Sustainable robust green synthesis of nanoparticles from waste aquatic plants and its application in environmental remediation

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ABSTRACT

Green synthesis of nanoparticles using natural materials is an emerging technique that fascinates the scientific community globally for the treatment of wastewater. In the present study, aquatic plants such as Piaropus crassipes (PC) and Lemna gibba (LG), were utilized to make low-cost nanoparticles, and its feasibility for the removal of Zn(II) ions was studied. The synthesized nano adsorbents were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectroscopy (FTIR), Brunauer Emmett-Teller (BET) analysis, and Zeta potential analysis. The optimal conditions were evaluated by batch adsorption studies, to investigate the parameters such as pH (2–7), adsorbent dosage (0.5–5 g/L), initial concentration (20–60 mg/L), and contact time (10–120 min) etc, respectively. The isotherm, and kinetic data results fit well with Langmuir, and pseudo-second order model. The anticipated monolayer adsorption capacity with respect to the PC, and LG was found to be 42.41 mg/g and 27.65 mg/g, respectively. Thermodynamic studies showed that the process is exothermic. The adsorption mechanism of PC/LG on Zn(II) exhibited surface complexation, ion exchange, and diffusion. Desorption studies were performed to analyze the recovery potential of Zn(II) ion. Hence, this article investigates the economic synthesis of green nanoparticles, and their potential utilization in heavy metal remediation.

Key words: green synthesis, isotherm, kinetics, mechanism, nanoparticles, thermodynamics, Zn(II) removal

HIGHLIGHTS

• Green nano particles were synthesized from waste aquatic weeds.
• Applicability of the prepared nano particles exploited for Zn(II) removal.
• Efficiency of nano adsorbents and regeneration capacity analyzed.
• Adsorption mechanism and economic feasibility of prepared nano particles proposed.

INTRODUCTION

Heavy metals are dispensed in the environment by diverse human activities that create serious contamination and found to be correlated with the occurrence of a lot of health effects. Quite a lot of ecotoxicological impact occurs due to dumping of heavy metals in the environment. Aquatic ecosystems are mostly at risk because they are often the final receiver of these elements (Gebretsadik et al. 2020). For example, electroplating, tannery, paint, mining, paper and pulp, iron and steel ventures, fertilizer industries explicitly release the abandoned wastewater directly into the water bodies (Peñafiel et al. 2019). Heavy metals such as copper, nickel, cadmium, zinc, lead, arsenic, mercury, and chromium are stable, carcinogenic and bioaccumulate easily. Among these, Zn(II) is toxic and non-bio-degradable.

Zn(II) finds its way into the environment through effluents from pharmaceuticals, galvanizing, paints, pigments, insecticides, and cosmetic industries that cause severe threats to the environment. Though, traces amount of Zn(II) is essential for humans for healthy function, at higher concentration it causes hazardous impact. As per the Bureau of Indian Standards (BIS) and World Health Organization (WHO), the threshold limit value of Zn(II) in drinking water is 5 mg/L. Beyond a permissible limit, the deficiency Zn(II) is associated with various syndromes such as short stature, hypoplasia of the immune system, poor wound healing, and attenuated neutrophils, etc. Therefore, effective removal of Zn(II) from the environment

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is necessary. Various strategies such as electro coagulation, chemical precipitation, membrane separation, filtration, oxidation, and ozonation, etc has been adopted for the removal of Zn(II). However, these techniques entail high capital investment, as well as inefficient when heavy metal exists in low concentration (Lou et al. 2018).

In this context, a new version of the technology with innovative materials for the application of wastewater treatment is necessary. In comparison with various methods, adsorption seems to be simple, and efficient method for the treatment of wastewater. Concerning heavy metal removal, adsorption process can completely remove the pollutant molecules, and regenerate the adsorbent, thereby reducing the capital cost (Sankaran et al. 2020). Various investigations have been carried out using bentonite, chitosan, tea waste, potato starch, etc., for adsorption of Zn(II) from aqueous solution (Saravanan et al. 2017; Bashir et al. 2020; Çelebi et al. 2020; Nasseri et al. 2020). However, factors such as waste disposal, secondary pollutant, economic feasibility, and stability play a vital role in the selection of an adsorbent. Therefore, researchers are focussing on low cost, biodegradable adsorbents particularly with high reactivity, and stability.

Nanotechnology plays a vital role in environmental remediation, owing to its large surface area, and high surface energy. Recently, synthesis of nano adsorbents using plant intermediates are in progress, and acclaimed as feasible, and efficient (Raman et al. 2021). Biomolecules of plants exhibit excellent potential to reduce metal ions in an eco-friendly manner. The reducing properties of plants towards heavy metals are due to high cellulose content. Also, the presence of functional groups such as hydroxyl, phenol, carboxyl makes it deliberate to apply it in wastewater treatment (Mohamed et al. 2019). With the available literature, it is observed that most of the studies were focussed on agricultural products or plants such as Hordeum vulgare, Mangifera indica, Amaranthus dubius, Rosmarinus Officinalis, etc for the synthesis of nano particles. But these plants require extreme care, and high capital cost, which restrict their usage on large scale. Thus, the present study focused on finding an alternative solution to high cost and its utilization on commercial scale. The objective was to select plants which are worthless for mankind but have favourable properties for heavy metal removal.

