Nano-chamomile Waste as a Low-cost Biosorbent for Rapid Removal of Heavy Metal Ions from Natural Water Samples

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Introduction

In recent years, nano-particle materials have been investigated for their potential as adsorbents. Their smaller size increases the surface area, which in turn increases their chemical activity for adsorption and confers remarkable capacities to take up many pollutants [1,2]. Water pollution caused by various heavy metal ions is a worldwide environmental problem. Heavy metals are not easily biodegradable or decomposable and even their trace amounts exert highly toxic effects to human, plants, and animals [3,4]. In order to achieve efficient removal of these pollutants from wastewater, nanoparticle adsorbents are becoming new alternatives for their treatment [5,6]. There are several methods available to detect trace metal ions such as chemical precipitation/co-precipitation [7], liquid-liquid extraction [8], and solid phase extraction (SPE) [9]. SPE has been considered as the most efficient technique compared with the others for its simplicity, economics, rapidity, and consumption of small volume of reagents. It is indispensable to find new sorbents to improve analytical sensitivity, affinity, capacity and precision in the SPE procedure. The main characteristics of an effective material to work as SP extractor are as follows: it should be stable and have an insoluble porous matrix.

In this study, we report the feasibility of using nano chamomile waste (NCW) as a selective solid phase extractor for heavy metal ions. The experimental parameters including pH (1.0–6.0), metal ion concentration (10–100 µmole), adsorbent dose (10–1000 mg), and biosorption time (0.5–90 min) were altered by using the batch technique to optimize the maximum capacity of this new biosorbent. The experimental data by NCW agreed with both Freundlich and Langmuir models ($R^2 = 0.999$) with maximum uptake capacities of 621.6 mg g$^{-1}$ (3 mmolg$^{-1}$) for Pb (II), 163.9 mg g$^{-1}$ (2.58 mmolg$^{-1}$) for Cu (II), and 522.7 mg g$^{-1}$ (9.36 mmolg$^{-1}$) for Fe (III). In addition, the values of metal uptake as a function of time agreed with the kinetic pseudo-second-order model. The kinetic experiments confirmed the fast accessibility of metal ions to the biosorbent surface resulting in equilibrium within 30 s. NCW was also characterized using FT-IR spectra and the crystallinity of the biosorbent was characterized using X-ray diffraction (XRD). The morphological characterization and particle size of NCW were obtained using SEM and TEM, respectively. Our method was investigated to measure Pb (II), Cu (II), and Fe (III) with a certain spiked amounts in natural water samples such as groundwater (GW), drinking tap water (DTW), natural drinking water (NDW), Nile River water (NRW), seawater (SW), and wastewater (WW). A removal efficiency of $\geq 98\%$ was obtained for all collected samples using batch experiments and without matrix interferences. Considering its cheap source, simple, economic and fast uptake process, NCW can be used as a low-cost nano biosorbent for the removal of metal ions from natural water samples.

Keywords: Nano chamomile waste, Heavy metal removal, Natural water samples, Adsorption isotherms, Kinetic studies, Biosorbance.
with proper active groups, it should behave like a typical chelating and inorganic ligand, which can selectively bind to the analytes, should also have a large adsorption capacity, good regenerability, and an active surface area. So far, only agricultural waste biomass has been used for biosorption procedure.

To understand the adsorption mechanism of metal ions process on the different adsorbents, it is an important issue to study their adsorption isotherm. From the adsorption isotherm equations, one can deduce some crucial information through the adsorption parameters interpretation. The Langmuir and Freundlich adsorption isotherms are the most well-known models which can be used in the interpretation of the adsorption mechanism. The molecular distribution of the adsorbed molecules on the adsorbent interface would be effectively described from the adsorption isotherm output.[10]

The use of waste materials is attractive because it helps in reducing the cost of waste disposal and minimizing the waste. These agricultural wastes include the shells and/or stones of fruits like coconut [11–13], peanuts [14], walnut [15], cashew [16,17]; fruit peels of orange [18,19], pomelo [20], citrus [21], banana [22]; rice husk [23–25]; and sugar cane bagasse [26]. These agricultural waste as adsorbents have been explored in SPE as low-cost nanometer-sized materials [27,28]. These adsorbents are normally modified by immobilizing organic and inorganic groups to their surfaces [14]. The functional materials obtained thus can effectively remove certain toxic metals from aqueous media. However, these modifications are usually time-consuming and most of these nano-adsorbents usually require an expensive mechanical grinder to obtain their particles in nanometer size [15,29]. Thus, the development of a new adsorbent is essential with a large adsorbent surface area and high uptake capacity using in a simple, fast and inexpensive method to overcome these limitations.

