Keywords: Phyllathus emblica; polymer nanocomposites; ion exchange process; heavy metals adsorption; potential donnan membrane effect; AgNPs; regeneration.

4.1. INTRODUCTION

Water contamination with heavy metal ions (Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$) is becoming a dangerous environmental and people’s health problem. Mercury is extremely toxic among the heavy metals. The major pathway for entering mercury waste into the environment from industrial processes such as thermometer manufacturing, alloy industrialized, batteries built-up, electrode manufacturing, etc [1]. In turn to reach the safer environment, various techniques like ion exchange, adsorption, precipitation, filtration, evaporation, flotation, oxidation, biosorption, reverse osmosis, electrochemical treatments and membrane processes are commonly used for the removal of heavy metals. Among these, ion exchange is a efficient technique to remove heavy metal ions [2]. This process does not require a sludge disposal problem and has the lead of recovery of metals. Among the resources used in ion exchange processes, the synthetic organic resins are the major type used nowadays since their characteristics can be modified to particular applications [3]. But the synthetic process was high expensive. Consequently, there is a present necessity to build-up LCIER. The LCIER was synthesized by blending the sulphonated carbons (SCs) prepared from waste flora resources within the synthetic organic resins. The earlier work carried out with the natural products like gum tree bark [4], Accacia nilotica [5]
etc. From the literature survey, it was found that so far CFR is not modified with sulphonated crateva nurvala charcoal (SCNC). The substitute didn’t cause any complex result on the properties, mainly on adsorption capacity. In the current work, seven ion-exchange resins (IERs) were synthesized by blending the quantity of SCNC in the CFR from 0 to 100% (w/w). The capability of the blends for removing heavy metals from aqueous solution was studied. The reports exposed that the adsorption capacity of these IERs reduced with increasing the % of blending CFR with SCNC. The substitutes up to 30% maintained almost all the essential properties of the original CFR (parent resin). Thus the blends made of 30% SCNC (w/w) in CFR will extremely lesser the 30% cost of IERs and act as LCIER. Though the adsorption capacity of the LCIER is fewer than that of the pure CFR because the potential Donnan membrane effect of the CFR is decreased by the impregnated SCNC. Now a days, the growth of nanoscience and nanotechnology has publicized extraordinary potential for the wastewater treatment [6]. As it was considered to increase the adsorption capacity of the LCIER by permanently impregnating 1% (w/w) of AgNPs. Previously, the AgNPs were synthesized by using different flora extracts such as Mentha piperita [7], Cassia auriculata [8] etc. Here, we have built-up a simple and green method to synthesize AgNPs with diameters in the range of 50–100nm using the phyllathus emblica leaf extract (PELE) as reductant and capping agent. Earlier, PNCs were synthesized by loading the zero valent nanoparticles within porous resins [9]. From the literature survey, it was found that the application of
PELE capped AgNPs (zero-valent metal) blended CFR for adsorbing heavy metals has not been reported yet. As a result in this work, PNCs was synthesized by encapsulating 1% (w/w) of AgNPs within the LCIER and these was explored for adsorbing Hg$^{2+}$ from aqueous media.

**4.2. EXPERIMENTAL**

**4.2.1. Materials**

Fresh leaves of Phyllathus emblica (P.emblica) and crateva nurvala plant waste (mavilingam pattai waste) were collected from virudhunagar district, tamilnadu. All the reagents were used in the experiments are analytical grade.

**4.2.2. Methods**

**4.2.2.1. Bio-synthesis of AgNPs**

The cleaned P.emblica leaf were washed thoroughly with sterile distilled water and dark dried for 1months. The dehydrated leaves were broken up to fine particles by using a mixer grinder. The PELE was prepared by 20 g of leaf powder was dissolved in 100 ml of deionized water in a 250ml iodine flask. Then the mixture was boiled at 60 °C for 15 min. The PELE was allowed to cool, filtered through Whatman No.1 filter paper and kept in a refrigerator for more use. 10 mL of PELE
was gradually mixed with 100 mL of 1mM AgNO$_3$ aqueous solution for the green synthesis of AgNPs. Subsequently the mixture was stirred for 20 min to obtain the AgNPs. At this time the formation of AgNPs was identified by the colour of the solution changed from light yellow to dark brown in colour (Fig.1). The environment ecofriendly reduced aqueous solution of Ag nanoparticles was used for further characterization.