Subsequently, aquatic weeds such as Piaropus crassipes (PC), and Lemna gibba (LG) were chosen, as they are considered as rampant colonizers, and blacklisted as notorious aquatic plants. Nevertheless, these weeds are rich in organic molecules, and polyphenols groups, which can be potentially employed for the synthesis purpose. The novelty of research focusses on the utilization of these weeds that offers a two-way management possibility in terms of their elimination, and custom for valuable products. The objective of the present work is (1) to explore the synthesized nanoparticles (PC and LG) as nano adsorbents, and to characterize their properties. (2) to evaluate the efficiency of PC and LG in the removal of Zn(II) ion from aqueous solution. (3) to investigate equilibrium, isotherm, kinetics, and thermodynamic studies of nano adsorbents (4) to propose reaction mechanism, and its regeneration capability.

**MATERIALS AND METHODS**

**Analytical reagents**

Chemicals such as ZnSO₄·7H₂O, Tetraethyl orthosilicate (TEOS), NaOH, C₂H₅OH of analytical grade were purchased from Sigma-Aldrich, and Merck, India used for the experimental purpose without any purification. The pH on Zn(II) removal was performed at different pH, and the desired pH was adjusted by adding 0.1 N HCl or NaOH solution. It was measured using by using a pH meter (Tesla Limited, India). Considering the experimental errors, and average values, three independent replicates confirmed that the results of Zn(II) removal were reproducible under same condition.

**Green synthesis of nanoparticles**

Aquatic plants (PC, LG) were collected from nearby villages, and the fresh leaves were washed several times with running water thoroughly followed by distilled water to remove impurities. It was sliced into pieces, dried in hot air oven (JSI mermo universal oven- JSI 101) at 70 °C for 2 h. It was then crushed, grounded, and sieved through BSS 250 μm sieve followed by 150 μm sieve, retaining 230–150 μm fraction.

Initially, 3 g (each) powdered PC, LG were mixed with ethanol (10 mL), NaOH (2.5 mL), and magnetically stirred (Royal scientific RSW 127, India), for 40 min. To this, 10 mL of TEOS was added slowly to the solution, and the mixture was stirred for 3 h to reach the homogeneity. As a result, a green colour gel was formed after the completion of the reaction. Then, the gel was heated for about 12 h in an oven at 100 °C. Finally, the dried gel was calcined for 700 °C for 2 h, in an electric furnace (Scientech SE-130) to produce fine nanoparticle samples (PC/LG). The schematic representation of the process is shown in Figure 1.
Various instrumentation methods were used to accomplish the characterization of synthesized nano adsorbent (PC/LM) in order to determine their morphologies, elemental properties, and surface properties. The surface texture, and morphology of the synthesized nano adsorbents were determined by Scanning Electron Microscopy (SEM), ZEISS Ultra 55-German. To evaluate the surface area, and pore size distribution Brunauer Emmett-Teller (BET) Analysis was carried out using N2 adsorption isotherm at 77 K using Quanta-IQ-MS/AR, USA. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the changes in the functional groups influenced due to adsorbent synthesis. The samples were analyzed in Bruker Optics Inc., Billerica, MA, USA, spectrophotometer ranges from 400 to 4,000 cm\(^{-1}\). In order to measure the electrical potential on the nanosorbent surface, zeta potential analysis was carried out using Nano Brook 90 Plus Zeta instrument.

**Batch adsorption studies**

Batch adsorption experiment was conducted with 100 mL sample of known Zn(II) ion concentration in a 250 mL conical flask. The experimental setup was placed in an incubation shaker (REMI CIS -18 T Bench top orbital shaking incubators, India) operating at 180 rpm for about 1–2 h. On reaching the desired contact time, the conical flask was taken out, and the solution was centrifuged. The supernatant was collected, and Zn(II) ion concentration was measured using an Atomic Absorption Spectrometer (AAS) (SL 176 Model, Elico Limited, Chennai, India). Various influencing factors such as solution pH (2–7), adsorbent dosage (0.5–5 g/L), initial concentration (20–60 mg/L), and contact time (10–120 min), etc were varied, and their effects were studied. The results obtained from batch adsorption studies were used to determine the percentage removal of Zn(II) ions by using the following reference Equation (1):

\[
\text{Percentage removal of metal ions (\%)} = \frac{C_i - C_f}{C_i} \times 100
\]

where, \(C_i\) and \(C_f\) are initial, and final concentration states of Zn(II) ion in the solution.

In the estimation of adsorption isotherms, adsorption studies were conducted by taking 2 g of PC/LG, and 100 mL of Zn(II) at different concentrations (20–60) mg/L in a series of flask. It was shaken for 30 min, at the optimum pH conditions and at a temperature of 30 °C. Once equilibrium time attained, mixture was centrifuged. The residual concentration in the solution was determined using AAS. The amount of Zn(II) ions adsorbed at equilibrium, \(q_e\) (mg/g), was calculated by the following
reference Equation (2):

\[ q_e = \frac{(C_i - C_e)V}{W} \]  

(2)

where, \( C_e \) is the concentration of Zn(II) ions in equilibrium (mg/L), \( V \) is the volume of Zn(II) solution treated (L), and \( W \) is the mass of PC/LG (g). Adsorption equilibrium data were applied to various isotherm models such as Langmuir, Freundlich, and Temkin.