In this study we’ve used nano-chamomile waste (NCW) as a selective solid phase extractor for removing some heavy metal ions i.e. Pb (II), Cu (II), and Fe (III) from different environmental water samples, via solid phase extraction method, under optimized conditions of pH, metal concentration, biosorbent dose, and adsorption time. The target samples have been examined using different adsorption isothermal models and the kinetics of the reactions have been studied as well. The overall study develops an environment-friendly and low-cost biomass technique.

**Experimental**

Reagents and materials

The metal salts ferric chloride hexahydrate \((\text{FeCl}_3 \cdot 6\text{H}_2\text{O})\), copper chloride dihydrate \((\text{CuCl}_2 \cdot 2\text{H}_2\text{O})\) and lead acetate trihydrate \((\text{Pb(CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O})\) were purchased from BDH (England) and Aldrich (USA). HCl, NaOH, and EDTA (ethylenediaminetetraacetic acid disodium salt dihydrate) were obtained from Merck (Germany). The natural groundwater (GW) and drinking tap water (DTW) were collected from Minia city, Egypt. The natural drinking-water (NDW) had the following parameters: total dissolved salts (TDS) expressed as \(\text{GW}_1\), \(\text{GW}_2\), \(\text{DTW}_1\) and \(\text{DTW}_2\), as 3090, 338, 177, 260 mg/L, respectively. The water samples from Nile River (NRW) were collected from Minia city, Egypt; wastewater (WW) was taken from Abu Korkas sugar Factory, Minia, Egypt; seawater (SW) was collected at Alexandria City, Egypt.

**Apparatus**

The functional groups of biosorbent before and after the metal ions biosorption were studied using FT-IR spectrophotometer model 410 JASCO (Japan). The pH values were measured using a Metrohm pH meter model 691. The morphological characterization of NCW was carried out using a scanning electron microscope (SEM) model JSM–5400 LV JEOL (Japan). NCW particle size was determined using a transmission electron microscope (TEM) model JEM100CXII JEOL (Japan). The crystallinity of the nanobiosorbent was recorded using a JEOL X-ray diffractometer (XRD) model JSX–60PA (Japan). The shaking was carried out using Gesellschaft Fur Labortechnehnik (GFL) model 3018. An atomic absorption spectrophotometer (AAS) supplied by Scientific Equipment PTY LTD (GBC) Model 902 was used to estimate the concentration of the metal ions.

Treatment of chamomile waste
The chamomile was purchased from the local market from Minia city, Egypt and its waste was collected after boiling it at least two times, then washed with double distilled water several times, filtered, and air dried. The dried chamomile waste was ground in a domestic mill and sieved until a powder form was obtained. If large particles were observed, it was ground again and sieved. Then it was dried well in an oven at 60 °C for 1 h, kept in closed glass bottles until utilization. The practical size of the powdered material was in the range of 20.6–28.3 nm measured by TEM.

Batch technique

The capacity of the new biosorbent to take up Pb (II), Cu (II) and Fe (III) ions from the different aqueous solutions was estimated using the batch technique. Typically, 10 mg of NCW was added to 0.5 mL of 0.1 M metal solution and final volume to 50.0 mL was made by DDW and pH adjusted by 0.1 M HCl or 0.1 M NaOH. Then mechanically shaken for 30 min in a 100 mL measuring flask at room temperature to get an equilibrium. After the equilibrium, the mixture was filtered, washed with double distilled water, and the residual metal ions in the filtrate were determined by complexometric EDTA titration using an appropriate indicator for each metal ion. The effects of metal ion concentration, biosorbent dose, and shaking time were monitored and evaluated by the same batch method. The metal uptake capacities were calculated using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W}$$  \hspace{1cm} (1)

$C_0$: initial concentrations of metal ion in mmol/L, $C_e$: concentration of the unsorbed metal ion in the filtrate in mmol/L of, $W$: mass of biosorbent waste in g, $q_e$: adsorption amount per unit gram of the adsorbent at equilibrium (mmol/g) and $V$: volume of the solution (L).

Adsorption isotherms models

Adsorption isotherm experiments were carried out by adding a fixed amount of NCW (20 mg L$^{-1}$) to a series of metal ions concentrations (0.2g L$^{-1}$) at pH 5.5 for Pb (II), 6.0 for Cu (II), and 3.3 for Fe (III) ions which chosen as an optimum pH values. The samples were shaken for 30 sec. in a mechanically shaker. The filtrate was carefully collected and quantified by complexometric EDTA titration and/or AAS. The amounts of adsorption at equilibrium, $q_e$(mmol/g) were calculated from Eq. (1).