4.2.2.2. Synthesis of composites

P-Cresol (12mL) and Con. H$_2$SO$_4$ (12.5mL) were mixed slowly with constant stirring and kept overnight [10]. crateva nurvala waste (500g) was broken into tiny pieces, then carbonized and sulphonated using Con. Sulphuric acid (500mL) and kept at room temperature (30 ± 1°C) for 24h and then heated at 90°C in a hot air-oven for 6 h. It was then cooled, washed several times with distilled water and finally with double distilled (DD) water to remove excess free acid (tested with BaCl$_2$ solution) and dried at 70°C for 12 h. It was labeled as SCNC. The planned quantities of SCNC were added to P-Cresol
sulphonic acid and thus retained the % (w/w) of the blended SCNC as 0, 10, 20, 30, 40 and 50. They correspond to the samples labeled as CFR, B, C, D, E and LCIER. All blend was polymerized with formaldehyde (12.5mL) at 110 °C and cured at this temperature for 3 h to yield a dark brown chunky mass, which was ground, washed, dried and sieved (210–250μm) using Jayant sieves (India) and preserved for characterization [11]. The sample CFR blended with 30% SCNC was labeled as LCIER due to the substitution up to 30% (w/w) blending of CFR with SCNC kept nearly the all necessary properties of the unique CFR.

4.2.2.3. Synthesis of PNCs

P-Cresol (10mL) and Con. H₂SO₄ (11.5mL) were mixed slowly with constant stirring and kept overnight. 30% (w/w) of SCNC and 1% (w/w) of AgNPs were added to P-Cresol sulphonic acid. The sample was labeled as PNCs. The blend was polymerized with formaldehyde (12.5mL) at 110 °C and cured at this temperature for 3 h to yield a dark brown chunky mass which was ground, washed, dried and sieved (250–300μm) using Jayant sieves (India) and preserved for characterization.

4.2.3. Characterization of AgNPs and PNCs:

To characterize the AgNPs and determine the surface functional groups lying on the IERs before and after ion-exchange experiments, the instruments like UV, FT-IR, SEM, EDX, XRD, AFM, TGA and DTA were used.
4.2.4. Adsorption studies by batch mode:

All the adsorption experiments were carried out without arresting any pre-equilibration methods for the operation of any experiments. The effects of adsorption experimental parameters such as initial concentration (30–150 Hg$^{2+}$ mg/L), contact time (10–50 min), resin dosage (0.010–0.030 g), grain size (210–300 μm) and temperature (30$^0$C–50$^0$C) on the removal of mercury ions from aqueous solution were studied in a batch mode system. 0.020 g of PNCs, CFR, B, C, D, E, F and SCNC was introduced into 40 mL solution of Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$ with 150 ppm concentration for 40 min onto the Remi rotator water bath shaker at 200 rpm stirring speed to calculate the adsorption capacity ($q_e$). Moreover, the adsorption experiments were done by 0.25 g of PNCs in 40 mL solution containing known Hg(II) concentration and the limited volume of opposing ions like Na(I), Mg(II), and Ca(II) were mixed into solution as preferred by dissolving their related nitrates with more concentration than the target toxic metal at 30$^0$C. The absolute solution volume was measured as 100 mL. The solution were then transferred to a 250 mL glass bottles and shaken at 200 rpm stirring speed onto the Remi rotator water bath shaker for 30 min. The all metal ions concentration in the supernatants after the adsorption onto the adsorbents was determined by using standard titration techniques as per the literature [12]. The equilibrium adsorption capacity of the adsorbents was estimated with the help of following equation:

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

4.2.5. Column adsorption studies

It was carried through fixed-bed glass column with 2.0 cm internal diameter and 35cm height and packed with 2 cm (4g) of CFR and PNCs were packed in two part columns. The column bed volume is 6.28 cm\(^3\). The glass wool beads were added to the develop the circulation of the influents. Mercury (II) ions solution (initial concentration= 5mg/L) and other co-ions were used as influent with high concentration than the target heavy metals and fed through the column at a constant flow rate of 5 mL/min in downflow mode. The effluent solution was collected at various time intervals and evaluated for Hg (II) content using EDTA titration techniques. Breakthrough curves were found by plotting volume of the influent against the proportion of Hg (II) ions concentrations in the effluent throughout the column for the adsorption of Hg (II) from aqueous solution. For regeneration and desorption of ion exchangers, the adsorbents were quickly rinsed with the limited volume of binary HCl-NaCl solution as the eluting agent and then washed several times with deionized water. After that, the adsorbents were dried in an air oven at 50°C. All the experiments were carried out in duplicate.

