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## Synthesis, Characterization and Application of Polymer Nanocomposites for Selective and Effective Cu (II) Removal

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**ABSTRACT:** In the current study built-up a novel polymer supported hybrid nanocomposites (PHNCs) by blending green synthesized Silver Nanoparticles (AgNPs) within a Low Cost ion Exchange Adsorbents [Phenol-Formaldehyde Resin (PFR) + 50% sulphonated Prosopis juliflora carbon (SPJC)] for extremely as well as efficiently removal of Cu (II) from polluted aqueous solution. Thermo gravimetric analysis (TGA), Differential thermal analysis (DTA), Scanning electron microscope (SEM), Energy-dispersive microanalysis (EDX), Fourier transform infra red (FT-IR) are used for characterizing the synthesized all composites structurally, thermally and morphologically. PHNCs exhibited a superior performance towards the removal of Cu (II) from polluted aqueous solution compared to the pure SPJC, PFR and PFR+50% SPJC due to the potential Donnan membrane effect applied by the immobilized negatively charged sulfonic acid groups ( $\text{SO}_3^-$ ) bound to the macroporous cation exchanger of Low Cost ion exchange Adsorbents (LCIEA) outcome in preconcentration and penetration enrichment of  $\text{Cu}^{2+}$  ions anterior to their effectual isolation by the doped AgNPs. The outcome of adsorption isotherms, kinetics, intraparticle diffusion, thermodynamics, grain size and its regeneration level were also studied. Moreover, the exhausted composite adsorbents are regenerated readily with binary 5% HCl-NaCl solution. Based on the obtained results, PHNCs could be applied competently for the removal of Cu (II) ions from polluted aqueous solution and industrial effluent.

**KEYWORDS:** Asparagus racemosus; Phenol Formaldehyde Resin ; ion exchanger; Cu (II) adsorption; AgNPs; potential donnan membrane effect.

### I. INTRODUCTION

Heavy metal ions are hazardous components of wastewaters due to their toxicity to living systems yet at very low concentrations [1]. Hence isolating of heavy metal ions from industrial effluent prior to their discharge to the milieu is a main crisis of current wastewater treatment. Among the heavy metal ions pollution, water pollution by Cu (II) ion is a severe one due to prolonged breathing of copper holding sprays is associated with an enlarge in lung cancer among displayed employees and then the Cu (II) in conjunction with Ar and Cu ions is distinguished as the maximum virtual mammal poisonous [2]. It is contamination begins from electroplating industries, too much utilize of Cu supported agri chemicals, copper mining, smelting, manufacture of brass etc. Upper accepted limit o concentration of Cu (II) in drinking water is less than  $3000 \text{ g/dm}^3$  [3]. Hence exclusion of Cu (II) from industrial effluent and wastewater has assumed as value. The usual techniques for removing heavy metal ions from water and wastewater include precipitation, membrane filtration, ion exchange, adsorption, oxidation, reduction. Ion exchange is an proficient system to eliminate copper due to this technique does not involve a sludge disposal problem [4]. Among all the ion exchange processes resources, Synthetic organic resins are the chief kind applied currently since their qualities can be tailored to particular applications among the ion exchange materials. However its synthetic process was luxurious [5]. Consequently there is an significant essential to develop LCIEA. The LCIEA was synthesized through blending the sulphonated carbons (SCs) prepared from waste plant sources in the synthetic organic resins. The previous effort was

