



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

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**I**N 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  $\mu\text{mole}$ ), 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  $621.6 \text{ mgg}^{-1}$  ( $3 \text{ mmolg}^{-1}$ ) for Pb (II),  $163.9 \text{ mgg}^{-1}$  ( $2.58 \text{ mmolg}^{-1}$ ) for Cu (II), and  $522.7 \text{ mgg}^{-1}$  ( $9.36 \text{ mmolg}^{-1}$ ) 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.

### 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

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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 addition to the previous adsorbents, nano-chamomile can be also used as an effective adsorbent due to its advantages and properties. It is a well-known and widely used plant for various gastro-intestinal disorders. Extracts of chamomile are used in cosmetics for anti-inflammatory and antiseptic properties. They may exert antioxidant effects within human body. The majority of their antioxidant activity is due to flavones, falvenols, isoflavones, flavonoids, anthocyanin, cumarin, tannins acid, and isocatechins [30].  
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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 ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ) were purchased from BDH (England) and Aldrich (USA). HCl, NaOH, and EDTA (ethylenediaminetetracetic 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 JEM100CX11 JEOL (Japan). The crystallinity of the nano-biosorbent was recorded using a JEOL X-ray diffractometer (XRD) model JSX-60PA (Japan). The shaking was carried out using Gesellschaft Fur Labortechnik (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):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$C_o$ : initial concentrations of metal ion in mmol/L,  $C_e$ : concentration of the unadsorbed 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<sup>-1</sup>) to a series of metal ions concentrations (0.2g L<sup>-1</sup>) 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<sup>-1</sup>. 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  $q_t$ (mmol/g) at time  $t$  (min) was calculated from Eq. (2)

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

$q_t$ : 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<sup>-1</sup>

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  $3422.57\text{ cm}^{-1}$  representing the presence of free-OH and stretching of hydroxyl groups. The bands at  $2923.03\text{ cm}^{-1}$  and  $2853.43\text{ cm}^{-1}$  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  $1756.32\text{ cm}^{-1}$  and a strong band near  $1635.68\text{ cm}^{-1}$  were attributed to C=O stretching of carboxylic acid [34,35]. The band observed at  $1550.44\text{ cm}^{-1}$  was due to C-OH stretching vibration [17]. The sharp bands at  $1517.62\text{ cm}^{-1}$  and  $1428.16\text{ cm}^{-1}$  were attributed to aromatic C=C ring structure [36]. Several peaks ranging from  $1383.99$  to  $1034.76\text{ cm}^{-1}$  may refer to C-O bonding of phenols and aliphatic and aromatic C-H group [24,37–39]. This splitting pattern is characteristic of several different C-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 C=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 -COOH and phenolic -OH groups were affected after the ion uptake as manifested by shifts in their absorption peaks from  $1034.76$ ,  $1635.68$ ,  $1726.32$  and  $3422.57\text{ cm}^{-1}$  to  $1036.58$ ,  $1634.34$ ,  $1731.85$  and  $3425.53\text{ cm}^{-1}$  for  $\nu$  (-C-O-),  $\nu$  (-C=O-),  $\nu$  (-COOH) and

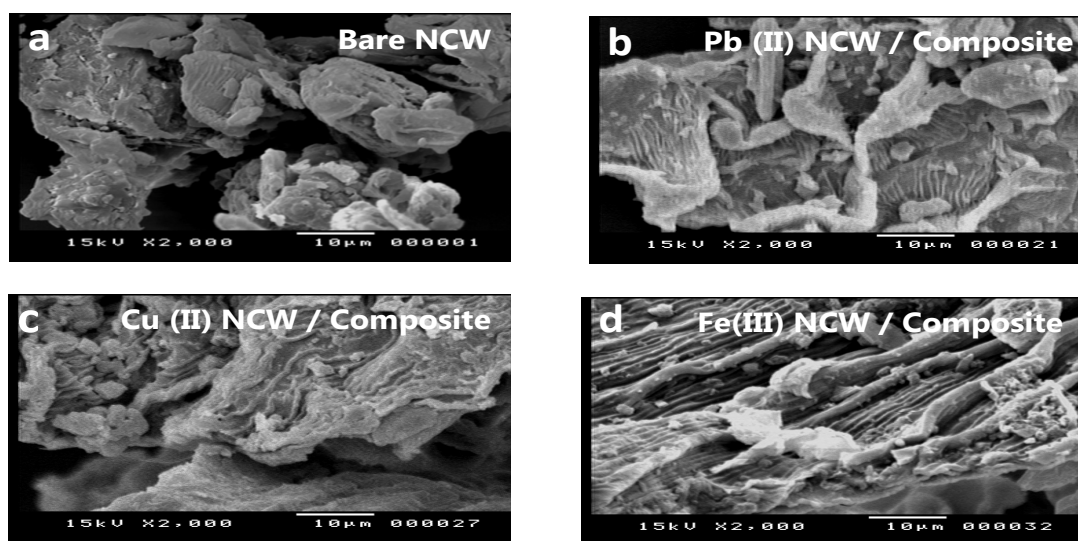


Fig. 1. SEM images of (a) bare NCW, and (b, c, d) NCW after Pb (II), Cu (II) and Fe (III) biosorption, respectively.

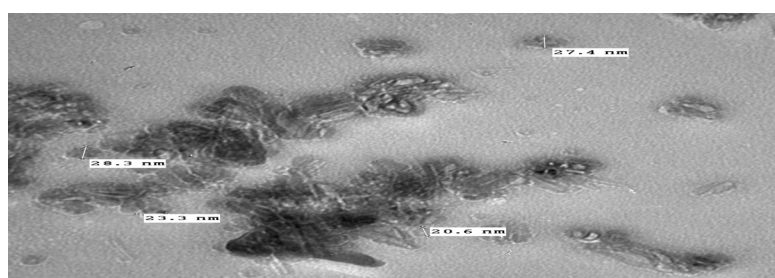


Fig. 2. TEM analysis of NCW biosorbent.