\[
% \text{ of Regeneration} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad \text{(2)}
\]

4.3. Results and discussion
4.3.1 Spectral characterization

4.3.1.1. UV–Vis spectra

10 mL of PELE was gradually mixed with 100 mL of 1mM AgNO$_3$ aqueous solution and the reduction of silver ions to silver nanoparticles after 30 min of reaction was monitored by UV/Vis absorption spectra (UV-1800SHIMADZU). Formation of silver nanoparticles was proved with UV–visible spectra and demonstrated surface Plasmon resonance at 420 (Fig.2). The surface Plasmon resonance band is broad as it indicates the formation of particles with broad size distribution [13].

![Fig.2. UV-Visible Spectra of the biologically synthesized AgNPs](image)

4.3.1.2. FT-IR spectra

FT-IR is an essential instrument in understanding the participation of functional groups in relation between AgNPs and biomolecules. Here, the FT-IR (SHIMATZ MODEL FT-IR spectrometer) analyses were studied to find out the probable organic compounds
liable for capping and stabilizing the silver nanoparticles. Fig.3 show spectral peaks suggesting the occurrence of bands relevant to intermolecular O-H stretching (3441 cm⁻¹), C-H aromatic stretching (2910 and 2918 cm⁻¹), C–O–H vibrations (1448 cm⁻¹), polyphenols (1267 cm⁻¹), C–N stretching (2366 cm⁻¹) amide group (1649 & 1743 cm⁻¹). This amide band arises due to carbonyl stretching and N–H deformation vibrations in the amide linkage of proteins present in it. The appeared functional groups may have an efficient function in the bio-synthesis of AgNPs [14]. Followed by the FT-IR spectra of the CFR (pure resin), LCIER (CFR blended with 30% (w/w) SCNC) and LCIER–AgNPs (CFR blended with 30% (w/w) SCNC and 1% AgNPs) before and after adsorption of Hg²⁺ were shown in Fig.4 a, b, c, d, e and f. It was confirmed the ion-exchangeable groups present

![Fig.3. IR Spectra of the synthesized AgNPs via green route](image-url)

...
in IERs [15]. The absorption bands at 1010–1050 cm\(^{-1}\) (S=O str.), 1184–1213 cm\(^{-1}\) (SO\(_2\) sym. Str.), 3392–3450 cm\(^{-1}\) (bonded -OH str.), 1643–1645 cm\(^{-1}\) (C-C str.) and 592–603 cm\(^{-1}\) (C–S str.) in CFR, LCIER and LCIER–AgNPs. As observed from Fig.4 d, e, and f, these peaks moved away or moved out after the adsorption of Hg\(^{2+}\) onto the IERs. It may be due to the bond of Hg\(^{2+}\) and sulfonic groups, which decreased the ion exchange capacity of the sulphonylic groups. After the regeneration, the absorption bands were identified at the same wave number with CFR verifying the return of sulphonic groups.

Fig.4 (a), (b), (c), (d), (e) and (f) FT-IR spectra of free and Hg\(^{2+}\) loaded CFR, LCIER and PNCs.
4.3.1.3. SEM

The surface morphology of the AgNPs was understood by SEM instrument (Vega3 Tescan). SEM images of the AgNPs (Fig.5a and b) were found to be spherical in shape. The size of the AgNPs was found to be 50-100nm.

![SEM image of the biologically reduced AgNPs](image)

Fig.5. SEM image of the biologically reduced AgNPs

![SEM images of free and Hg^{2+} loaded CFR](image)

Fig.6 (a) and (b) SEM images of free and Hg^{2+} loaded CFR
Fig. 7 (a) and (b) SEM images of free and Hg$^{2+}$ loaded LCIER

Fig. 8 (a) and (b) SEM images of free and Hg$^{2+}$ loaded PNCs

Fig. 9. EDX spectra of AgNPs
Then the SEM images of CFR, LCIER, PNCs, Hg (II) – CFR, Hg (II) – LCIER and Hg (II) – PNCs were shown in Fig.6a, 7a, 8a, 6b, 7b and 8b these showed that the surface of the resin before adsorption was somewhat clear. As can be seen in these figures after adsorption,
some of the solid particles were adsorbed onto the resin, indicating that the adsorption of mercury ions on the surface of the IERs [16].