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done by using the natural products as spent coffee [6], Curcuma longa [7] etc. From the literature survey, it was found that PFR was not modified with sulphonated Prosopis juliflora carbon (SPJC). In the present work, low cost ion exchange resins were synthesized by blending 0, 10, 20, 30, 40, 50, 60 and 70 percentage of SPJC within PFR and labelled as PFR, A, B, C, D, LCIEA, E and F. As synthesized the above all adsorbents were applied for the removal of Cu (II) from polluted aqueous solution. Then the replacement didn't produce any difficult outcome on the properties essentially on adsorption capacity up to blending of 50% of SPJC within PFR. Beyond that started to produce tremendous difference in the all properties of PFR particularly on adsorption capacity. As a result the best polymer composite 50% SPJC (w/w) in PFR will extremely reduce the 50% cost of pure PFR as well as called as LCIEA. However the adsorption capacity of the LCIEA is less than that of the pure PFR due to the potential Donnan membrane effect of the PFR gets decreased by the closing the pores of the PFR with impregnated SPJC. currently a days, the application of nanoparticles has broadcasted amazing potential for the wastewater treatment [8]. Since it was regarded as to rise the adsorption capacity of the LCIEA by eternally infusing 1% (w/w) of AgNPs. The adsorption capacity of the LCIEA was developed by permanently drenched AgNPs within LCIEA due to the impregnated AgNPs released the pores locked by SPJC and also produced the new pores in the LCIEA as well as improved potential donnan membrane effect of the LCIEA [9]. In the present work, AgNPs were synthesized through environmental eco-friendly method by using Asparagus racemosus leaf extract (ARLE) as reductant and capping agent. From the literature survey, it was detected that the ARLE capped AgNPs (zero-valent metal) blended PFR for adsorbing Cu(II) ions has not been reported so far. Thus in the current work, PHNCs was urbanized by impregnating 1% (w/w) of AgNPs within the LCIEA as well as these was applied for the elimination of  $\text{Cu}^{2+}$  from polluted aqueous media.

## II. EXPERIMENTAL METHODS

### MATERIALS

The fresh plant material utilized in the current research work was Asparagus racemosus (A.racemosus) and Prosopis juliflora. These plant materials were generously existing in Tamil Nadu, India (Fig.1). Phenol and formaldehyde utilized were Fischer reagents (India). LR grade (purity: 98.3%) of concentrated Sulphuric acid (Sp.gr = 1.82) was used. Silver Nitrate ( $\text{AgNO}_3$ ) was purchased from A.R grade SD Fine chemicals.



Fig.1. Images of the (a) Prosopis juliflora & (b) Asparagus Racemosus

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### BIO-SYNTHESIS OF AGNPS

The sanitized *A. racemosus* leaf were cleaned well with deionized water and dark desiccated for 15 days. The dehydrated leaves were cut into fine particles with mixer grinder. The ARLE was prepared with 20 g of leaf powder was dissolved in 100 ml of deionized water in a 250ml winkler's flask. Subsequently the mixture was heated at 60°C for 20 min. The ARLE was let to cool, filtered throughout Whatman No.1 filter paper and preserved in a refrigerator for applying additionally. 20 mL of ARLE was progressively mixed up with 50 mL of 1mM AgNO<sub>3</sub> aqueous solution for the green synthesis of AgNPs with stirring (150RPM) in a magnetic stirrer as well as obtained AgNPs in 40 min through the colour of the solution turned from light green to dark brown in colour.

### SYNTHESIS OF POLYMER COMPOSITES

Phenol (10mL) and Conc.H<sub>2</sub>SO<sub>4</sub> (14mL) were mixed gradually with regular stirring to form phenol-Sulphonic acid and this compound was set aside overnight. *Prosopis juliflora* waste (100g) was wrecked into small bits, followed by carbonized and sulphonated using Conc. Sulphuric acid (100mL) and set aside at room temperature for 1 day and subsequently heated at 70°C in a hot air-oven for 8h to obtain the activated carbon. The prepared activated carbon was washed several times with deionized water to eliminate surplus unreacted acid (tested with BaCl<sub>2</sub> solution) and dried at 50°C for 1 day and this was labelled as SPJC. The designed percentage of SPJC were added to phenol sulphonic acid as 0, 10, 20, 30, 40, 50, 60 and 70 as well as labelled PFR, A, B, C, D, LCIEA, E and F. The above labeled blends were polymerized individually with formaldehyde (11mL) at 90°C and treated at that temperature for 3 h to get a dark brown thick mass. The synthesized all polymer composites were crunched, washed, dried and sieved (250– 300µm) with Jayant sieves (India) as well as protected for the further characterization. The polymer composite PFR blended with 50% SPJC was labelled as LCIEA because of blending of 50% SPJC with PFR retains practically the entire essential properties of the Pure PFR [10].