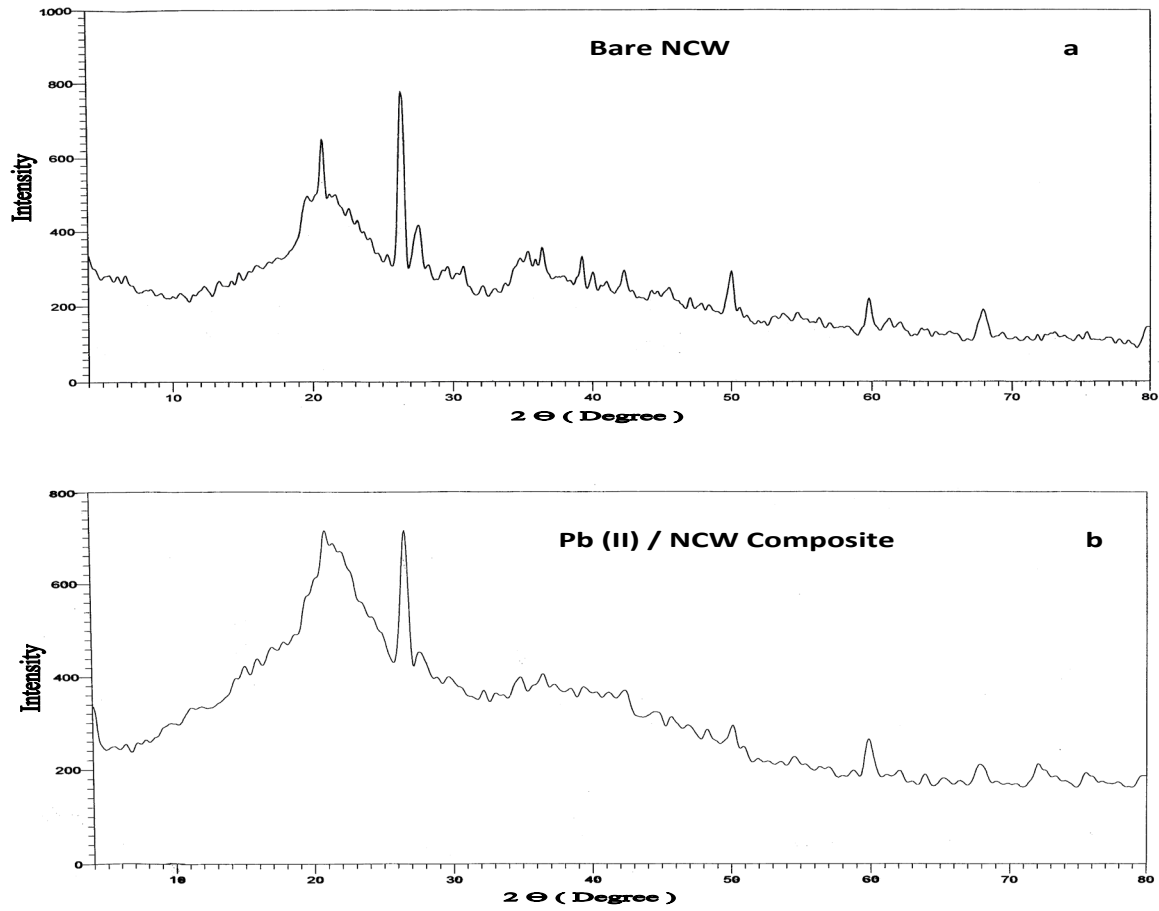
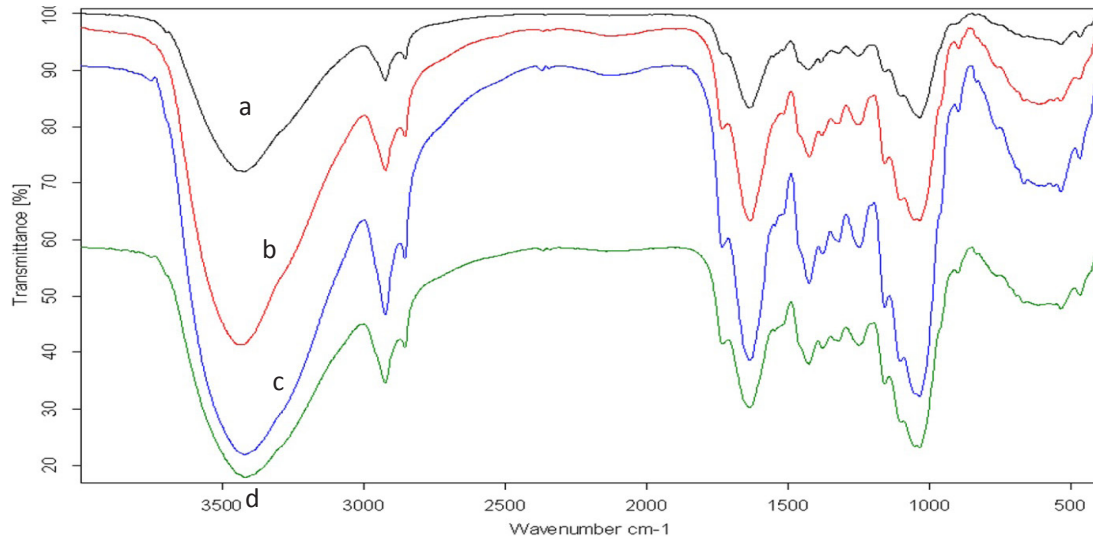
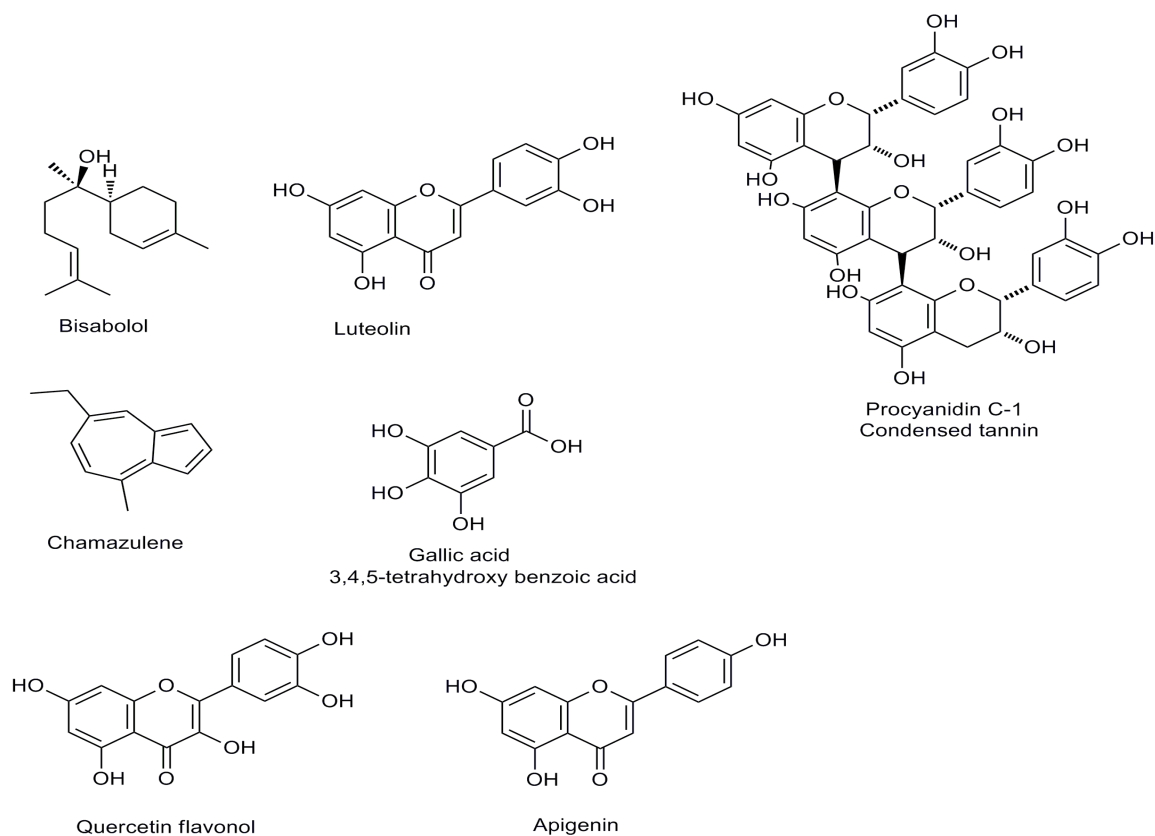