Adsorption kinetics

Adsorption kinetics of Pb (II), Cu (II) and Fe (III) on NCW performed with an initial concentration of 0.04 mol/L$^{-1}$. Basically, the adsorption kinetic experiments were identical to those of isotherm experiments. At various time intervals from 0.5 to 90 min, the solid NCW was filtrated, while the concentration of metal ions remains in the filtrate was determined by the same batch method mentioned above. The amount of adsorbate adsorbed $q_e$(mmol/g) at time t (min) was calculated from Eq. (2)

$$q_t = \frac{(C_0 - C_t)V}{W}$$  \hspace{1cm} (2)

$q_e$: metal ions adsorbed at time t (mg/g), $C_t$: solution concentrations at time t, V: volume of the liquid phase (L).

Results and Discussion

Characterization of the biosorbent

SEM is an important tool for determining the morphology of the biosorbent surface. Figure 1 shows the differences in the morphological surface of nano-chamomile waste before and after the metal ions uptake. The SEM images before the metal ions biosorption show large separate particles with little fibers, whereas the merged particles with clear and more fibers were observed after the biosorption of metal ions. The differences in the structure of the biosorbent support the biosorption of the selected metal ions on their surfaces. The TEM analysis indicated that NCW particle size is in the range 20.6 to 28.3 nm (Fig. 2). The X-ray diffraction (XRD) analysis of NCW indicated that the bands of NCW were broad[31] confirming an amorphous surface of the biosorbent (Fig. 3a). After biosorption of Pb (II), for example, the intensity of the bands increased as shown in Figure 3b.

Nano-chamomile waste is rich in phenolic compounds[30] as shown in scheme 1. Gallic acid is a natural phenolic compound widely present in plants (which is the main compound acting as a multidentate ligand with high affinity to metal ions, thus making the plant materials suitable to be used as biosorbents) [32,33]. The main functional groups are C=O, COO, C–O, and O–H, which are responsible for metal adsorption from a solution as confirmed by FT-IR analysis.

The FT-IR spectra of NCW before and after the metal ions biosorption were recorded to measure the vibration frequency changes in these functional groups in the range of 4000–400 cm$^{-1}$.
as shown in Fig. 4. The assignment determination supports the complex nature of the observed biosorbent with the target metal ions. NCW before metal ion biosorption showed an absorption band around 3422.57 cm\(^{-1}\) representing the presence of free–OH and stretching of hydroxyl groups. The bands at 2923.03 cm\(^{-1}\) and 2853.43 cm\(^{-1}\) were attributed to the antisymmetric and symmetric stretching of \(-\text{CH}_2–\) bond of methylene groups and \(-\text{CH}–\) bond of a methyl group, respectively [33]. A sharp band near 1756.32 cm\(^{-1}\) and a strong band near 1635.68 cm\(^{-1}\) were attributed to \(\text{C}=\text{O}\) stretching of carboxylic acid [34,35]. The band observed at 1550.44 cm\(^{-1}\) was due to \(\text{C}–\text{OH}\) stretching vibration [17]. The sharp bands at 1517.62 cm\(^{-1}\) and 1428.16 cm\(^{-1}\) were attributed to aromatic \(\text{C}=\text{C}\) ring structure [36]. Several peaks ranging from 1383.99 to 1034.76 cm\(^{-1}\) may refer to \(\text{C}–\text{O}\) bonding of phenols and aliphatic and aromatic \(\text{C}–\text{H}\) group [24,37–39]. This splitting pattern is characteristic of several different \(\text{C}–\text{O}\) bonding due to different phenols and confirms that chamomile is rich in tannins and gallic acid [32]. An obvious color change was observed after metal ions biosorption by NCW biosorbent due to the complex formation or ion exchange mechanism. For example, the color change of NCW from pale brown to blue and deep brown can be ascribed to the biosorption of Cu (II) and Fe (III), respectively. On the basis of these results, it can be suggested that the metallic ions would bind to NCW biosorbent by an interaction with the active OH of phenolic groups and COOH of carboxylic acids. The presence of active groups (i.e., –OH and \(\text{C}=\text{O}\)) also emphasizes the presence of carboxylic groups. On the other hand, by comparing the FT-IR spectra of NCW biosorbent before and after Pb (II) biosorption, it was clearly demonstrated that the carboxyl \(-\text{COOH}\) and phenolic \(-\text{OH}\) groups were affected after the ion uptake as manifested by shifts in their absorption peaks from 1034.76, 1635.68, 1726.32 and 3422.57 cm\(^{-1}\) to 1036.58, 1634.34, 1731.85 and 3425.53 cm\(^{-1}\) for \(\nu (-\text{C}-\text{O}-)\), \(\nu (-\text{C}=\text{O}-)\), \(\nu(-\text{COOH})\) and

Fig. 1. SEM images of (a) bare NCW, and (b, c, d) NCW after Pb (II), Cu (II) and Fe (III) biosorption, respectively.