### SYNTHESIS OF PHNCS

Phenol (11mL) and Conc.H<sub>2</sub>SO<sub>4</sub> (12 mL) were mixed gradually with steady stirring to obtain Phenol-Sulphonic acid and set aside overnight. 50% (w/w) of SPJC and 1% (w/w) of AgNPs were added to Phenol- sulphonic acid as well as that sample was labelled as PHNCS. Then the blend was polymerized with formaldehyde (13mL) at 90°C and alleviated at this temperature for 3 h to give a dark brown chunky mass. The synthesized PHNCS was broken, Powdered, washed, dried and sieved (250– 300µm) using Jayant sieves (India) and then protected for further characterization [11].

### ADSORPTION STUDIES THROUGH BATCH APPROACH

Batch approach used for studying the Adsorption works by shaking 0.020g of PFR, A, B, C, D, LCIEA, E, F, Pure SPJC and PHNCS in 20 mL solution of Cu (II) with 400 ppm concentration for 50 min in the Remi rotator water bath shaker at 150 rpm stirring rate. . Cu (II) concentration in the supernatants after the adsorption onto the different adsorbents was calculated with standard titration techniques as per the literature [12]. The equilibrium adsorption capacity of the all adsorbents was found with this equation:

$$q_e = (C_o - C_e) \times V / M \text{ ----- (1)}$$

Where  $q_e$  is the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_o$  and  $C_e$  is the initial and final Cu (II) ion concentration ( $\text{mg L}^{-1}$ ) at equilibrium,  $V$  is the volume of solution (L) and  $M$  is the weight (g) of adsorbent.

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## III. RESULTS AND DISCUSSION

### CHARACTERIZATION OF AGNPS BY UV-VIS, FT-IR, SEM & EDX

UV/Vis absorption spectra (UV-1800SHIMADZU) was applied to confirm the presence of silver nanoparticles in the ARLE. As a result, the surface Plasmon resonance appeared at 420nm(Fig.2).

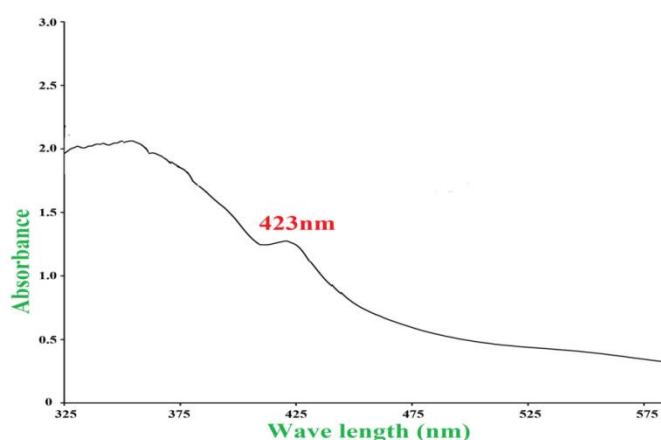


Fig.2. UV-Visible Spectra of the AgNPs

FT-IR (SHIMATZ MODEL) spectrometer was applied to find out the possible organic compounds responsible for capping and bracing the AgNPs. Fig.3 indicate the bands at 3541, 1272, 2412 and 1751  $\text{cm}^{-1}$  are respective to presence of the following functional groups as intermolecular O-H stretching, C-H aromatic stretching, polyphenols, C-N stretching, amide and carbonyl group. This amide band occurs because of carbonyl stretching and N-H bending vibrations in the peptide linkage of proteins present in ARLE. The seemed functional groups could encompass an competent role in the green synthesis of AgNPs.