Fig. 3. X-ray diffraction of (a) bare NCW before and (b) after Pb (II) biosorption.



|   |         |                    |            |
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| C:\Program Files\OPUS_65\MEAS\2 OF 12.0 | 2 OF 12 | Sample Compartment | 28/02/2017 |
| C:\Program Files\OPUS_65\MEAS\3 OF 12.0 | 3 OF 12 | Sample Compartment | 28/02/2017 |
| C:\Program Files\OPUS_65\MEAS\TAGRE 1.0 | TAGRE 1 | Sample Compartment | 09/03/2016 |

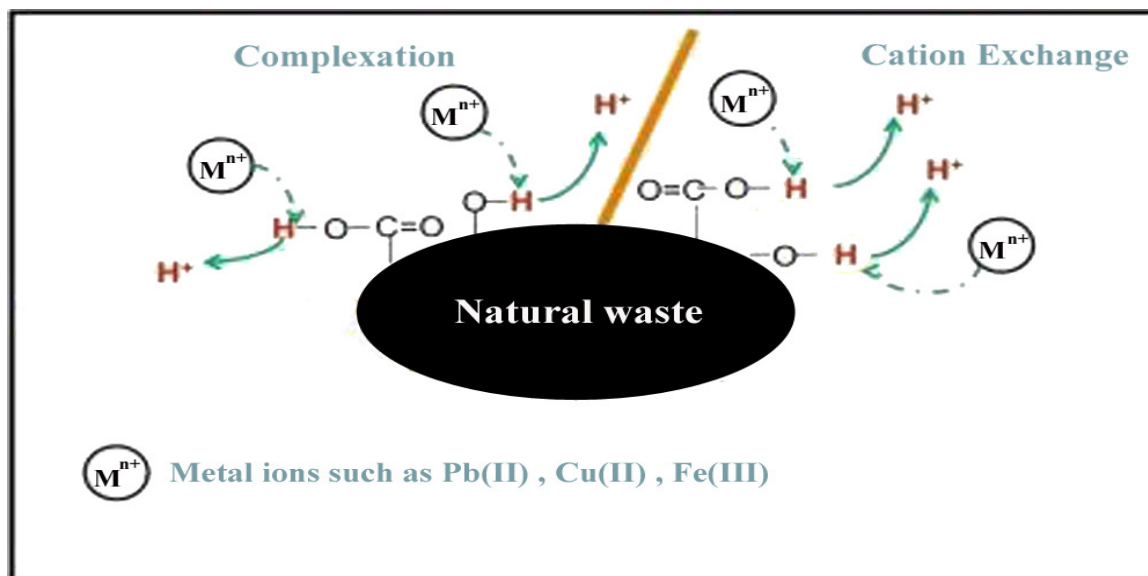
Fig. 4. FTIR spectra of (a) bare NCW and (b, c, d) NCW after Pb (II), Cu (II) and Fe (III) biosorption, respectively.