Fig. 2. TEM analysis of NCW biosorbent.

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Fig. 3. X-ray diffraction of (a) bare NCW before and (b) after Pb (II) biosorption.

Fig. 4. FTIR spectra of (a) bare NCW and (b, c, d) NCW after Pb (II), Cu (II) and Fe (III) biosorption, respectively.

TABLE 1. Fundamental FT-IR bands for a NCW sample before and after metal ions biosorption

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Band position (cm⁻¹)</th>
<th>Fe (III)</th>
<th>Cu (II)</th>
<th>Pb (II)</th>
<th>Before biosorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretch, H bonded, alcohol, phenol</td>
<td></td>
<td>3418.63</td>
<td>3420.28</td>
<td>3425.54</td>
<td>3422.57</td>
</tr>
<tr>
<td>C–H stretching vibrations of–CH₂ and –CH₃ functional group</td>
<td>2922.92</td>
<td>2922.48</td>
<td>2922.22</td>
<td></td>
<td>2923.03</td>
</tr>
<tr>
<td>C=O stretch of carbonyl</td>
<td>1731.43</td>
<td>1732.57</td>
<td>1731.85</td>
<td>1726.33</td>
<td>1726.33</td>
</tr>
<tr>
<td>C=O stretching of carboxylate ion</td>
<td>1636.21</td>
<td>1633.56</td>
<td>1634.34</td>
<td>1631.68</td>
<td>1631.68</td>
</tr>
<tr>
<td>C–OH stretching vibration</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1551.44</td>
</tr>
<tr>
<td>C=C ring stretch aromatic</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1517.62</td>
</tr>
<tr>
<td>C–C stretch (in ring), aromatics</td>
<td>1427.09</td>
<td>1425.48</td>
<td>1425.72</td>
<td>1428.16</td>
<td></td>
</tr>
<tr>
<td>C-H aromatic and carboxyl-carbonate structure</td>
<td>1377.06</td>
<td>1378.58</td>
<td>-</td>
<td>1383.99</td>
<td></td>
</tr>
<tr>
<td>C–H aliphatic –CH₃ or –CH₂</td>
<td>1322.10</td>
<td>1321.79</td>
<td>1322.50</td>
<td>1321.34</td>
<td></td>
</tr>
<tr>
<td>C=O stretch of carboxylate group</td>
<td>1248.65</td>
<td>1250.05</td>
<td>1250.05</td>
<td>1253.00</td>
<td></td>
</tr>
<tr>
<td>C–OH stretching of phenol</td>
<td>1159.05–1034.63</td>
<td>1158.65–1035.14</td>
<td>1158.40–1036.58</td>
<td>1158.23–1034.76</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 1. Structures of organic compounds found in studied waste (NCW)
NANO-CHAMOMILE WASTE AS A LOW-COST BIOSORBENT FOR RAPID ...

Equilibration studies of nano-chamomile waste for uptake of Pb (II), Cu (II) and Fe (III) as a function of pH, biosorbent dose, and contact time

The removal of heavy metal ions from the different aqueous waste solutions by NCW is pH dependent as shown in Fig. 5. The uptake was quite weak at lower pH. In such an environment, the surface area of biosorbent was more protonated and the arrival of positive metal ions was hampered because of repulsive forces. In addition to this, a competitive adsorption appeared between H\(^+\) and metal cations toward the negative active sites on NCW surface. An increasing pH enhanced negative charges on the NCW surface and so the adsorption due to the high electrostatic attraction between the negatively charged surface of NCW and metal cations. The metal uptake capacities increased with an increasing pH and reached the maximum level at pH 5.5 for Pb (II), 6.0 for Cu (II) and 3.3 for Fe (III). At pH values higher than 5.5, 6.0, and 3.3 for Pb (II), Cu (II) and Fe (III), respectively, a transformation to M(OH) or precipitation as M(OH)\(_2\) occurs [27,40]. Therefore, pH 5.5 for Pb (II), 6.0 for Cu (II), and 3.3 for Fe (III) ions were chosen as optimum pH values. At these pH values, the maximum uptake of Pb (II), Cu (II) and Fe (III) was found to be 1.57 mmol g\(^{-1}\), 1.7 mmol g\(^{-1}\), and 1.3 mmol g\(^{-1}\), respectively.