4.3.1.4. EDX

In the SEM-EDX pattern, the silver nanoparticles commonly exhibit the absorption peak about at 3 keV due to surface plasmon resonance [17]. In this work, the SEM-EDX (Bruker EDX machine) pattern were shown strong absorption signal in the silver region (3 keV) and confirmed the formation of AgNPs. Extra elemental signals were evidenced may be due to elements from enzymes or proteins present within the PELE (Fig.9). The SEM-EDX spectrum of free and Hg (II) loaded CFR and PNCs were shown in Fig 10a, 10b, 11a and 11b. Comparison of this SEM-EDX spectrum before and after Hg (II) sorption shows that the presence of Hg (II) peak in the spectrum confirms the adsorption of Hg (II) onto the IERs [18].

4.3.1.5. XRD

The absorption peak detected in XRD pattern of the synthesized AgNPs via green route using the PELE additional deep-rooted and confirmed the presence of silver nanoparticles (Fig.12 and Table.1). The main diffraction peaks monitored are (1 0 0), (1 0 1), (1 0 3), (0 0 6), (1 1 0) and (2 0 2) and telling that the prepared silver nanoparticles pure crystalline in nature (JCPDS file no. 87-0598). The average crystallite size calculated from the XRD patterns is 28.07 nm using the Debye–Scherrer equation [19].
Fig. 12. X-ray diffraction pattern of AgNPs

Table 1 XRD Profile of the synthesized AgNPs

<table>
<thead>
<tr>
<th>Peak Pos. [°2\theta]</th>
<th>FWHM Left [°2\theta]</th>
<th>d-spacing, [Å]</th>
<th>hkl values</th>
<th>Crystallite size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.3873834</td>
<td>0.2</td>
<td>3.46911</td>
<td>1 0 0</td>
<td>18.53</td>
</tr>
<tr>
<td>30.8462905</td>
<td>0.08</td>
<td>3.12773</td>
<td>1 0 1</td>
<td>42.85</td>
</tr>
<tr>
<td>43.3207463</td>
<td>0.28</td>
<td>2.99868</td>
<td>1 0 3</td>
<td>13.83</td>
</tr>
<tr>
<td>56.3349622</td>
<td>0.16</td>
<td>2.77329</td>
<td>0 0 6</td>
<td>29.42</td>
</tr>
<tr>
<td>61.592655</td>
<td>0.09</td>
<td>2.65427</td>
<td>1 1 0</td>
<td>58.29</td>
</tr>
<tr>
<td>70.2087961</td>
<td>1.22</td>
<td>2.43529</td>
<td>2 0 2</td>
<td>5.54</td>
</tr>
</tbody>
</table>

Average crystallite size (nm) **28.07**

4.3.1.6. AFM
Fig. 13. AFM topographical image of AgNPs

Fig. 14. AFM size distribution image of AgNPs
The AgNPs through environmental eco-friendly way using the PELE were analyzed by AFM to find out its particle size, surface morphology, size distribution and shape of the particles. As may be seen from fig 13, 14 and 15, the prepared AgNPs are in the range of 60 nm. The histogram graph was clearly indicated that the size distribution of the AgNPs range from 3 to 20nm (Fig.14). The AgNPs are mainly at 10nm was demonstrated in the line shape. The statistics graph was showed that the size distribution of nanoparticles range around from 30 to 40 nm. The inset image (Fig.15) was visibly shown that the shape of the AgNPs are in spherical nature.

4.3.1.7. TGA & DTA

TGA and DTA analysis of the free and metal loaded adsorbents were shown in (Fig.16a and b & Fig.17a and b). These were showing a shift in temperature dominant peaks related with the loaded metal may be due to the metal binding process taking place at the surface of IERs [20].
Fig. 16 (a) and (b) TGA analysis of free and Hg\textsuperscript{2+} loaded PNCs.