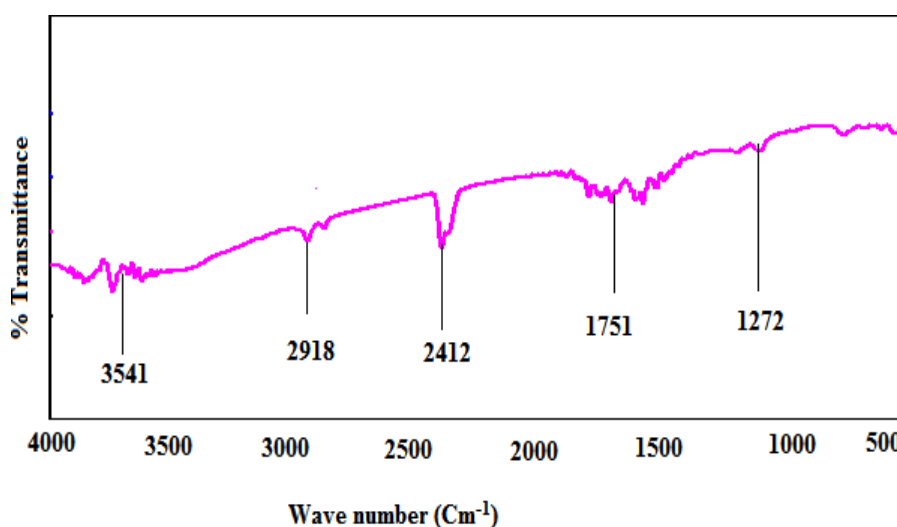


Fig.3. IR Spectra of the synthesized AgNPs

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Scanning Electron Microscope was applied to detect the surface morphology of the AgNPs (Vega3 Tescan). SEM pictures of the AgNPs (Fig.4) were discovered as spherical in shape. The size of the AgNPs was found to be 50-100nm.