Scheme 1 . Structures of organic compounds found in studied waste (NCW)

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

| Assignment   | Band position (cm <sup>-1</sup> ) |                 |                 |                    |
|--|-----------------------------------|-----------------|-----------------|--------------------|
|  | After biosorption                 |                 |                 | Before biosorption |
|  | Fe (III)                          | Cu (II)         | Pb (II)         |                    |
| O–H stretch, H bonded, alcohol, phenol   | 3418.63                           | 3420.28         | 3425.54         | 3422.57            |
| C–H stretching vibrations of–CH <sub>2</sub> and –CH <sub>3</sub> functional group | 2922.92                           | 2922.48         | 2922.22         | 2923.03            |
|  | 2853.86                           | 2853.76         | 2853.53         | 2853.43            |
| C=O stretch of carbonyl  | 1731.43                           | 1732.57         | 1731.85         | 1726.33            |
| C=O stretching of carboxylate ion  | 1636.21                           | 1633.56         | 1634.34         | 1631.68            |
| C–OH stretching vibration  | -                                 | -               | -               | 1551.44            |
| C=C ring stretch aromatic  | -                                 | -               | -               | 1517.62            |
| C–C stretch (in ring), aromatics   | 1427.09                           | 1425.48         | 1425.72         | 1428.16            |
| C-H aromatic and carboxyl-carbonate structure                                      | 1377.06                           | 1378.58         | -               | 1383.99            |
| C–H aliphatic –CH <sub>3</sub> or –CH <sub>2</sub>                                 | 1322.10                           | 1321.79         | 1322.50         | 1321.34            |
| C=O stretch of carboxylate group   | 1248.65                           | 1250.05         | 1250.05         | 1253.00            |
| C–OH stretching of phenol  | 1159.05–1034.63                   | 1158.65–1035.14 | 1158.40–1036.58 | 1158.23–1034.76    |



Scheme 2 . Suggested mechanism for the interaction of metal ions on active binding sites of NCW biosorbent.

v(-OH), respectively (Table 1). Moreover, the absence of C–O band stretching of carboxylic acid and a C=C band of aromatic rings after the metal ion biosorption indicated the involvement of these groups in the biosorption, emphasizing a chemical interaction occurring between the metal and carboxylate groups onto the NCW surface.

The mechanism suggests for removal of Pb (II), Cu (II) and Fe (III) ions by the NCW can be explained mainly by the complexation adsorption model, in addition to the affinity of hydroxyl groups of the NCW biosorbent to metal ions or ions exchange with a single carboxylic group as shown in scheme 2.

*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 metalcations. 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  $1.57 \text{ mmol g}^{-1}$ ,  $1.7 \text{ mmol g}^{-1}$ , and  $1.3 \text{ mmol g}^{-1}$ , 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  $\text{mmol g}^{-1}$  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

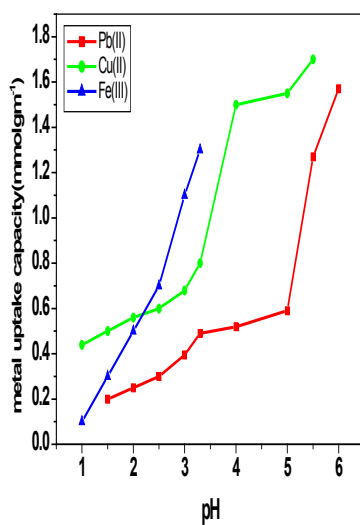


Fig. 5. Effect of pH on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).

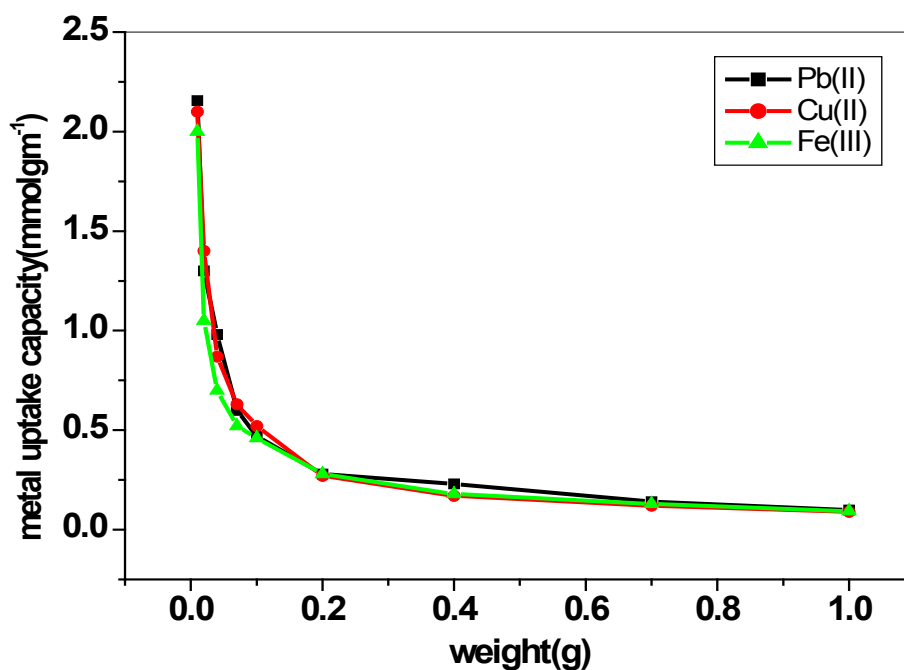


Fig. 6. Effect of weight on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).