The NCW dose was also observed to be an important parameter for the quantitative removal of metals from wastewater. In the experiment, 10.0 to 1000 mg of NCW was added to 1.0 mL of 0.1 M of the metal solution and final volume was made to 50.0 mL by DDW. The pH was adjusted to the optimum value for each metal and then the solution was shaken for 30 min. The biosorbent dose versus metal uptake capacity was plotted (Fig. 6). As can be seen from the plot, with an increasing biosorbent dose, the uptake capacities of Pb (II), Cu (II) and Fe (III) were decreased. When the weight of the biosorbent was increased from 10 to 1000 mg, the capacities were decreased from 2.0 to 0.099, 2.15 to 0.093, and 2.1 to 0.09 mmol g\(^{-1}\) for Pb (II), Cu (II) and Fe (III), respectively.

The effect of contact time was studied to determine the optimum time for the maximum metal uptake capacity of NCW. In a set of experiment, 10 mg of NCW was added to 1 mL of 0.1 M metal solution and a final volume of 50.0 mL was made by DDW. The optimum pH value...
Fig. 5. Effect of pH on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).

Fig. 6. Effect of weight on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).
Fig. 7. Effect of contact time on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).

Fig. 8. Pseudo-second-order kinetic model for Pb (II), Cu (II), and Fe (III) adsorption on NCW.
for each metal ion was set by HCl or NaOH. The resultant solutions were mechanically shaken for 0.5, 1, 2, 5, 10, 20, 30, 45, 60 and 90 min at room temperature to get an equilibrium. The plot of metal ion adsorbing capacities of NCW versus time showed that the adsorption process was very rapid for all metals and attained the equilibrium in just 30 s of contact (Fig. 7). These extremely rapid adsorption rates emphasize an easy interaction and accessibility of the available binding sites by the metal ions in a short time. It is easy to spot that the metal ion biosorption on the NCW is very quick. Therefore, the optimum equilibrium time was taken as 30 s in the further batch experiments.

**Adsorption isotherms**

The equilibrium adsorption and the adsorption efficacy of NCW biosorbent for metals adsorption were determined by the adsorption isotherms. An equilibrium was achieved when the adsorbate concentration in the solution was in an equilibrium with the adsorbent concentration. The isotherm adsorption constants indicate the affinity of the NCW biosorbent surface toward metal ions. An adsorption isotherm analysis also gives information on the pathways of adsorption reaction [37,41,42]. In the current study, , Langmuir and Freundlich models are applied to determine the adsorption equilibrium between NCW as biosorbent and Pb (II), Cu (II), and Fe (III) metal ions in the target water samples. Table 2 illustrates the adsorption constants values of the two models via the linear regression analysis.

**Freundlich isotherm**

The Freundlich model was employed to describe that the metal ions were adsorbed on the heterogeneous biosorbent surfaces and there was an interaction among the adsorbed molecules [43-45]. The simple form of the Freundlich model (Eq. 3) is described by:

\[ q_e = k_f \cdot C_e^{1/n} \]  
(exponential form)  (3)

where \( k_f \), \( 1/n \), \( C_e \) and \( q_e \) are the constants attributed to adsorption capacity and intensity, the equilibrium concentration of the solution and equilibrium concentration of a solute on the surface of an adsorbent, respectively. The linear form of the Freundlich model (Eq. 4) can be expressed as:

\[ \log q_e = \log k_f + \frac{1}{n} \log C_e \]  
(linear form)   (4)

The constants \( (k_f) \) and \( (1/n) \) are the intercept and slope of the plot, respectively, between \( \log q_e \) versus \( \log C_e \). Furthermore, the Freundlich exponent \( 1/n \) indicates the favorability of biosorption. As represented in Table 2, the obtained values of \( (1/n) \) were < 1.0 indicating an efficient biosorption of metal ions onto NCWbiosorbentsurface [46]. Moreover, the correlation coefficients \( (R^2) \) values obtained from Freundlich adsorption model are in between 0.993-0.996, which indicates the validation of this adsorption model to describe the adsorption process mechanism.