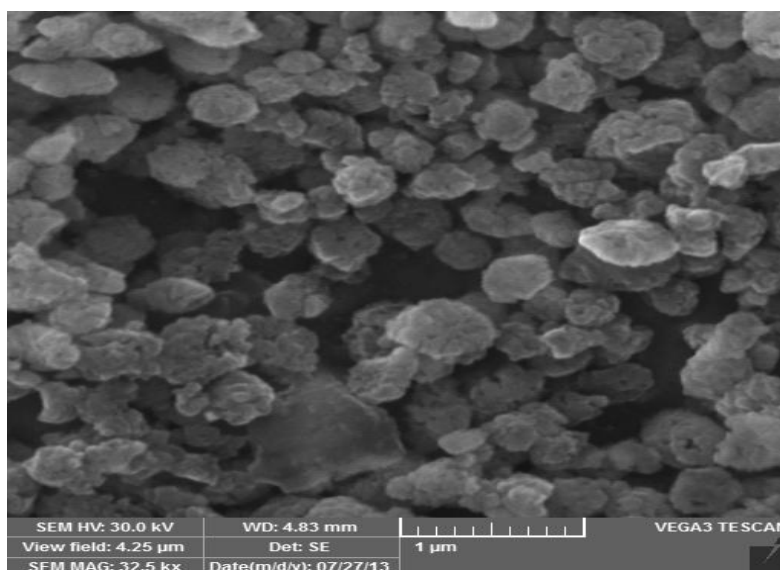


Fig.4. SEM image of the AgNPs

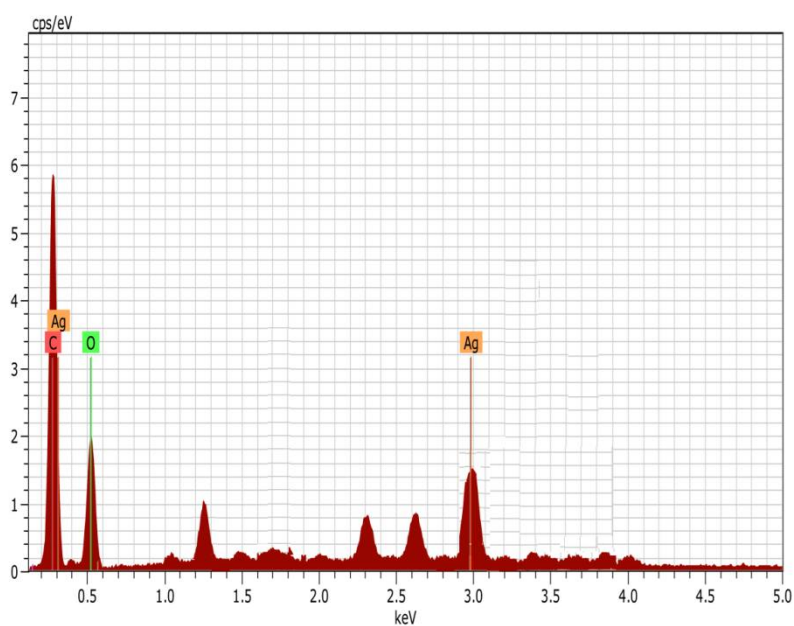


Fig.5. EDX image of the AgNPs

### STUDY OF PHNCs BEFORE & AFTER CU (II) ADSORPTION BY IR, SEM, TGA & DTA

As viewed from fig.6 (a) & (b), these bands were shifted away or disappeared after the adsorption of Cu (II) onto the PHNCs due to development of chemical bond interaction between Cu (II) in polluted aqueous solution and sulfonic acid groups in the PHNCs.

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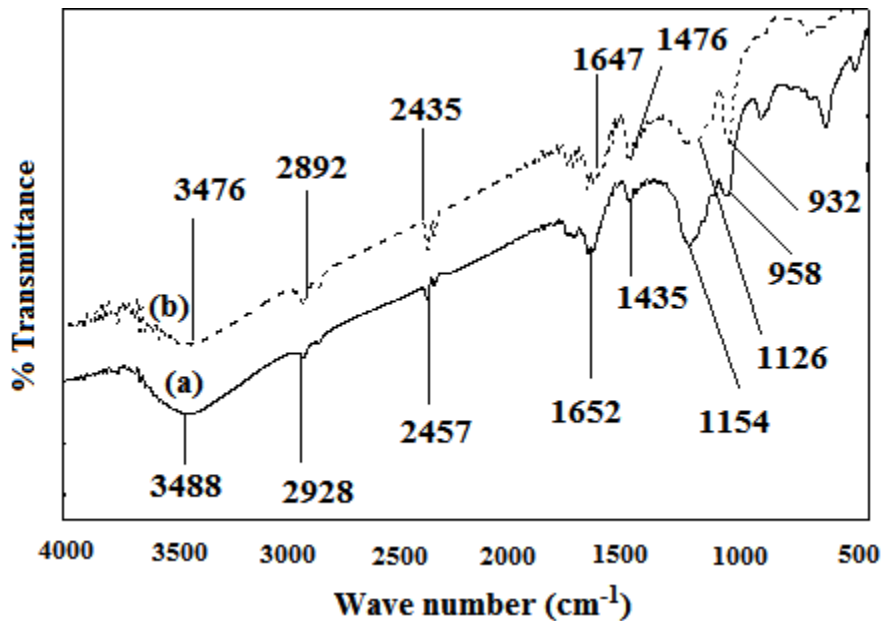


Fig.6. FT-IR spectra of free (a) and Cu(II) loaded (b) PHNCs

As detected from SEM images 7 (a) & (b), a noticeable modification appeared in the surface morphology of the PHNCs after Cu (II) adsorption due to may be happened ion exchange reaction between Cu (II) and PHNCs.