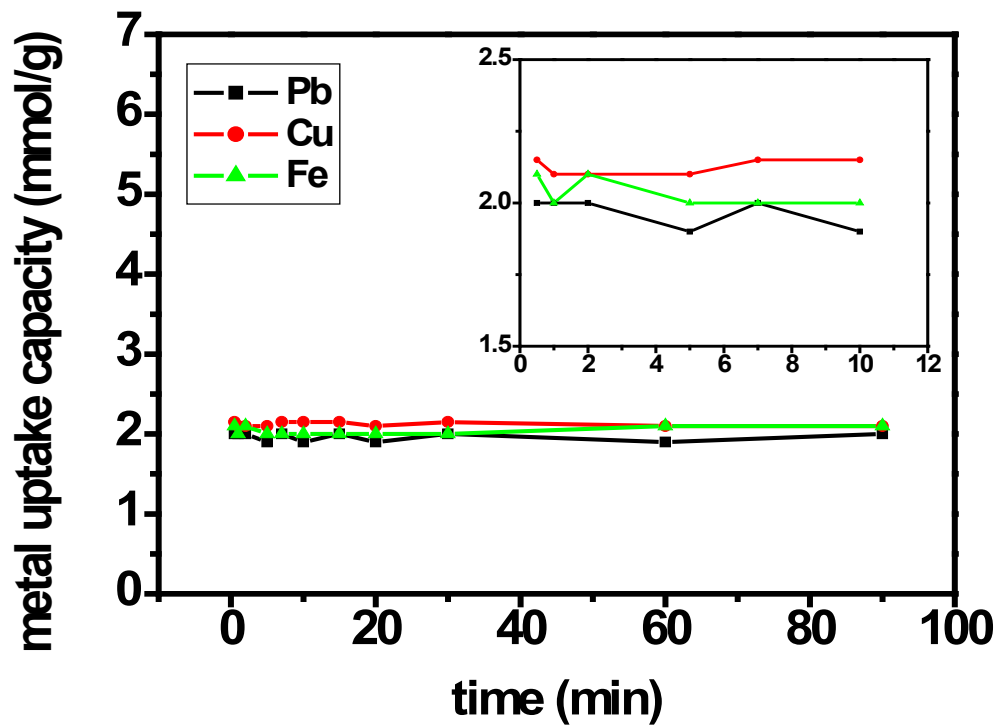


Fig. 7. Effect of contact time on the metal uptake capacity of NCW biosorbent for Pb (II), Cu (II), and Fe (III).

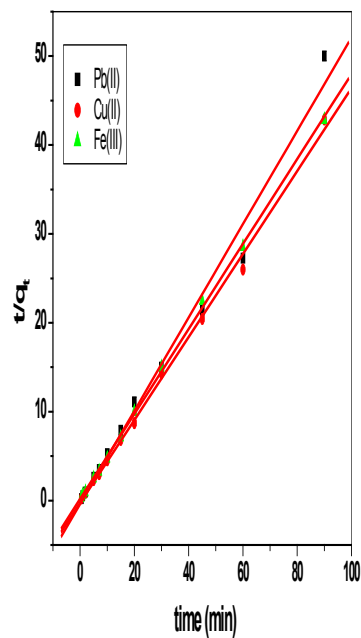


Fig. 8. Pseudo-second-order kinetic model for Pb (II), Cu (II), and Fe (III) adsorption on NCW.

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:

$$q_e = k_f \cdot C_e^{1/n} \quad (\text{exponential form}) \quad (3)$$

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:

$$\log q_e = \log k_f + 1/n \log C_e \quad (\text{linear form}) \quad (4)$$

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 NCW biosorbent surface [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

$$1/q_e = 1/q_m + 1/q_m b C_e \quad (\text{linear form}) \quad (5)$$

where  $q_e$  ( $\text{mmol g}^{-1}$ ) is the equilibrium adsorption capacity at the equilibrium concentration  $C_e$  ( $\text{mmol ml}^{-1}$ ),  $q_m$  ( $\text{mmol g}^{-1}$ ) is the maximum adsorption capacity on a Langmuir monolayer and  $b$  ( $\text{ml mmol}^{-1}$ ) 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 2. Langmuir and Freundlich isothermic constants for the biosorption of Pb (II), Cu (II) and Fe (III) on NCW at room temperature.**

| Freundlich model |       |       | Langmuir model |                     |       | Metal Ions |
|------------------|-------|-------|----------------|---------------------|-------|------------|
| $R^2$            | $1/n$ | $k_f$ | $R^2$          | $q_{\max}$ (mmol/g) | $b$   |            |
| 0.995            | 0.38  | 24.56 | 0.995          | 3.0                 | 0.142 | Pb (II)    |
| 0.993            | 0.32  | 16.93 | 0.998          | 2.58                | 0.299 | Cu (II)    |

$1/q_t$  and  $1/C_e$ . 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 ( $R^2$ ) of NCW arranged 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).

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t \quad (6)$$

where  $q_t$  and  $q_e$  are the metal uptake capacity at time  $t$  (min) and at an equilibrium (mmol/g), respectively, and  $k_1$  ( $\text{min}^{-1}$ ) 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 ( $q_e$ ) remained constant with changing time. The kinetics of metals adsorption on NCW is also described as pseudo-second order Eq. (7) [48]:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (7)$$

where  $k_2$  ( $\text{gmmol}^{-1} \text{min}^{-1}$ ) 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  $t/q_t$  versus  $t$ . As shown in Fig. 8, a good fit (correlation coefficient  $R^2 = 0.999$ ) is obtained and the theoretical values of  $q_{e(\text{Theoretically})}$  also agree with the experimental values ( $q_{e(\text{Experimentally})}$ ), indicating that the adsorption conforms to the pseudo-second-order mechanism and the adsorption rate is controlled by chemical adsorption.