**Langmuir isotherm**

The Langmuir model assumes that adsorption occurs with a mono-molecular layer arrangement onto a completely homogeneous surface and the interactions between the adsorbed molecules are negligible. The simple Langmuir [43,44,47] isotherm equation (Eq. 5) is

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \]  
(linear form)   (5)

where \( q_e \) (mmol/g) is the equilibrium adsorption capacity at the equilibrium concentration \( C_e \) (mmol/l), \( q_m \) (mmol g\(^{-1}\)) is the maximum adsorption capacity on a Langmuir monolayer and \( b \) (mlmmol\(^{-1}\)) is the Langmuir constant attributed to the energy of adsorption, and could be estimated from the intercept \( (1/q_m b) \) and slope \( (1/q_m) \) of a linear plot between

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
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<tbody>
<tr>
<td>( R^2 )</td>
<td>( 1/n )</td>
<td>( k_f )</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>0.995</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>0.993</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**TABLE 2. Langmuir and Freundlich isothermic constants for the biosorption of Pb (II), Cu (II) and Fe (III) on NCW at room temperature.**

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1/q and 1/C. The results revealed that the monolayer adsorption was the likely mechanism of metal sorption onto the NCW biosorbent and the available binding sites were fully saturated with the metal ions (Table 2). Furthermore, the correlation coefficients (R²) of NCW ranged between 0.995 - 0.998, indicating a good fit of the mono-layer Langmuir model to the adsorption of metals by NCW biosorbent. Additionally, the q max values indicate the high adsorption efficiency of NCW biosorbent due to its high surface area. In conclusion, the experimental data fitted well with Freundlich and Langmuir isotherm models both.

Kinetic Studies
The kinetic experiment provides valuable insight into the reaction pathways and gives an idea of the rate at which an adsorbent attracts adsorbates from the solution phase and eventually achieves the equilibrium. The adsorption of metals ions quickly attained an equilibrium and was stable for a long time change. Many models, namely pseudo-first- and second-order kinetic equations are used to study the adsorption mechanism. The pseudo-first-order kinetic model is known as the Lagergren equation (6).

\[
\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{6}
\]

where \( q_t \) and \( q_e \) are the metal uptake capacity at time \( t \) (min) and at an equilibrium (mmol/g), respectively, and \( k_1 \) (min⁻¹) is the constant of pseudo-first-order rate. The adsorption process does not follow pseudo-first-order because the adsorption of Cu(II), Pb(II) and Fe(III) on biosorbent (NCW) is fast and the values of adsorption uptakes \( q_t \) remained constant with changing time. The kinetics of metals adsorption on NCW is also described as pseudo-second order Eq. (7) [48]:

\[
t/q_i = 1/k_2 q_i^2 + 1/q_e t \tag{7}
\]

where \( k_2 \) (mmol⁻¹ L min⁻¹) is the constant of pseudo-second-order rate. The value of \( q_e \) and \( k_2 \) are experimentally determined from the slope and the intercept of the plot \( t/q_i \) versus \( t \). As shown in Fig. 8, a good fit (correlation coefficient \( R^2 = 0.999 \)) is obtained and the theoretical values of \( q_e \) (Theoretically) also agree with the experimental values \( q_e \) (Experimentally), indicating that the adsorption conforms to the pseudo-second-order mechanism and the adsorptions rate is controlled by chemical adsorption.

The theoretical values of \( q_e \) (Theoretically) (2.09, 2.14 and 1.90 mmol g⁻¹) agree with the experimental values \( q_e \) (Experimentally) = 2.10, 2.15 and 2.00 mmol g⁻¹ suggesting that the present adsorption system can be described more favorably by the pseudo-second-order system for nano chamomile waste (Table 3).

Comparison with various low-cost natural biosorbents
The comparison of adsorption results of NCW biosorbent with different natural biosorbents published recently in the literature for measuring of Pb (II), Cu (II), and Fe (III) is given in Table 4. This clearly indicated that NCW has higher metal uptake capacity for Pb (II), Cu (II), and Fe (III) ions as compared other natural biosorbents. The presented data showed a high adsorptive capacity with a large adsorptive surface area of the NCW for the uptake of lead, copper, and iron. Furthermore, NCW biosorbent is simple and inexpensive and prepared by a rapid method without modification and use of solvents in an eco-friendly manner.

