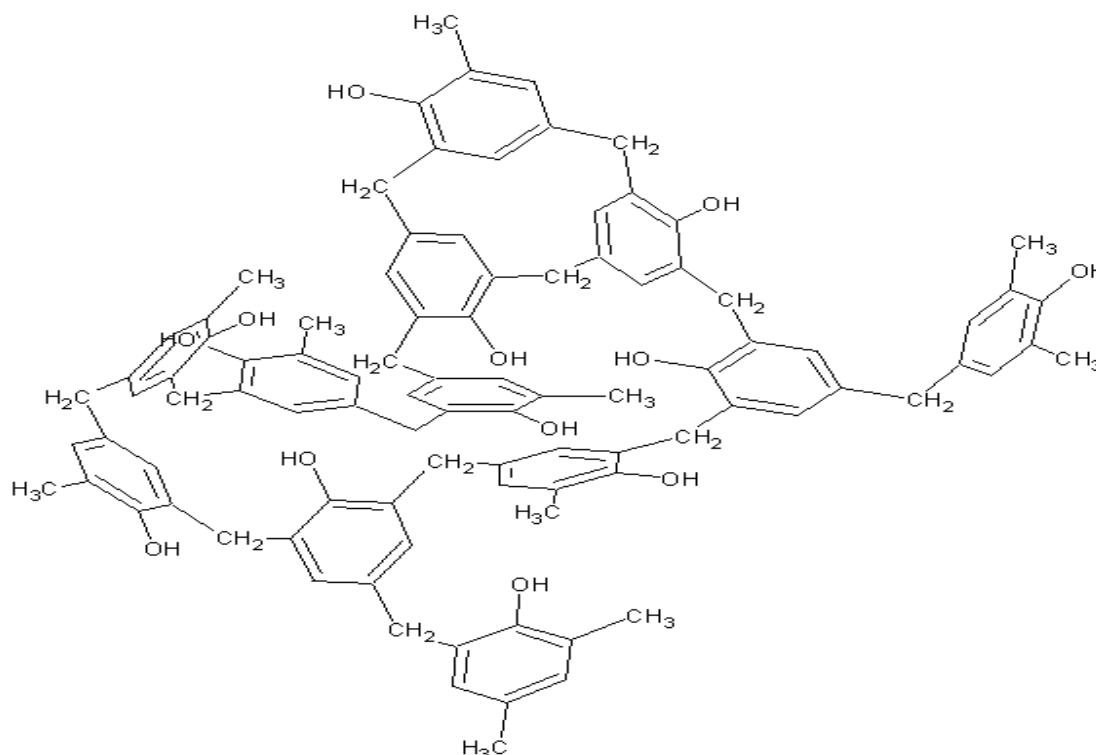


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(RESORCINOL – FORMALDEHYDE SULPHONIC ACID CATION RESIN)



RESORCINOL – FORMALDEHYDE SULPHONIC ACID CATION RESIN (RFR) (Macro Polymer)

**CATION EXCHANGE capacity (CEC) in meq g⁻¹ for various metal ions at 35⁰C
(for 0.1m solution)**

Sample	% of HESC in resin (w/w)	Ca ⁺	Mg ²⁺	Zn ²⁺	Pb ²⁺	Ni ²⁺	Cu ²⁺
RFR	0	17.85	16.12	16.75	18.98	17.92	18.59
A	10	18.15	17.61	17.29	19.18	20.23	19.57
B	20	19.83	18.64	18.21	20.32	23.69	20.58
C	30	22.40	19.37	19.42	24.06	30.06	21.36
D	40	21.81	18.63	14.56	21.93	25.43	20.85
E	50	20.40	17.39	13.11	18.45	21.97	19.35
HESC	100	12.12	11.20	10.24	13.21	13.61	13.45

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Characterization of IERs

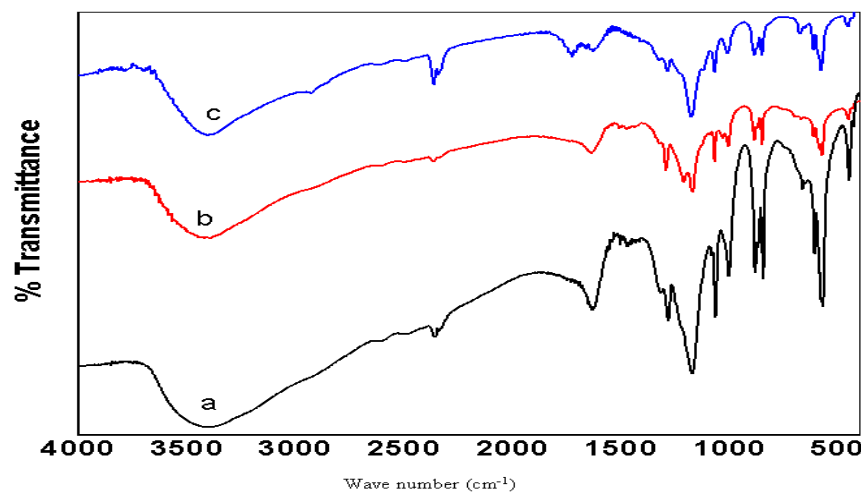
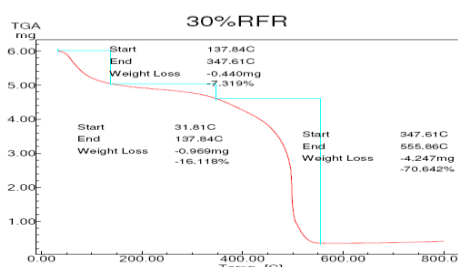
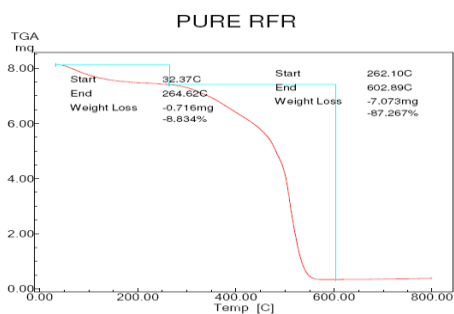