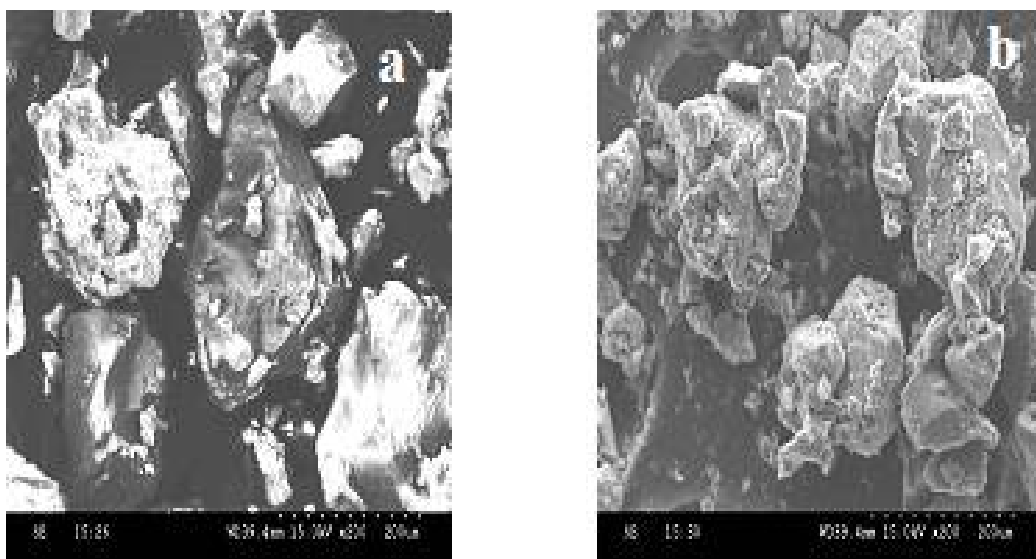


Fig.7 (a) & (b) SEM images of free (a) and Cu(II) loaded (b) PHNCs

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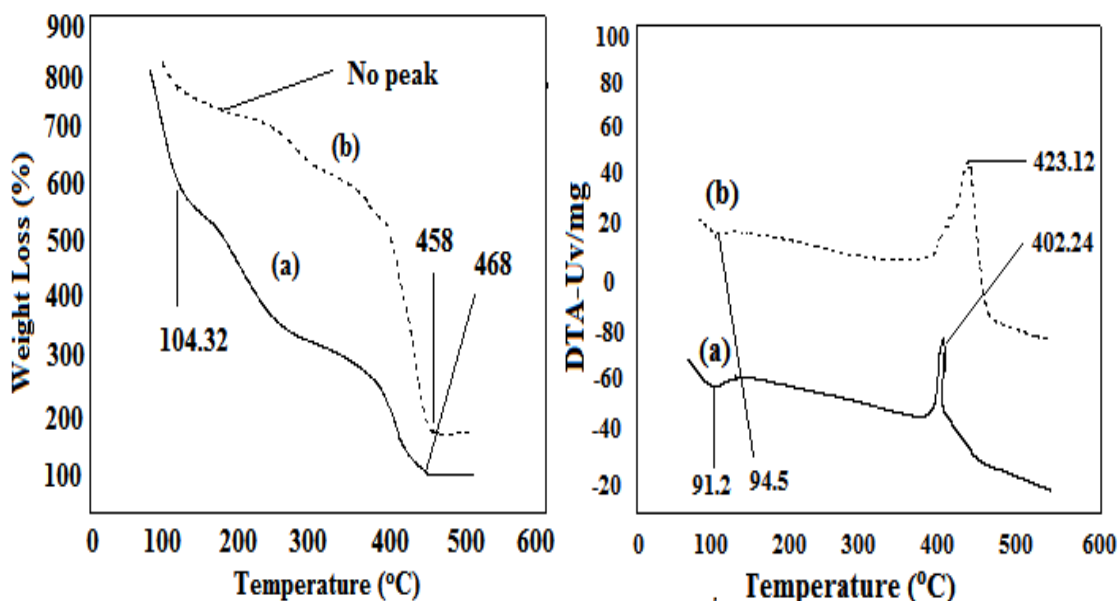


Fig.8 TGA analysis of free (a) and Cu (II) loaded (b) PHNCs. Fig.9 DTA analysis of free (a) and Cu (II) loaded (b) PHNCs.

TGA [8 (a) & (b)] and DTA [9 (a) & (b)] images were shown clearly that the transfer in temperature foremost peaks narrated with the packed Cu (II) ions possibly owing to the Cu (II) holding process happening at the exterior of the PHNCs [14].