Fig. 17 (a) and (b) DTA analysis of free and Hg\textsuperscript{2+} laded PNCs.
4.3.2. Effects of resin dosage

The effect of resin dosage is one of the significant factors affecting strappingly the adsorption capacity. The Hg\(^{2+}\) adsorption from aqueous medium

![Graph showing the effect of resin dosage on the removal of Hg (II) from aqueous solution](image)

**Fig.18. Effect of resin dosage on the removal of Hg (II) from aqueous solution**

onto the PNCs was studied by differing the quantity of the resin from 0.010 to 0.030g/L. The limit adsorption capacity was found as 0.020g/L. Fig.18 was indicating that the adsorption capacity of mercury increased with increasing resin amount from 0.010 to 0.020g/L due to the raise in IERs site existing for the adsorption of Hg(II) ions and then it was decreased with an increase in resin amount from 0.020 to 0.030g/L. This progress may be attributed to the formation of clusters in IERs ensuing decreased surface area [21].

4.3.3. Effect of grain size on adsorption capacity

Fig.19 shows that the removal of Hg(II) from aqueous solution by the PNCs was grain size dependant behavior. The effect of grain size on the adsorption of  Hg (II) onto
PNCs was studied at grain size range 210-300. From the plot, it is clear that the optimum grain was 210–250 micron for the removal amount of Hg(II) for the removal of mercury from aqueous solution.

![Effect of particle size on PNCs for Hg$^{2+}$ removal](image)

**Fig.19. Effect of particle size on the removal of Hg (II) from aqueous solution**

4.3.4. **Adsorption isotherm study**

The isotherm graph in Fig.20 specified as the $C_0$ increases from 30 to 150 mg L$^{-1}$, the adsorption capacity of PNCs at 30°C for Hg(II) increases in the series of 26.66-173 mg.g$^{-1}$ due to the initial concentration makes necessary driving force to trounce the conflict to the mass transfer of metal ions between the adsorbate and the adsorbent. The relation between Hg(II) and PNCs can be determined with the different adsorption isotherm representations like Freundlich[22] and Langmuir isotherm[23] models.
Fig.20. Effect of concentration on the removal of Hg (II) from aqueous solution

Table 2 Nature of adsorption isotherm and the feasibility

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Adsorption process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

Table 3 Adsorption isotherm factors for Hg$^{2+}$ removal from aqueous solution onto the PNCs
The parameters were calculated from fig.21a and b and are calculated in table 3:

**Freundlich isotherm**: \( \log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \) \quad (3)

**Langmuir isotherm**: \( \left( \frac{C_e}{q_e} \right) = \left( \frac{1}{Q_o b} \right) + \left( \frac{C_e}{Q_o} \right) \) \quad (4)

Where \( K_F \) (mg g\(^{-1}\)) is the Freundlich constant and ‘\( n \)’ the freundlich exponent. Where \( q_e \) (mg g\(^{-1}\)) is the adsorbed amount of Hg (II) at equilibrium, \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of Hg (II), \( Q_o \) (mg g\(^{-1}\)) and \( b \) (L mg\(^{-1}\)) are Langmuir constants related to adsorption capacity and energy of adsorption. Further, the Langmuir isotherm important parameter like separation factor (\( R_L \)) can be calculated by the equation 5.

\[
R_L = \frac{1}{1 + bQ_o} \quad (5)
\]

The \( R_L \) value believed the nature and the feasibility of adsorption process are mentioned in table 2. As exposed in table.3, the experimental data could be well fitted by Langmuir \( (R^2=0.9783) \) as compared to the Freundlich isotherm models \( (R^2=0.9729) \). The \( R_L \) value range from 0 to 1 (0.3871) which confirmed that the adsorption process is favorable for the IERs [24]. The magnitude of the exponent 1/\( n \)

**Table 4 Comparison of adsorption capacities of different adsorbents with PNCs for Hg\(^{2+}\) removal**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Hg (II)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine functionalised bentonites</td>
<td>102.7</td>
<td>[26]</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>cross-linked magnetic chitosan-phenylthiourea resin</td>
<td>135</td>
<td>[27]</td>
</tr>
<tr>
<td>Ethylenediamine modified peanut shells</td>
<td>30.78</td>
<td>[28]</td>
</tr>
<tr>
<td>Thiol containing polymer encapsulated magnetic Nanoparticles</td>
<td>16.02</td>
<td>[29]</td>
</tr>
<tr>
<td>PNCs</td>
<td>104.16</td>
<td>Present work</td>
</tr>
</tbody>
</table>

(0.6273) lying between 0 and 1 and also the value of n (1.5941) greater than 1 showed favorable environments for adsorption [25]. The adsorption capacities of the PNCs and other adsorbents for the removal of Hg\(^{2+}\) from aqueous solution or wastewater are mentioned in Table 4 [26–29].