Adsorption kinetics studies were performed by mixing 2 g/L of PC/LG with 100 mL Zn(II) ion solution (20 mg/L) at pH of 5.2 (PC), and 5.4 (LG) in a stoppered conical flask. The conical flask was shaken for 50 min in an incubator shaker. 10 mL of the sample was withdrawn, from conical flask at regular time intervals ranging from 10–120 min, centrifuged, and finally the residual Zn(II) ion concentration was determined using AAS. To estimate the adsorption mechanism, and rate determining step, various kinetic models such as using pseudo-first order, and pseudo-second order models, and intraparticle diffusion model were applied.

Thermodynamic studies were carried out by shaking mixture in temperature controlled incubation shaker for different temperature (303 K, 313 K, 323 K, and 333 K) at an optimum condition (Zn(II) ion concentration = 20 mg/L, pH = 5.2 (PC)/5.4 (LG), dosage = 2 g, contact time = 80 min (PC), 70 min (LG), and volume of sample = 100 mL). After the predetermined time interval, the residual Zn(II) concentration was analysed using AAS. The adsorption data were fitted to thermodynamic equations to evaluate the thermodynamic parameters.

Desorption studies were carried out to determine the consecutive reuse capability of PC and LG for Zn(II) removal. About 2 g of synthesized nano adsorbent (PC/LG) was added to cone shaped stoppered flasks containing 100 mL of 0.1 M HCl solution, and kept in a rotary shaker at 200 rpm at 30 °C for 60 min. The desorbed material was separated out, and recovered by filtration operation. The concentration of Zn(II) ions in the supernatant was measured by using AAS. This cycle was repeated upto 3 times.

RESULTS AND DISCUSSION

Characterization of adsorbent

The surface morphology, porosity, and texture of nanoparticles were examined by using SEM analysis and their images are depicted in Figure 2(a) and 2(b). Based on the analysis, the shape of PC, and LG appears to be non-aggregated with small flakes, and craggy structure. The surface appears to be curled, and has a large number of uneven porous sites with an interconnected framework. It indicates that PC, and LG have more sufficient space for the adsorption of Zn(II) ions. The high cellulosic content of the nano adsorbent boosts the binding capacity of metal ions, and the occurrence of polyfunctional metal binding sites for both anionic and cationic complexes, thereby enhancing rapid channels to transmit heavy metal ions into the adsorbent core during the adsorption process. The synthesized PC, and LG nanoparticles were not perfectly spherical. Slight clusters occurred on the surface of the particles, because of non-mineral elements such as Na, K, etc., present in the sample.

The value of BET surface area (m²/g), pore volume as well as average pore diameter measurement for PC, and LG were determined by the BET adsorption method using Quanta-IQ-MS/AR instrument. The results were tabulated in Table 1. Figure 2(b) shows the nitrogen adsorption-desorption isotherm curves of PC/LG, using TEOS as precursor. Figure 2(a) and 2(b) shows the mesopore diameter of the synthesized materials can vary from 2–35 Å, depending upon the amount of precursor used in the preparation of nano adsorbent.

As depicted in Table 1, the BET surface area of synthesized PC, and LG was found to be 259 m²/g, and 193 m²/g, respectively. The surface area of LG is lower than PC ascribed to creation of tightly packed aggregates owing to hydrophobic interactions between the particles. It is noted that components such as traces of sugars, lignin will consistently block the pores on adsorbent material, causing further exposure to the adsorbent surface. The pore volume of LG (0.42 cm³/g) decreased which might be due to the close filling of adjacent particles, whereas the pore volume of PC (0.63 cm³/g) increased due to the development of a new annullled aggregates. Moreover, the pore volume did not decrease correspondingly with surface area in turn it led to increase in average pore diameter.
Also, Figure 2(a) and 2(b) shows a clear hysteresis loop in the nitrogen adsorption and desorption isotherms. Based on the classification, the isotherm in Figure 2(a) and 2(b) belongs to Type IV, out of six isotherm group. It suggests the capillary compression with H1 type hysteresis loop, and further it indicates cylindrical pore geometry, with uniform porosity, and pore connectivity. The results found to have good agreement with the average pore size ranging from 20–50 nm. Figure 2(c) and 2(d), indicates the presence of mesopore structure formation. It predominates in the order PC > LG. A comparative study has been made with present experimental work with the reported values for other adsorbents in the published literature (Table 2). Interestingly, the obtained specific surface area from the present study was higher than most of the documented green synthesized nano particles.