The theoretical values of  $q_{e(\text{Theoretically})}$  (2.09, 2.14 and  $1.90 \text{ mmolg}^{-1}$ ) agree with the experimental values ( $q_{e(\text{Experimentally})} = 2.10, 2.15$  and  $2.00 \text{ mmolg}^{-1}$ ) suggesting that the present adsorption system can be described more favorable 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), 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

|       |       |        |       |      |        |          |
|-------|-------|--------|-------|------|--------|----------|
| 0.996 | 0.944 | 972.75 | 0.997 | 9.36 | 0.0182 | Fe (III) |
|-------|-------|--------|-------|------|--------|----------|

TABLE 3. Pseudo-second-order rate constants and equilibrium metal uptake for Pb (II), Cu (II) and Fe (III) binding onto NCW.

| Second-order kinetics |                            |           |                             | Metal Ions |
|-----------------------|----------------------------|-----------|-----------------------------|------------|
| $R^2$                 | $q_e$ Theoretical (mmol/g) | $k_{ads}$ | $q_e$ Experimental (mmol/g) |            |
| 0.990                 | 1.9                        | 0.280     | 2.00                        | Pb (II)    |

|       |      |       |      |          |
|-------|------|-------|------|----------|
| 0.998 | 2.14 | 0.186 | 2.15 | Cu (II)  |
| 0.999 | 2.09 | 1.237 | 2.10 | 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.**

| Reference         | Modification procedure   |                                  |                  | Adsorbent dose (g/L) | pH         | Contact time   | Adsorption capacity (mgg <sup>-1</sup> ) | Adsorbent                                     | Metal          |
|-------------------|--|----------------------------------|------------------|----------------------|------------|----------------|--|---|----------------|
|                   | Reagents used for modification   | Time needed for modification (h) | No. of Steps     |                      |            |                |  |   |                |
| [15]              | NaOH<br>Fe <sub>3</sub> O <sub>4</sub>   | >20 h                            | Many steps       | 2                    | 5          | 4 min.         | 28.57                                    | Modified walnut shell                         |                |
| [49]              | Dimethyl formamide (DMF) + tripolyphosphate (STTPP)  | 24 h                             | Many steps       | 1                    | 5          | -              | 305 ±4.7                                 | Tripolyphosphate modified waste Lyocell fiber |                |
| [27]              | Ethanol + tetrahydrofuran (THF) + tartaric acid  | 24 h                             | Many steps       | 5                    | 5          | 90 min.        | 93.45                                    | Modified rice husk                            |                |
| [50]              | NaOH + acetone + CS <sub>2</sub>   | >1.5 h                           | Many steps       | 1                    | 5          | 5 min.         | 531.29 ±0.28                             | Chemically modified Lyocell fiber             | <b>Pb (II)</b> |
| [51]              | NaOH + H <sub>2</sub> SO <sub>4</sub> + CS <sub>2</sub>  | >12 h                            | Many steps       | 0.8                  | 4          | 5 min.         | 178.57                                   | Xanthate modified apple pomace                |                |
| [52]              | NaOH + Fe <sub>3</sub> O <sub>4</sub> + Na <sub>3</sub> P <sub>3</sub> O <sub>10</sub> (TPP) + H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub> | 24 h                             | Single step      | 10                   | 5          | -              | 16.247                                   | Chemical treated olive stone                  |                |
| [53]              | NaOH + HCL + HNO <sub>3</sub>  | 12 h                             | Many steps       | 1                    | 5          | -              | 50.12                                    | Treated guava bagasse                         |                |
| [54]              | NaOH + ethanol Mercapto-acetic acid  | >24 h                            | Many steps       | 5                    | 5          | -              | 164                                      | Sulfured orange peel                          |                |
| <b>This study</b> | <b>No reagent</b>  | -                                | <b>Bare* NCW</b> | <b>0.2</b>           | <b>5.5</b> | <b>30 sec.</b> | <b>621.6</b>                             | <b>Nano chamomile waste</b>                   |                |
| [50]              | NaOH + acetone + CS <sub>2</sub>   | >1.5 h                           | Many steps       | 1                    | 4          | 5 min.         | 123.08 ±0.26                             | Chemically modified Lyocell fiber             |                |
| [55]              | NaOH + KCl   | >12 h                            | Many steps       | 5                    | 5–5.5      | 120 min.       | 59.77                                    | K type orange peel                            | <b>Cu (II)</b> |
| [55]              | NaOH + MgCl <sub>2</sub>   | >12 h                            | Many steps       | 5                    | 5–5.5      | 120 min.       | 40.37                                    | Mg type orange peel                           |                |
| <b>This study</b> | <b>No reagent</b>  | -                                | <b>Bare NCW</b>  | <b>0.2</b>           | <b>6</b>   | <b>30 sec.</b> | <b>163.9</b>                             | <b>Nano chamomile waste</b>                   |                |