4.3.5. Adsorption kinetics study

The Fig. 22 evidently indicated that the adsorption process was fast at the begin of reaction and completes within 40 min. Subsequently a time-consuming next stage for the Hg\(^{2+}\) adsorption on PNCs was completed within 50 min. Thus the equilibrium time was 40 min for this adsorption and then no significant change was observed due to may be more active sites were obtainable on PNCs at the start of reaction (or) more active sites may not be available on PNCs after 40 min.
Fig. 22. Effect of contact time on the removal of Hg (II) from aqueous solution

Fig. 23 (a) and (b) Pseudo first and Pseudo second order plots for Hg (II) removal

The pseudo-first-order and pseudo-second-order kinetic models were used to explain such adsorption as [30]

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{---------- (6)}
\]

\[
t / q_t = \frac{1}{k_2} q_e^2 + t / q_e \quad \text{---------- (7)}
\]

Table 5 The kinetic factors for the removal of Hg (II) from aqueous solution onto the PNCs
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Experimental $q_e$ (mg/g)</th>
<th>Pseudo-I-Order constants</th>
<th>Pseudo-II-Order constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>$K_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>173</td>
<td>2147</td>
<td>0.2233</td>
</tr>
</tbody>
</table>

Where $k_1$ is the pseudo-first-order rate constant (min$^{-1}$), $q_e$ (mg g$^{-1}$) is the adsorption capacity at equilibrium, $q_t$ (mg g$^{-1}$) is the adsorbed amount of metal ion after time $t$ (min), $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$). From fig.23a and b, the entire values were calculated and tabulated in table 5. The $R^2$ value for pseudo second-order kinetic model is higher than pseudo-first order kinetic model. moreover the experimental $q_e$ value is very closer to the calculated $q_e$ value for pseudo-second-order kinetic model. Thus the adsorption process was followed second order model kinetic model.

4.3.6. **Intra-particle diffusion model (Waber–Morris model)**

It is used to highlight the rate-limiting step of the adsorption process and this was suggested by Weber and Morries. The scheme is based on the account that if the plot of $q_t$ versus $t^{1/2}$ origin to be a straight line and surpass throughout the origin, intra-particle diffusion is the resource of rate-limiting step. This equation can be uttered as

$$q_t = k_{id} t^{1/2} + c \quad \text{---------- (8)}$$
Fig. 24. Weber–Morris intra particle diffusion model for the Hg (II) removal using the PNCs.

Table 6: The intraparticle diffusion factors for Hg$^{2+}$ removal from aqueous media onto the PNCs.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Intraparticle diffusion parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{id}$ (g mg$^{-1}$ min$^{-1/2}$)</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>32.221</td>
</tr>
</tbody>
</table>

Where $q_t$ is the adsorption capacity at any time $t$ and $k_{id}$ is the intra particle diffusion rate constant and $C$ is the film thickness. From fig.24, the values $K_{id}$, $C$ and $R^2$ calculated and tabulated in Table 6. Larger the value of $C$ tells that the effect of boundary layer on adsorption process was superior. The deviation of the scheme from the linearity gives an idea about the rate-limiting step must be controlled boundary layer diffusion. Fig.24 point out that the two or more steps control the adsorption process. The two straight
lines are in fig.24 tell as the one portion is owing to the film diffusion and the second linear portion is owing to the pore diffusion[31].

4.3.7. Adsorption Capacity study ($q_e$)

As observed from Fig.25, the adsorption capacity value of IERs has been lessening with rising the % of SCNC in CFR owing to the potential donnan membrane effect was lessen by infusing SCNC in the CFR. However the replacement up to 30% of SCNC in CFR maintains the all fundamental properties of pure CFR and as the blending of CFR with 30% SCNC was labeled as LCIER. Although the adsorption capacity of the LCIER is less than that of the CFR due to the decreased potential donnan membrane effect by substituted SCNC for removing heavy metals.