Table -2 IR spectral studies (ν in cm^{-1})

Group	Pure PFR(A)	30% SAMC(D)	Pure SAMC(G)
S=O	1068	1070	1068
SO ₂	1170	1176	1176
C-S	572	574	576
Bonded OH str	3398	3410	3402
CH ₂ -def	1473	1473	1464
C-C str	1635	1629	1627
C-H def	887	887	887

Thermal studies:



Between 200 - 520⁰C there is 90% weight loss in RFR and

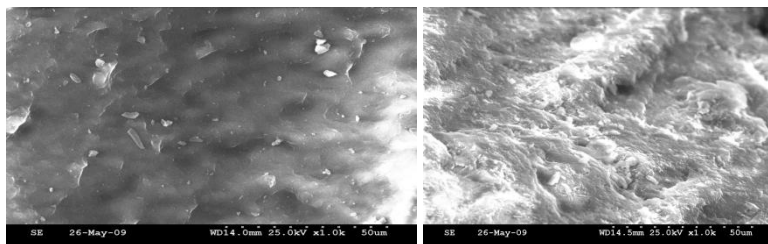
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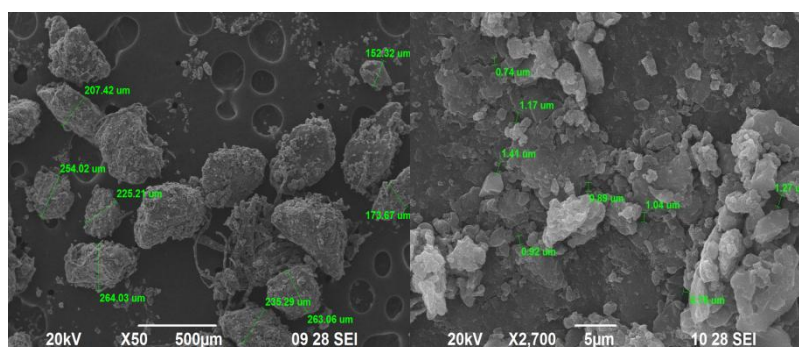
60% loss in weight in blend with 30 % (w/w) of HESC was observed.

Porosity: (SEM)

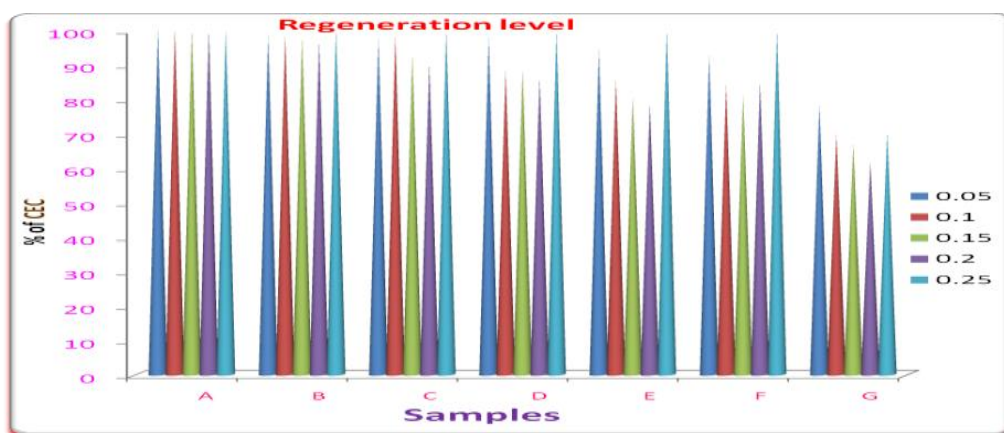


The high macroporous carbon obtained from **HES charcoal** form the reservoir in which the **resorcinol-formaldehyde** sulphonic acid particles are deposited.

SEM ANALYSIS OF RFR WITH 30% CONDENSATE.



Regeneration of IERs



[FIG.5 Regeneration level for PFR,its composite,and SAMC by using NaCl,after exchange with Ni²⁺ ions]

VI. CONCLUSION

The mathematical modeling has been useful for theoretically predicting the CES values under various experimental conditions. The balanced nature of a statistical design leads itself to an organized method of experimentation and to a

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straight forward approximation to data analysis. Graphical presentation is facilitated with such results from designed experiments. The variable such as % (w/w) of HESC in condensate, particle size and initial concentration of Ca^{2+} ions are proved to be the most significant parameters for the maximum CEC for Ca^{2+} ions as evidenced from the MLR equations. The results obtained could be used for better designing cost-effective IERs for effluent / water treatment plant, for the economic removal of metal ions general and in particular by ion exchange process. Recorcinol – formaldehyde ion exchange resin could be blended by sulphonated charcoal obtained from *Hybanthus enneaspermus* upto 30% (w/w) without affecting its physical, chemical, thermal, spectral and column capacity such blended macro reticular composite ion exchange resin could be employed as low cost materials in the water softening process waste water treatment process, especially for the removal of meta ions.

The Composite containing *Hybanthus enneaspermus* (L.) F. v. Muell charcoal of 30% is found to have high density values than the pure RFR, which is contrary effect with the already reported resins. It's a good swelling behavior comparable attritional resistance efficient column and absolute capacities sufficient thermal stability, and is particularly macro-porous and cheap

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