Applications
The applicability and usefulness of this

<table>
<thead>
<tr>
<th>Second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Ions</td>
</tr>
<tr>
<td>Pb (II)</td>
</tr>
<tr>
<td>q e Theoretical (mmol/g)</td>
</tr>
<tr>
<td>k ads</td>
</tr>
<tr>
<td>q e Experimental (mmol/g)</td>
</tr>
</tbody>
</table>

0.96 0.094 972.75 0.997 9.36 0.0182 Fe (III)
TABLE 4. Comparison of NCW with other novel biosorbents as a function of metal ion uptake, contact time, pH, adsorbent dose, and modification procedures for the removal of Pb (II), Cu (II), and Fe (III) from aqueous media.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Modification procedure</th>
<th>Time needed for modification (h)</th>
<th>No. of Steps</th>
<th>Adsorbent dose (g/L)</th>
<th>pH</th>
<th>Contact time</th>
<th>Adsorption capacity (mg g(^{-1}))</th>
<th>Adsorbent</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15]</td>
<td>NaOH + Fe(_2)O(_3)</td>
<td>&gt;20 h</td>
<td>Many steps</td>
<td>2</td>
<td>5</td>
<td>4 min.</td>
<td>28.57</td>
<td>Modified walnut shell</td>
<td>Pb (II)</td>
</tr>
<tr>
<td></td>
<td>Dimethyl formamide (DMF) + tripolyphosphate (STTP)</td>
<td>24 h</td>
<td>Many steps</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>305 ±4.7</td>
<td>Triopolyphosphate modified waste Lyocell fiber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol + tetrahydrofuran (THF) + tartaric acid</td>
<td>24 h</td>
<td>Many steps</td>
<td>5</td>
<td>5</td>
<td>90 min.</td>
<td>93.45</td>
<td>Modified rice husk</td>
<td></td>
</tr>
<tr>
<td>[27]</td>
<td>NaOH + acetone + CS(_2)</td>
<td>&gt;1.5 h</td>
<td>Many steps</td>
<td>1</td>
<td>5</td>
<td>5 min.</td>
<td>531.29 ±0.28</td>
<td>Chemically modified Lyocell fiber</td>
<td></td>
</tr>
<tr>
<td>[50]</td>
<td>NaOH + H(_2)SO(_4) + CS(_2)</td>
<td>&gt;12 h</td>
<td>Many steps</td>
<td>0.8</td>
<td>4</td>
<td>5 min.</td>
<td>178.57</td>
<td>Xanthate modified apple pomace</td>
<td></td>
</tr>
<tr>
<td>[51]</td>
<td>NaOH + Fe(_3)O(_4) + Na(_2)P(_3)O(_9) (TPP) + H(_2)SO(_4) + HNO(_3)</td>
<td>24 h</td>
<td>Single step</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>16.247</td>
<td>Chemical treated olive stone</td>
<td></td>
</tr>
<tr>
<td>[52]</td>
<td>NaOH + HCl + HNO(_3)</td>
<td>12 h</td>
<td>Many steps</td>
<td>1</td>
<td>5</td>
<td>-</td>
<td>50.12</td>
<td>Treated guava bagasse</td>
<td></td>
</tr>
<tr>
<td>[53]</td>
<td>NaOH + ethanol Mercapto-acetic acid</td>
<td>&gt;24 h</td>
<td>Many steps</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>164</td>
<td>Sulfured orange peel</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>No reagent</td>
<td>-</td>
<td>Bare* NCW</td>
<td>0.2</td>
<td>5.5</td>
<td>30 sec.</td>
<td>621.6</td>
<td>Nano chamomile waste</td>
<td></td>
</tr>
<tr>
<td>[50]</td>
<td>NaOH + acetone + CS(_2)</td>
<td>&gt;1.5 h</td>
<td>Many steps</td>
<td>1</td>
<td>4</td>
<td>5 min.</td>
<td>123.08 ±0.26</td>
<td>Chemically modified Lyocell fiber</td>
<td></td>
</tr>
<tr>
<td>[55]</td>
<td>NaOH + KCl</td>
<td>&gt;12 h</td>
<td>Many steps</td>
<td>5</td>
<td>5–5.5</td>
<td>120 min.</td>
<td>59.77</td>
<td>K type orange peel</td>
<td></td>
</tr>
<tr>
<td>[55]</td>
<td>NaOH+ MgCl(_2)</td>
<td>&gt;12 h</td>
<td>Many steps</td>
<td>5</td>
<td>5–5.5</td>
<td>120 min.</td>
<td>40.37</td>
<td>Mg type orange peel</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>No reagent</td>
<td>-</td>
<td>Bare NCW</td>
<td>0.2</td>
<td>6</td>
<td>30 sec.</td>
<td>163.9</td>
<td>Nano chamomile waste</td>
<td></td>
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</table>
method were tested for removal of metals on NCW biosorbent by spiking a known amount (2.5, 2.5 and 10.0 ppm) of Pb (II), Cu (II), Fe (III) ions, respectively, in different environmental water samples (DTW, NDW, NRW, GW, WW, SW). As determined by atomic absorption spectrometry (AAS), the results confirmed an efficient removal of ≥ 98% of Pb (II), Cu (II), and Fe (III), spiked in natural water samples. Thus, this supports the validity of the procedure in removing the specific metal ions from water samples with no effect of the matrix as described in Table 5.