FTIR investigations were carried on synthesized nano adsorbents and are the results are shown in Figure 2(g). The cell wall of PC and LG is composed of a large number of complex organic components along with proteins, carbohydrate polymers

Figure 2 | (a, b) SEM Images (c, d) BET Plots (e, f) BJH Plots (pore size) (g) FTIR Spectra (h) Zeta Potential as a function of pH and pH_{PZC} for PC and LG Samples. (Continued)
such as cellulose, xylene and inorganic ions such as Ca$^{2+}$, Mg$^{2+}$, etc. However, the cell wall composed of acidic functional groups such as carboxylic, phosphate groups have a direct influence on the sorption capacity. The peak at 3,742.88 cm$^{-1}$, 3,914.48 cm$^{-1}$ of PC and LG corresponds to OH-stretching of polymeric compounds. The peak

Table 1 | Surface characteristic analysis of PC and LG

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PC</td>
<td>259</td>
<td>0.63</td>
<td>1.89</td>
</tr>
<tr>
<td>2</td>
<td>LG</td>
<td>193</td>
<td>0.42</td>
<td>5.10</td>
</tr>
</tbody>
</table>
and the formation of Zn(OH)$_2$ species was observed. Higher effects of pH was not studied beyond 6, in order to avoid the removal efficiency. The adsorption capacity was less at initial pH values owing to the competition between the Zn(II) ions. When the initial pH value was higher than 5.6, the adsorption capacity gradually decreased.

The removal of Zn(II) on surface of PC/LG can be described in terms of the adsorbent pH$_{pzc}$. The pH$_{pzc}$ of synthesized nano adsorbents (PC, LG) was found to be 7.2, and 8.1, respectively. The surface of the adsorbent is protonated if pH $<$ pH$_{pzc}$, and positively charged. Conversely, the active sites are deprotonated, and the charge is negative when pH $>$ pH$_{pzc}$. Thus, the competition between H$^+$ and Zn$^{2+}$ ions decreases, on increasing the due to decrease in the repulsive force. However, in the present study, the adsorption of Zn(II) at pH $<$ pH$_{pzc}$ was observed signifying the adsorption of Zn(II) may occur under acidic condition. Subsequently, the Zn(II) adsorption decreased under alkaline conditions. Also electrostatic repulsion that occurred between adsorbate species, and adsorbent caused the reduction in the Zn(II) removal capacity.

Table 2 | Comparative studies on the surface area of different adsorbents with PC and LG

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PC</td>
<td>259</td>
<td>Present study</td>
</tr>
<tr>
<td>2</td>
<td>LG</td>
<td>193</td>
<td>Present study</td>
</tr>
<tr>
<td>3</td>
<td><em>Moringa oleifera</em> extracts</td>
<td>87.07</td>
<td>Gautam <em>et al.</em> (2020)</td>
</tr>
<tr>
<td>4</td>
<td><em>F. chinensis Roxb</em> extract</td>
<td>115.42</td>
<td>Ali <em>et al.</em> (2018)</td>
</tr>
<tr>
<td>5</td>
<td><em>Psidium guajava</em> extract</td>
<td>20</td>
<td>Mahmoud <em>et al.</em> (2021)</td>
</tr>
</tbody>
</table>

2,893.03 cm$^{-1}$ corresponds to symmetric vibration of -CH$_2$ (Khalaf *et al.* 2021). The band around 1,065.94 cm$^{-1}$, and 1,639.02 cm$^{-1}$ was attributed to the asymmetric stretching vibration of the -NH$_2$ group.

Similarly, the peak located at 2,393.59 cm$^{-1}$ is the vibration of -COO group stretching. The corresponding peak observed at 873 cm$^{-1}$ is the Si-H band (Syafri *et al.* 2019). The C-O-C stretching of polysaccharides was in the range of 1,000 cm$^{-1}$–800 cm$^{-1}$. The spectral band at 593 cm$^{-1}$, and 603 cm$^{-1}$ corresponded to the fingerprint zone of sulphur and phosphorous present in the nano adsorbents. The outcome of functional group characterization of PC, and LG contains diversified functional groups such as phosphate, amide, carboxyl, thiol, hydroxide groups which can serve as a potential binder for Zn(II) ions removal.

Zeta Potential (ZP) value exhibits information about the stability, and surface charge of the prepared nano adsorbent. Figure 2(h) demonstrates the attained zeta-potential values as a function of pH for PC and LG, respectively. The range of zeta potential value is positioned below $-30$ mV or above $+30$ mV. A high value of zeta-potential produces electrostatic repulsion thereby stopping particles to form flocculates, and aggregates When the value of pH $< 6$, the surface charge illustrates a strong positive zeta potential value equal to $+28$ mV for PC, and $+25$ mV for LG. On further increase in pH, the point of zero charge (pHpzc) is reached at 7.2 (PC), and 8.1 (LG), respectively. When the pH$_{pzc} >$ pH, anion adsorption is favourable. However, when pH $<$ pH$_{pzc}$, the adsorbent surface is positively charged, and electrostatic attraction is accomplished for Zn(II) adsorption (Rodrigues *et al.* 2020).

Effect of pH

Generally, the pH value of an aqueous solution has a greater effect on adsorption rate, and can even entirely interchange the activity of binding sites. In the present study, the effect of pH on the adsorption was determined by shaking 2 g/L of PC/LG with 100 mL Zn(II) solution of 20 mg/L concentration at various pH values ranging from 2 to 7. Figure 3(a) represents the adsorption capacity of PC/LG as a function of pH. As the initial pH varies from 2 to 7, the adsorption ability of Zn(II)-PC/LG increased gradually, and the maximum removal efficiency was achieved at pH = 5.2 and 5.4, respectively. When the initial pH value was higher than 5.6, the adsorption capacity gradually decreased.