![Fig.25](image)

**Fig.25. Adsorption Capacity of H⁺ Form of IERS for Various Metal ions relative to CFR**

Consequently fasten the potential donnan membrane effect principle prepared a novel nanocomposite ion exchanger (PNCs) by impregnating AgNPs within a macroporous cation exchanger LCIER. The adsorption capacity of the novel adsorbent was also
studied and compared with CFR and LCIER for removing Hg (II) from aqueous solution. While compared to CFR and LCIER, the prepared nanocomposites PNCs rendered superior selective for removal of mercury from aqueous medium. It was generally recognized to two features, the host material LCIER and AgNPs particles. In this work, confirmed that the immobilized
Fig. 26. Effect of competing ions on Hg (II) retention by CFR and PNCs at 30°C.

negatively charged sulfonic acid groups bound to LCIER matrix would significantly develop permeation and preconcentration of the target heavy metal cations from aqueous media to interior of the polymeric phase [32], and in order to build positive conditions for mercury removal by AgNPs particles.

4.3.8. Effect of competitor ions

Alkali and alkaline earth metals are generally present in the natural and industrial waste water effluents. Though they are normally not hazardous to us, particularly alkaline earth metals tightly compete with heavy metals for active sites of a used adsorbent [33]. So, it is essential to find out the % of adsorption to PNCs toward Hg (II) ions in the existence of co-ions. Here, we studied the effects of Na⁺, Mg²⁺ and Ca²⁺ on Hg (II) adsorption with the adsorbent along with the host cation exchanger RFR was also involved for reference. Fig. 26 was shown that the Na⁺ adding together induces negligible effect on Hg (II) adsorption in the test concentration series, while the divalent opposing ions such as Mg²⁺ and Ca²⁺ effect in a significant drop in Hg (II) adsorption on
both adsorbents. Generally, divalent cations are adsorbed comparatively greater than the monovalent cations and divalent cations with lower hydration energies are adsorbed relatively over those with higher hydration energies [34]. The adsorption capacity of the CFR was almost zero with rising the concentration of these divalent cations. While, increasing the Mg$^{2+}$ and Ca$^{2+}$ from 0 to 5 times of the Hg (II) concentration found as apparent drop of its % of adsorption from 100 to 50–60 for PNCs. Then, increasing the whole

![Breakthrough curves of Hg (II) retention by PNCs and CFR in two separate fixed-bed column cycles.](image)

**Fig. 27.** comparing of breakthrough curves of Hg (II) retention by PNCs and CFR in two separate fixed-bed column cycles.

these opposing ions still to 3 times of Hg (II) concentration, no more drop in the adsorption capacity value due to the AgNPs immobilized in the polymer, which selectively sequestrate Hg (II) ions through inner-sphere complexation of Hg (II) on AgNPs [35].

4.3.9. Fixed-bed column adsorption studies:
Fig. 27 illustrates a complete effluent history of a separate fixed-bed column packed with both PNCs and CFR for a feeding solution containing Hg\textsuperscript{2+} and rival cations (Na\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+}). Fig. 27 shows that the Hg\textsuperscript{2+} breaks through rapidly onto the CFR due to its too little selectivity towards Hg\textsuperscript{2+} with the proficient treatment volume is almost 800 bed volumes (BV). Quite the reverse, appropriate breakthrough results were determined for PNCs as about 7000BV under identical conditions. The concentration of Hg\textsuperscript{+} in the effluent decreased significantly from 5 to less than 0.001mg/L, this limit was accepted by WHO. Then, the used PNCs column was regenerated by a binary NaCl-HCl solution and the results are shown in Fig. 28. It was shown that the preloaded mercury can be effectively desorbed with 11-12BV regenerates. Besides, we carried out a continuous adsorption–desorption runs for PNCs bed-column to prove its feasibility. The imbrication of mercury breakthrough curves for the 1st and 3rd cycle confirmed that PNCs can be employed for multiple use with negligible capacity loss.
Fig. 28. A column desorption history of mercury preloaded onto PNCs and CFR.