### IV. CONCLUSION

PHNCs (Polymer Hybrid Nanocomposites) was synthesized by the doping of AgNPs in a low cost ion exchange adsorbents (LCIEA) through fresh method by using formaldehyde as a cross linking agent and the synthesized PHNCs adsorbent was approachable for perceptive Cu(II) removal founded on potential donnan membrane principle. As well, PHNCs was exhibited that the preminent choice for the removal of copper(II) from polluted aqueous medium as compared to PFR and LCIEA due to the AgNPs unlocked the pores blocked by SPJC and also the created the new pores in the structure of LCIEA as well as improved the potential donnan membrane effect of the LCIEA. In this work, AgNPs was synthesized via easy and green route by using the ARLE as reductant and capping agent. Moreover, the exhausted PHNCs was amenable to an effectual restoration by 8-10 BV of binary HCl-NaCl solution for its repeated exploit. Ultimately the current research work exposed that the development of PHNCs could be applied for the removal of Cu (II) from industrial effluent and reduced 50% cost for the making ion exchange resin.

### V. ACKNOWLEDGEMENT

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### REFERENCES

- [1] F.M.Perez, F.A.Castro, J. Benito, Kinetics of exchange reactions in a cation-exchange resin. *J.Macromol.Sci.* 24 ,155-165, (1987).
- [2] S.Y. Quek, D.A.J. Wase, C.F. Forster, The use of sago waste for the sorption of lead and copper. *Water SA.* 24 (3) 1998.
- [3] L. Uzun, F. Güzel, Adsorption of some heavy metal ions from aqueous solution by activated carbon and comparison of percent adsorption results of activated carbon with those of some other adsorbents. *Turk J Chem.* 24, 291- 297, (2000).

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- [4] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J. Hazardous Mater. B* (141),77-85, (2007).
- [5] O. Bonner, G. Easterling, D. Weit, V. Holland, Osmotic and activity coefficients of p-toluene sulfonic acid and p-ethylbenzenesulfonic acid and their relationship to ion exchange equilibria. *J. Am. Chem. Soc.* 77, 242-244, (1955).
- [6] D. Kathiresapandian, S. Krishnamoorthy, Resorcinol-formaldehyde cationic matrices by Curcuma longa charcoal. *Indian. J. Technol.* 29, 487-488, (1991).
- [7] A. Mariamichel, S. Krishnamoorthy, Synthesis and characterization of new composite ion exchangers. *Asian J. Chem.* 56, 680-685, (1997).
- [8] B. Pan, B. Pan, W. Zhang, L. Lv, Q. Zhang and S. Zheng, "Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters." *Chem. Eng. J.*, 151, 19-29, 2009.
- [9] S. Siva, S. Sudharsan, R. Sayee Kannan, Synthesis, characterization and ion-exchange properties of novel hybrid polymer nanocomposites for selective and effective mercury (II) removal. *RSC Adv.* 5, 79665-79678, (2015).
- [10] N. Kannan, R. K. Seenivasan, Synthesis, characterization and application of phenol formaldehyde resin blend with sulphonated achyranthes aspera linn., carbon. *J. Ion Exchange.* 16, 164-172 (2005).
- [11] P. Vasudevan, N.L.N. Sharma, Composite cation exchangers. *J. Appl. Poly. Sci.* 23, 1443-1448, (1979).
- [12] F. M. Perez, F. A. Castro, J. F. P. Benito, "Kinetics of exchange reactions in a cation-exchange resin," *J. Macromol. Sci.*, vol. 24, pp. 155-165, 1987.
- [13] D. Philip, Green synthesis of gold and silver nanoparticles using Hibiscus Rosa sinensis. *Physica E.* 42, 1417-1424, (2010).
- [14] M. L. Rao, N. Savithamma, Biological Synthesis of Silver Nanoparticles using Svensonia Hyderabadensis Leaf Extract and Evaluation of their Antimicrobial Efficacy. *J. Pharm. Sci. & Res.* 3, 1117-1121, (2011).