On further increase in pH, the point of zero charge (pHpzc) is reached at 7.2 (PC), and 8.1 (LG), respectively. When the pH$_{pzc} >$ pH, anion adsorption is favourable. However, when pH $<$ pH$_{pzc}$, the adsorbent surface is positively charged, and electrostatic attraction is accomplished for Zn(II) adsorption (Rodrigues *et al.* 2020).
Effect of adsorbent dosage

The effect of adsorbent dose on Zn(II) adsorption onto PC and LG was examined by varying the doses from 0.5 to 5 g/L in 100 mL solution containing 20 mg/L Zn(II) concentration at a fixed pH. The schematic illustration is presented in Figure 3(b).

As represented in Figure 3(b), it is evident that on increasing the adsorbent dosage upto 2 g/L, the percentage of metal uptake (0–97%) increased. The degree of adsorption of metal ions increased with an increase in adsorbent concentration owing to an increment in the overall surface area, which automatically increases the number of binding sites (Afroze et al. 2016). Further, an increase in adsorbent dosage beyond 2 g/L, no considerable improvement in yield was observed. It is due to the distribution of the PC and LG on the surface of Zn(II) ions. On the contrary, the metal uptake decreased with an increase in adsorbent concentration.
Moreover at higher adsorbent dosage, the existing metal ions were inadequate to cover all the transferable sites on the nanoparticles, resulting in the decline of metal uptake. Hence, an adsorbent dosage of 2 g/L was chosen as an optimum value for further experimental studies, as it showed relatively excellent removal efficiencies.

Effect of initial concentration

The initial concentrations of Zn(II) ions act as a driving force to overcome mass transfer resistance for metal ion transport between the surface of adsorbent, and the solution. The influence of Zn(II) ion concentration on adsorption by PC and LG was shown in Figure 3(c). The percentage removal of Zn(II) ion was observed in the range from 97% to 86% for PC, and 94% to 82% for LG, respectively. It can be examined from Figure 3(c) an increase in Zn(II) ion concentration, the amount of Zn(II) retained on the tested PC and LG increased, whereas Zn(II) ion removal efficiency decreased. This increase in trend may be attributed to the rise in the driving force of the Zn(II) ion concentration gradient generated by the increase of the Zn(II) ion concentration. Similarly, the lower adsorption percentage at higher Zn(II) ion concentration might be directly related to inadequate binding sites for the adsorption (Bao et al. 2015).

Effect of contact time

The effect of contact time on the adsorption of Zn(II) for PC and LG was studied by taking 20 mg/L of Zn(II) solution with 2 g/L of adsorbent dosage at pH 5.5. The adsorption process of Zn(II) ions onto PC and LG increased rapidly in the beginning, owing to the large availability of active sites on the surface of PC, and LG, respectively. It was clear from Figure 3(d), LG posed maximum removal with an increase in contact time up to 80 min for Zn(II) ions, thereafter it remains constant. Similarly, maximum removal (97%) was achieved at 70 min (PC) for Zn(II) ions. These findings are in agreement with the examination of other researchers for the removal of Zn(II) ions by eggshell and neem leaf, etc (Senthil Kumar et al. 2012).

Adsorption isotherm

Adsorption isotherms were applied to various models such as Langmuir, Freundlich, and Temkin to determine the feasibility of the adsorption system. Nonlinear regression analysis was performed by applying the experimental data (Ce and qe) to the isotherm models using Origin 2017 software. The constant parameters, correlation coefficients (R²), Sum of Error Squared (SSE), and the Root Mean Square Error (RMSE) are tabulated in Table 3. Based on the results attained from aforementioned analysis, suitable adsorption isotherm model was chosen based on the higher correlation coefficient (R²) and low error values. The Langmuir isotherm model is given by Equation (3):

\[
q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}
\]

(3)

Table 3 | Isotherm parameters for the removal of Zn(II) by PC, and LG

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Piaropus Crassipes (PC)</th>
<th>Lemna gibba (LG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>q_m (mg/g)</td>
<td>43</td>
<td>28.15</td>
</tr>
<tr>
<td></td>
<td>K_L (L/mg)</td>
<td>3.90</td>
<td>8.67</td>
</tr>
<tr>
<td></td>
<td>R_L</td>
<td>4 × 10^{-3}</td>
<td>2 × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K_f (mg^{1-1/n}/g)</td>
<td>4.33</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>n (g/L)</td>
<td>1.81</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>0.07</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.13</td>
<td>0.31</td>
</tr>
<tr>
<td>Temkin</td>
<td>A (L/g)</td>
<td>41.22</td>
<td>31.89</td>
</tr>
<tr>
<td></td>
<td>B (l/mol)</td>
<td>14.9</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>1.18</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.62</td>
<td>0.60</td>
</tr>
</tbody>
</table>
where, $q_m$ (mg/g) is adsorption capacity, and $K_L$ (L/mg) is Langmuir constant related to the rate of adsorption. The value of $q_m$ (mg/g), $K_L$ (L/mg), is estimated from the plot $C_e$ vs. $q_e$. The Freundlich model (multilayer adsorption process) is expressed by Equation (4):