4.3.10. Thermodynamics study

The cause of temperature on the adsorption of Hg(II) ions onto PNCs was known from the scheme of the thermodynamic equilibrium constant values ($K_c$) versus absolute temperatures ($T$) in Fig. 29. It was shown that the $\log K_c$ increased with $T$ increasing, so the adsorption process in exothermic nature. Thermodynamic parameters such as standard free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and
entropy change (\(\Delta S^o\)) can be determined by using following equations [36]:

\[ K_C = \frac{C_{ad\ (solid)}}{C_e\ (solution)} \quad \text{------------- (9)} \]

\[ \Delta G^o = -2.303\ RT\ \log K_C \quad \text{--------------(10)} \]

\[ \log K_C = -\left[\frac{\Delta H^o}{2.303\ RT}\right] + \left(\frac{\Delta S^o}{2.303R}\right) \quad \text{--------------(11)} \]

Where \(K_C\) is the thermodynamic equilibrium constant, \(T\) is the absolute temperature (K) and \(R\) is universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). The \(\Delta H^o\) and \(\Delta S^o\) values

Table 7 Thermodynamic factors for the removal of Hg\(^{2+}\) from aqueous solution onto the PNCs.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(-\Delta G^o\ (kJ\ mol^{-1}))</th>
<th>(-\Delta S^o\ (J\ mol^{-1}K^{-1}))</th>
<th>(-\Delta H^o\ (kJ\ mol^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>236</td>
<td>292.18</td>
<td>15.36</td>
</tr>
<tr>
<td>40°C</td>
<td>249</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50°C</td>
<td>292.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
were calculated from the logKc vs 1/T plot and were tabulated in Table 7. The negative \( \Delta G^\circ \) & \( \Delta H^\circ \) values were shown that the adsorption process exothermic in nature. Besides the negative sign of \( \Delta S^\circ \) value exemplified drop in attraction between PNCs and Hg(II) ions.

4.4. Conclusion

AgNPs was determinedly impregnated in the interior a low cost macroporous cation ion exchange resin (LCIER) via novel method using CFR as a cross linking agent, as well as a novel polymer nanocomposites (PNCs) adsorbent was accessible for sensitive Hg(II) removal based on potential donnan membrane principle. Besides, PNCs were exposed that the best selective for the removal of mercury(II) from aqueous medium while Compared to CFR and LCIER and it was attributed to the potential donnan membrane effect exercised by impregnating AgNPs. These were synthesized through trouble-free and environment eco-friendly method using the PELE as reductant and capping agent. Also, the used PNCs were conformable to an effective regeneration by binary HCl-NaCl solution for its frequent use. All the results proved that the synthesized PNCs are a extremely attractive ion exchanger for efficient heavy metal removal from industrial wastewater and polluted aqueous solution.

4.5. References:


Selective Co (II) Removal from Aqueous Media by Immobilizing the Silver Nanoparticles within a Polymer-Matrix through Formaldehyde Cross Linking Agent

Abstract:
Silver nanoparticles (AgNPs) were synthesized by a biological reduction method using Cyperus rotundus grass extract (CRGE) and these were found to contain a regular diameter of 1-100 nm. The Polymer nanocomposites (PFR-AgNPs) were then built-up by encapsulating green synthesized AgNPs within a phenol-formaldehyde resin (PFR) as a cross linking agent using polycondensation method and applied to sorption of Co (II) from aqueous solution in a batch adsorption system as an initial concentration (30–150mg/L), contact time (10–50min) and temperatures (303–333 K). The non-diffusible negatively charged sulphonic acid groups bound to PFR template should significantly develop penetration and preconcentration of the goal metal cations from aqueous solution to interior plane of the polymeric matrix as well as make constructive conditions for Co (II) removal by AgNPs particles. Then the column adsorption studies were carried out for the Co (II) retention in the presence of alkali and alkaline earth metals (Na⁺, Ca²⁺ and Mg²⁺). While compared to PFR, PFR-AgNPs demonstrated extremely penetrative cobalt removal from wastewaters in the subsistence of contending Ca²⁺, Mg²⁺, and Na⁺ at a large amount than the target heavy metal. Pseudo first order reaction, pseudo second reaction and Weber–Morris intraparticle diffusion models were used to analyze the data. The adsorption equilibrium data was explored by the Freundlich and Langmuir adsorption isotherm models and the reaction was found to show a relationship well with a Langmuir adsorption model. Free PFR-AgNPs and Co²⁺ loaded PFR-AgNPs were characterized by the FT-IR spectra (FT-IR), Scanning electron microscope (SEM), energy-dispersive microanalysis (EDX), thermo gravimetric analysis (TGA), and differential thermal analysis (DTA). The regenerant used for regeneration of the cation-exchange resin was