**Conclusion**

The present work investigated the efficiency of NCW as biosorbent for the removal of Pb (II), Cu (II) and Fe (III) ions, under optimized conditions of pH, metal concentration, biosorbent dose, and adsorption time. The adsorption process is extremely fast and attains an equilibrium within 30 s of contact between adsorbent and adsorbate. The equilibrium data comply well with the Langmuir and Freundlich models both. The equilibrium binding showed a pseudo-second-order reaction. NCW biosorbent showed a high affinity for removal of Pb (II), Cu (II), and Fe (III) comparing with other sorbents reported recently in the literature. Being a waste product, it also resolves the waste disposal problem. Further, the accuracy of NCW biosorbent was tested for removal of heavy metal ions in different environmental water samples with high removal values.

**Acknowledgements**

We wish to thank Minia University for its support and assistance in pursuing this research. We would like to express our gratitude to plant, water and soil analysis laboratory at Minia University for carrying out the atomic absorption analysis of Pb (II), Cu (II), and Fe (III).

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**TABLE 5. The removal efficiency of NCW for Pb (II), Cu (II) and Fe (III) in the spiked natural water samples by the batch technique.**

<table>
<thead>
<tr>
<th>Recovery (%)</th>
<th>Mass of the adsorbent (g)</th>
<th>Spiked (ppm)</th>
<th>Water sample</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.00 ±1</td>
<td>0.01</td>
<td>10</td>
<td>TW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>99.00 ±1</td>
<td>0.01</td>
<td>10</td>
<td>TW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>99.00 ±1</td>
<td>0.01</td>
<td>10</td>
<td>MDW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>99.00 ±1</td>
<td>0.05</td>
<td>10</td>
<td>GW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>99.00 ±1</td>
<td>0.01</td>
<td>10</td>
<td>GW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>98.00 ±1</td>
<td>1.0</td>
<td>10</td>
<td>SW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>98.00 ±1</td>
<td>1.0</td>
<td>10</td>
<td>WW</td>
<td>Pb (II)</td>
</tr>
<tr>
<td>91.00 ±3.6</td>
<td>0.1</td>
<td>2.5</td>
<td>TW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>91.00 ±3.6</td>
<td>0.1</td>
<td>2.5</td>
<td>TW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>91.00 ±3.6</td>
<td>0.05</td>
<td>2.5</td>
<td>MDW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>89.33 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>GW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>91.00 ±3.6</td>
<td>0.1</td>
<td>2.5</td>
<td>GW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>91.00 ±3.6</td>
<td>0.1</td>
<td>2.5</td>
<td>RW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>89.33 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>SW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>89.33 ±3</td>
<td>4.0</td>
<td>2.5</td>
<td>WW</td>
<td>Cu (II)</td>
</tr>
<tr>
<td>93.00 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>TW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>93.00 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>TW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>99.00 ±1</td>
<td>0.01</td>
<td>2.5</td>
<td>MDW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>89.33 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>GW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>93.00 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>GW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>93.00 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>RW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>89.33 ±3</td>
<td>0.1</td>
<td>2.5</td>
<td>SW</td>
<td>Fe (III)</td>
</tr>
<tr>
<td>87.66 ±2.5</td>
<td>4.0</td>
<td>2.5</td>
<td>WW</td>
<td>Fe (III)</td>
</tr>
</tbody>
</table>

*a average of three estimates ± standard deviation (S.D.)
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NANO-CHAMOMILE WASTE AS A LOW-COST BIOSORBENT FOR RAPID ...  

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NANO-CHAMOMILE WASTE AS A LOW-COST BIOSORBENT FOR RAPID ...  

in this work, it is proposed to use nano waste from the chamomile leaves as an effective and low-cost solid extractant for the rapid removal of metal ions from aqueous solutions. A series of tests were conducted to investigate the removal of metal ions such as Pb(II), Fe(III), and Cu(II) from aqueous solutions. The results showed that the use of this waste has a high potential for the removal of metal ions from aqueous solutions. The use of this waste as a biosorbent is also environmentally friendly due to its low cost and its ability to remove metal ions from aqueous solutions.