Freundlich isotherm: $q_e = K_F(C_e)^{1/n}$

where, $K_F$ (mg$^{1-1/n}$/g), and $1/n_F$ (g/L) are Freundlich constants that corresponds to binding energy, and measure of deviation from linearity. The value of ‘$n$’ is used to assess whether the adsorption process is linear ($n = 1$), physical ($n > 1$), or chemical ($n < 1$) in nature. The plot between $C_e$ vs. $q_e$ using Equation (4) predicts the value of $K_F$ and $n_F$, respectively. The Temkin model is represented by Equation (5):

Temkin isotherm: $q_e = B \ln K_T + B \ln C_e$

where, $B$ is Temkin constant presented as the heat of adsorption (J/mol), and $A_T$ is the adsorption isotherm constant (L/g). The graphical representation of the isotherm plots was presented in Figure 4(a) and 4(b), respectively.

As presented in Table 3, Langmuir isotherm correlation coefficient ($R^2$) values for the PC fitted well ($R^2 = 0.99$) followed by LG ($R^2 = 0.97$) for Zn(II) ion. The maximum adsorption capacity, $q_m$ (mg/g) was found to be 43 mg/g and 28.15 mg/g, respectively. The $n$ value of Freundlich adsorption was found to be 1.81 (PC), and 2.2 (LG) for Zn(II) ions, respectively. Since the $n$ value lies between 1 and 10, it indicates that the adsorption of Zn(II) ions onto the PC and LG is a physical process. The values of the Temkin plot determined as: $A_T = 41.22$ (PC), and 31.89 (LG) L/g, B = 14.9 (PC), and 11.6 (LG) J/mol indicates the heat of sorption is physical process. Based on the experimental results, Langmuir model provides higher regression coefficient ($R^2 = 0.99, 0.97$) with low error values (SSE = 0.01, 0.03) than other models discussed. Hence, it is clear that Langmuir isotherm model gives best fit to the experimental data, implies monolayer adsorption takes place on the surface of PC, and LG.

Table 4 shows the comparison between different adsorbents applied for Zn(II) adsorption in terms of the maximum adsorption capacity ($q_m$). As shown in Table 4, the $q_m$ value for PC and LG was found to be 43 mg/g and 28.15 mg/g which is good, and comparatively higher as compared to the other adsorbents presented in the literature.

![Figure 4](image_url) | Adsorption isotherm plots on the adsorption of Zn(II) by (a) PC, (b) LG.
Adsorption kinetics

The adsorption kinetics for the removal of Zn(II) ions from the aqueous solution was carried out to determine the reaction rate and controlling mechanism of the adsorption process. In this study, adsorption of Zn(II) ions onto the adsorbents (PC and LG) was studied by using various kinetic models, such as pseudo-first order, pseudo-second order, and intraparticle model. The adsorption kinetic parameters, correlation coefficient values ($R^2$) and sum of error squared (SSE), and the root mean square error (RMSE) are listed in Table 5 and plotted in Figure 5(a) and 5(b), respectively. The pseudo-first-order model is given by Equation (6):

$$q_t = q_e(1 - \exp(-k_1t))$$  \hspace{1cm} (6)

where, $q_e$ and $q_t$ are the amounts of Zn(II) ions adsorbed at equilibrium (mg/L), and at time $t$ (min). $k_1$ ((1/min) is the adsorption rate constant. Pseudo-second order equation is represented as in Equation (7):

$$q_t = \frac{q_e^2k_2t}{1 + q_ek_2t}$$  \hspace{1cm} (7)

where, $k_2$ (gmg$^{-1}$/min) is the rate constant of second order adsorption. The intraparticle diffusion model is given by Equation (8):

$$q_t = kp t^{1/2} + C$$  \hspace{1cm} (8)

| Table 4 | Comparative studies on the adsorption capacity of Zn(II) onto different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piaropus crassipes (PC)</td>
<td>43</td>
<td>Present work</td>
</tr>
<tr>
<td>Lemna gibba (LG)</td>
<td>28.15</td>
<td>Present work</td>
</tr>
<tr>
<td>Red algae</td>
<td>18.51</td>
<td>Anilkumar et al. (2016)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>20.52</td>
<td>Kouakou et al. (2013)</td>
</tr>
<tr>
<td>Xanthate modified magnetic chitosan</td>
<td>20.8</td>
<td>Zhu et al. (2012)</td>
</tr>
</tbody>
</table>

| Table 5 | Parameters of kinetic models for the adsorption of Zn(II) by PC and LG