**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.

| Recovery <sup>a</sup> (%) | Mass of the adsorbent (g) | Spiked (ppm) | Water sample    | Metal    |
|---------------------------|---------------------------|--------------|-----------------|----------|
| 99.00 ±1                  | 0.01                      | 10           | TW <sub>1</sub> | Pb (II)  |
| 99.00 ±1                  | 0.01                      | 10           | TW <sub>2</sub> |          |
| 99.00 ±1                  | 0.01                      | 10           | MDW             |          |
| 99.00 ±1                  | 0.05                      | 10           | GW <sub>1</sub> |          |
| 99.00 ±1                  | 0.01                      | 10           | GW <sub>2</sub> |          |
| 99.00 ±1                  | 0.01                      | 10           | RW              |          |
| 98.00 ±1                  | 1.0                       | 10           | SW              |          |
| 98.00 ±1                  | 1.0                       | 10           | WW              |          |
| 91.00 ±3.6                | 0.1                       | 2.5          | TW <sub>1</sub> | Cu (II)  |
| 91.00 ±3.6                | 0.1                       | 2.5          | TW <sub>2</sub> |          |
| 91.00 ±3.6                | 0.05                      | 2.5          | MDW             |          |
| 89.33 ±3                  | 0.1                       | 2.5          | GW <sub>1</sub> |          |
| 91.00 ±3.6                | 0.1                       | 2.5          | GW <sub>2</sub> |          |
| 91.00 ±3.6                | 0.1                       | 2.5          | RW              |          |
| 89.33 ±3                  | 0.1                       | 2.5          | SW              |          |
| 89.33 ±3                  | 4.0                       | 2.5          | WW              |          |
| 93.00 ±3                  | 0.1                       | 2.5          | TW <sub>1</sub> | Fe (III) |
| 93.00 ±3                  | 0.1                       | 2.5          | TW <sub>2</sub> |          |
| 99.00 ±1                  | 0.01                      | 2.5          | MDW             |          |
| 89.33 ±3                  | 0.1                       | 2.5          | GW <sub>1</sub> |          |
| 93.00 ±3                  | 0.1                       | 2.5          | GW <sub>2</sub> |          |
| 93.00 ±3                  | 0.1                       | 2.5          | RW              |          |
| 89.33 ±3                  | 0.1                       | 2.5          | SW              |          |
| 87.66 ±2.5                | 4.0                       | 2.5          | WW              |          |

<sup>a</sup> average of three estimates ±standard deviation (S.D.)

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.

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## References

- Gubin S. P., Koksharov Y. A., Khomutov G. B. and Yurkov G. Yu., Magnetic nanoparticles: preparation, structure and properties. *Russian Chemical Reviews*, **746**, 489–520 (2005).
- Santhosh C., Velmurugan V., Jacob G., Jeong S. K., Grace A. N. and Bhatnagar A., Role of nanomaterials in water treatment applications. *Chemical Engineering Journal*, **306**, 1116–1137 (2016).
- Bhatnagara A. and Sillanp M., Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment. *Chemical Engineering Journal*, **157**, 277–296 (2010).
- Anjum M., Miandad R., Waqas M., Gehany F. and Baraka M.A.T., Remediation of wastewater using various nanomaterials. *Arabian Journal of Chemistry*, <http://dx.doi.org/10.1016/j.arabjc.2016.10.004> in press).
- Djerahov L., Vasileva P., Karadjoval., Kurakalva R.M. and Aradhi K. K., Chitosan film loaded with silver nanoparticles – sorbent for solid phase extraction of Al (III), Cd (II), Cu (II), Co (II), Fe (III), Ni (II), Pb (II) and Zn (II). *Carbohydrate Polymers*, **147**, 45–52 (2016).
- Bao S., Li K., Ning P., Peng J., Jin X. and Tang L., Highly effective removal of mercury and lead ions from wastewater by mercaptoamine-functionalised silica-coated magnetic nano-adsorbents: Behaviours and mechanisms. *Applied Surface Science*, **393**, 457–466 (2017).
- Firouzabadi Z.D., Haji Shabani A. M., Dadfarnia S. and Ehrampoush M.H., Preconcentration and speciation of thallium by ferrofluid based dispersive solid phase extraction and flame atomic absorption spectrometry. *Microchemical Journal*, **130**, 428–435 (2017).
- Shi C., Jing Y., Xiao J., Wang X. and Jia Y., Liquid-liquid extraction of lithium using novel phosphonium ionic liquid as an extractant. *Hydrometallurgy*, **169**, 314–320 (2017).
- Srivastava B., Barman M.K., Chatterjee M., Roy D. and Mandal B., Solid phase extraction, separation and preconcentration of rare elements thorium (IV), uranium (VI), zirconium (IV), cerium (IV) and chromium (III) amid several other foreign ions with eriochrome black T anchored to 3-D networking silica gel. *Journal of Chromatography*, **1451**, 1–14 (2016).  
*Egypt. J. Chem.* **62**, No. 5 (2019)
- Negm N. A., Abd El Wahed M.G., Hassan A.A. and Abou Kana M. T.H., Feasibility of metal adsorption using brown algae and fungi: Effect of biosorbents structure on adsorption isotherm and kinetics. *Journal of Molecular Liquids*, **264**, 292–305 (2018).
- Malik R., Dahiya S. and Iata S., An experimental and quantum chemical study of removal of utmostly quantified heavy metals in wastewater using coconut husk: A novel approach to mechanism. *International Journal of Biological Macromolecules*, **98**, 139–149 (2017).
- Shrestha S., Son G., Lee S.H. and Lee T. G., Isotherm and thermodynamic studies of Zn (II) adsorption on lignite and coconut shell-based activated carbon fiber. *Chemosphere*, **92**, 1053–1061 (2013).
- Shen Y. S., Wang S. L., Huang S. T., Tzoua Y. M. and Huang J. H., a Biosorption of Cr (VI) by coconut coir: Spectroscopic investigation on the reaction mechanism of Cr (VI) with lignocellulosic material. *Journal of Hazardous Materials*, **179**, 160–165 (2010).
- Rozumová L., Životský O., Seidlerová J., Motykaa O., Šafařík I., iková M. Š. Magnetically modified peanut husks as an effective sorbent of heavy metals. *Journal of Environmental Chemical Engineering*, **4**, 549–555 (2016).
- Safinejad A., Chamjangali M. A., Goudarzi N., Bagherian G., Synthesis and characterization of a new magnetic bio-adsorbent using walnut shell powder and its application in ultrasonic assisted removal of lead. *Journal of Environmental Chemical Engineering*, **5**, 1429–1437 (2017).
- Kumar P. S., Ramalingam S., D.Kirupha S., Murugesan A., Vidhyadevic T. and Sivanesan S., Adsorption behavior of nickel (II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design. *Chemical Engineering Journal*, **167** 122–131 (2011).
- Senthil Kumar P., Ramalingam S., Sathyaselvabala V., Kirupha S. D. and Sivanesan S., Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination*, **266** 63–71 (2011).
- Romero-Cano L. A., Gonzalez-Gutierrez L. V. and Baldenegro-Perez L. A., Biosorbents prepared from orange peels using Instant Controlled Pressure Drop for Cu (II) and phenol removal. *Industrial*