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Piaropus Crassipes (PC)</th>
<th>Lemna gibba (LG)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>3.80</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>$k_2 \times 10^{-3}$</td>
<td>2.50</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.87</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>63.3</td>
<td>132.1</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>2.16</td>
<td>3.09</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>$k_2 \times 10^{-3}$</td>
<td>2.50</td>
<td>6.80</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>38.9</td>
<td>37.2</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (exp) (mg/g)</td>
<td>38.6</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>11.57</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Intra particle diffusion</td>
<td>$k_p \times 10^{-3}$</td>
<td>2.10</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.90</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.85</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>SSE</td>
<td>1.626</td>
<td>1.829</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>10.16</td>
<td>11.93</td>
</tr>
</tbody>
</table>
where, $k_p$ is the intraparticle diffusion rate constant (mg/gmin$^{0.5}$), $t$ is the time (min), and $C$ is the constant. The best fitted kinetic model was identified based on the comparison between the calculated ($q_e$ (cal)), and experimental ($q_e$ (exp)) adsorption capacity, and correlation coefficients ($R^2$). From the experimental results, it is evident that the pseudo-first-order model predicts a low value for the calculated adsorption capacity than the experimental value, making the model unsuitable. Conversely, Table 5 shows that the pseudo-second order model has higher correlation coefficient values ($R^2 = 0.99$, and 0.99 for PC and LG), and low error values (SSE = 11.57, RMSE = 0.90, and SSE = 12.20, RMSE = 0.90 for PC and LG) when compared to other models. This suggests that the adsorption of Zn (II) ions onto the adsorbent (PC and LG) is fitted well with pseudo-second order model. It is also inferred that the adsorption process is controlled by chemisorption model.

The intraparticle diffusion model was plotted to see the influence of mass transfer resistance for the binding of Zn(II) ions to PC and LG. Due to unreliable range in adsorption process in the initial and final stages, dual nature is observed in the adsorption process. During the initial periods, the Zn(II) removal was due to the frontier layer diffusion whereas, part particle diffusion occurs in the latter part. As seen from Figure 5(a) and 5(b), the diffusion part plot does not pass through the origin, indicating that intraparticle diffusion is not the only rate-limiting step but there are other processes that operates parallelly.

**Thermodynamic study**

The thermodynamic study on the adsorption of Zn (II) ions onto PC and LG were investigated by using thermodynamic parameters such as enthalpy $\Delta H^o$, entropy $\Delta S^o$, and free energy $\Delta G^o$. These parameters were calculated by using the following Equations (9) and (10), respectively.

$$\Delta G^o = -RT \ln k_c$$  \hspace{1cm} (9)

$$\log k_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$$  \hspace{1cm} (10)

where, $k_c$ is equilibrium constant, $R$ is the universal gas constant (8.314 J/K/mol), $T$ is temperature(K). The value of $\Delta S^o$, and $\Delta H^o$ was calculated from the slope and intercept of the linear plot ($1/T$ vs $\ln k_c$), respectively. The thermodynamic parameters

![Figure 5](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.471/954189/wst2021471.pdf)
are determined from Figure 6, and the values are listed in Table 6. As represented in Table 6, during the adsorption of Zn(II), the change in entropy ($\Delta S^\circ$) depicts the randomness at PC, and LG interface.

As seen from the Table 6, the value of Gibbs free energy ($\Delta G^\circ$) is small, and negative values for all the investigated temperatures for the adsorption of Zn(II) on nanoparticles indicate that the process is spontaneous, and feasible. Similarly, the negative values of $\Delta G^\circ$ increased with a decrease in temperature designate that the adsorption process is much favourable at a low temperature. The negative value of entropy, and enthalpy determined the adsorption between metal ion, and adsorbent is exothermic due to the weak force of attraction between the Zn (II) and nano adsorbent.

**Plausible mechanism of Zn(II) ions onto PC and LG**

The synthesized nanoparticles PC and LG posed various functional groups such as carbonyl, hydroxyl, silicate and so on, which in turn provided an active binding site for the adsorption of Zn(II) ions. The availability of many active binding sites on the surface of the nanoparticles, and affinity of the pollutant onto the nanoparticle surface along with various functional groups exhibit an acceptor-donor interaction with Zn(II) ions. It would affect the adsorption process. The adsorption of PC/LG for Zn(II) adsorption is a combination of physical adsorption on the surface, ion exchange, surface complexation mechanism, intraparticle diffusion, and greatly influenced by pH.

Based on the Surface Complexation Model (SCM), cations with the hydroxyl group on the surface of PC and LG could create a surface complex mechanism. PC/LG is the symbol of adsorbent hydroxyl surface. Also, the adsorption of Zn(II) ions results in the development of more than one kind of surface complex mechanism. The mechanism can be deduced as follows in Equations (11) and (12), respectively.

\[
\begin{align*}
\text{PC}/\text{LG} - \text{OH} + \text{Zn}^{2+} &\leftrightarrow (\text{PC}/\text{LG})\cdot\text{Zn}^{2+} + \text{H}^+ \\
\text{PC}/\text{LG} - \text{OH} + \text{Zn}^{2+} + \text{H}_2\text{O} &\leftrightarrow [\text{PC}/\text{LG} - \text{ZnO}^+] + 2\text{H}^+ \\
\end{align*}
\]

Generally, pH influences the sorbent surface charge. As a result of increased pH, less competition from protons to reaction sites increased the concentration of Zn(OH)$^+$ species, and therefore a large amount of Zn(II) ions was observed up to pH 5.5.

![Figure 6](image)

**Figure 6** | Thermodynamic Plot on the Adsorption of Zn(II) by PC and LG.

**Table 6** | Thermodynamic results for the removal of Zn(II) ions by PC and LG

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\Delta S^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>Zn(II) -PC</td>
<td>$-27$</td>
<td>$-63$</td>
<td>$-9$</td>
</tr>
<tr>
<td>Zn(II) -LG</td>
<td>$-17$</td>
<td>$-32$</td>
<td>$-7.4$</td>
</tr>
</tbody>
</table>
The total adsorption density of Zn(II) ions is a sum of surface concentrations of $[\text{PC/LG}^-\text{O}^-\text{Zn}^{2+}]$ and $[\text{PC/LG}^-\text{O}^-\text{ZnOH}^+]$. Also, $[\text{PC/LG}^-\text{O}^-\text{ZnOH}^+]$ was predominant on Zn$^{2+}$ surface species for the pH value $\geq 5$.

**Regeneration studies**

The removal efficiency of Zn(II) decreased with increase in the number of reuses owing to the adsorption sites on the fact that surface of the PC/LG are gradually occupied by Zn(II) ions. However, the PC still had a high regeneration capacity after three adsorption–desorption cycles, which indicates that PC is a promising adsorbent than LG. However, the PC still had a high regeneration capacity after three adsorption–desorption cycles, indicating that PC is a promising adsorbent than LG.

**Figure 7** | Plausible mechanism for the adsorption of Zn(II) by PC and LG.

**Figure 8** | Regeneration study for the adsorption of Zn(II) PC and LG.
Cost estimation for the production of nanoparticles (PC and LG)

Cost analysis is an important factor that implies the successful implementation of the process in the application part. The availability and production at an affordable cost determine the successful operation of any treatment process. In the present study, the cost analysis for the production of PC and LG was evaluated. Cost analysis includes various parameters such as raw material collection, cleaning, drying, and sol-gel treatment. The step-wise cost estimation for 1 kg of the sample (PC/LG) is as follows:

1. Raw material cost = 0.0 INR (raw material is collected from local ponds).
2. Washing (tap + distilled water) and drying = 1.35 INR (The raw material is washed using distilled water prepared from laboratory set up. For the drying process, the cost consumption for 1 unit is 0.3 kWh x 4.5 INR = 1.35 INR).
3. Sol-gel treatment (10 mL ethanol, 2.5 mL NaOH, 10 mL TEOS) = 22 INR.
4. Crushing = 0 INR (manually done using mortar and pestle).
5. Calcination (0.7 kWh x 4.5 INR) = 3.15 INR.

The total cost can be determined by the sum of the cost comprised from steps 1 to 5. The overhead charges will be added for the commercial operation. Hence, the cumulative cost for producing 1 kg of nanoparticles (PC/LG) was found to be 31.80 INR [26.50 INR (Material processing cost) 5.30INR (overhead charges)]. Thus, the overall estimated cost in the production of PC/LG indicates that nanoparticles prepared from waste aquatic plants are very cheap and profitable. Also, the cost was found to be substantially very low compared to other products prepared from tea waste and bio-char, respectively (Banerjee et al. 2016).

CONCLUSION AND FUTURE PERSPECTIVES

In the present study, the reported work highlighted utilization of aquatic weeds (PC, LM) as nano adsorbent by a simple, efficient technique. Systematic characterization of PC/LG revealed its morphological character, surface area, and nanoscale dimension (30 nm). The zeta potential measurements showed that the point of zero charge (pH_Pzc) of PC, and LG was 7.20, and 8.10, respectively. The effects of pH, adsorbent dosage, initial Zn(II) concentration, and contact time on the Zn(II) adsorption were precisely investigated. Maximum percentage removal (97%) was obtained at the optimum condition of pH (5.2), adsorbent dosage (2 g/L), initial concentration (20 mg/L), and time (70 min) for Zn(II) ions removal by PC. Similarly, 94% removal was achieved by 20 mg/L of Zn(II) by utilizing 2 g/L of LG in 80 min at 5.6 pH, respectively. The Zn (II) adsorption onto PC, and LG indicate a reasonable fit to the isotherm models such as Langmuir, Freundlich, and Temkin. The fitting of Langmuir adsorption isotherm indicates that the adsorption sites were consistent with monolayer adsorption coverage. Kinetic study fits well with pseudo second-order model. This suggests adsorption process is chemisorption in nature. The thermodynamic study revealed that the adsorption process is spontaneous, and exothermic. The adsorption mechanisms could be determined as the combination of diffusion, ion-exchange, surface complexation, and precipitation between Zn(II) and the functional groups on PC/LG, respectively. Moreover, the nano adsorbents could regain the adsorption property for three cycles towards Zn(II) ions.

Based on the exploration of experimental findings, PC and LG can be utilized as highly efficient adsorbents for the removal of heavy metals from wastewater. In addition, this study provides a useful tool for future study combined with utilization of waste materials for heavy metal removal. Also, it aids in planning wastewater treatment framework for the harmful metal removal in a cost-effective manner, and assist in reducing the negative effects on water quality. Therefore, it can be concluded that, an integrated approach of nanotechnology and waste management can be coupled for wastewater treatment, which in turn opens a new venture in the environmental pollution in near future.

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CONFLICT OF INTEREST

We declare that there is no conflict of interest concerning this publication.
DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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