- Crops and Products*, **84**, 344–349 (2016).
19. Guiza S., Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel. *Ecological Engineering*, **99**, 134–140 (2017).
  20. Tasaso P., Adsorption of Copper Using Pomelo Peel and Depectinated Pomelo Peel. *Journal of Clean Energy Technologies*, **2** 154–157 (2014).
  21. Bhatti H. N., Zaman Q., Kausar A., Noreen S. and Iqbal M., Efficient remediation of Zr (IV) using citrus peel waste biomass: Kinetic, equilibrium and thermodynamic studies. *Ecological Engineering*, **95**, 216–228 (2016).
  22. Ali A., Saeed K. and Mabood F., Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. *Alexandria Engineering Journal*, **55**, 2933–2942 (2016).
  23. Tavlieva M. P., Genieva S.D., Georgieva V.G. and Vlaev L. T., Thermodynamics and kinetics of the removal of manganese (II) ions from aqueous solutions by white rice husk ash. *Journal of Molecular Liquids*, **211**, 938–947 (2015).
  24. Yadav D., Kapur M., Kuma P. R and Mondal M.K., Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue. *Process Safety and Environmental Protection*, **94**, 402–409 (2015).
  25. Georgieva V.G., Tavlieva M. P., Genieva S. D. and Vlaev L. T., Adsorption kinetics of Cr (VI) ions from aqueous solutions onto black rice husk ash. *Journal of Molecular Liquids*, **208**, 219–226 (2015).
  26. Hafshejani L.D., Hooshmand A., Naseria A.A., Mohammadia A.S., Abbasib F. and Bhatnagar A., Removal of nitrate from aqueous solution by modified sugarcane bagasse biochar. *Ecological Engineering*, **95**, 101–111 (2016).
  27. Masoumi A., Hemmati K. and Ghaemy M., Low-cost nanoparticles sorbent from modified rice husk and a copolymer for efficient removal of Pb (II) and crystal violet from water. *Chemosphere*, **146**, 253–262 (2016).
  28. López-Téllez G., Barrera-Díaz C. E., Balderas-Hernández P., Roa-Morales G. and Bilyeu B., Removal of hexavalent chromium in aquatic solutions by iron nanoparticles embedded in orange peel pith. *Chemical Engineering Journal*, **173**, 480–485 (2011).
  29. Feng N., Guo X., Liang S., Zhu Y. and Liu J., Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials*, **185**, 49–54 (2011).
  30. Guimarães R., Barros L., Dueñas M., Calheta R. C., Carvalho A. M., Santos-Buelga C., Queiroz M. J. and Ferreira I. C., Infusion and decoction of wild German chamomile: Bioactivity and characterization of organic acids and phenolic compounds. *Food Chemistry*, **136**, 947–954 (2013).
  31. Ahmad R. and Haseeb S., Adsorptive removal of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> from the aqueous solution by using ground nut husk modified with Guar Gum (GG): Kinetic and thermodynamic studies. *Ground Water for Sustainable Development*, **1**, 41–49 (2015).
  32. Bahtiti N. H. and Hassan N., Chemical analysis and biological activity of Jordanian chamomile extracts. *Advance Journal of Food Science and Technology*, **4** (1), 22–25 (2012).
  33. Xie F., Lin X., Wu X. and Xie Z., Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry. *Talanta*, **74**, 836–843 (2008).
  34. Nayak A., Bhushan B., Gupta V. and Sharma P., Chemically activated carbon from lignocellulosic wastes for heavy metal wastewater remediation: Effect of activation conditions. *Journal of Colloid and Interface Science*, **493**, 228–240 (2017).
  35. Basu M., Guha A.K., Ray L., Adsorption of Lead on Cucumber Peel. *Journal of Cleaner Production*, **151**, 603–615 (2017).
  36. Vaghetti J. C.P., Lima E.C., Royer B., da Cunha B.M., Cardoso N. F., Brasil J.L. and Dias S. L.P., Pecan nutshell as biosorbent to remove Cu (II), Mn (II) and Pb (II) from aqueous solutions. *Journal of Hazardous Materials*, **162**, 270–280 (2009).
  37. Ben-Ali S., Jaouali I., Souissi-Najar S. and Ouederni A., Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *Journal of Cleaner Production*, **142**, 3809–3821 (2017).
  38. Ben-Ali S., Souissi-Najar S. and Ouederni A., Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *Journal of Cleaner Production*, **154**, 269–275 (2017).

39. Moyo M., Guyo U., Mawenyiyo G., Zinyama N. P. and Nyamun B. C., Marula seed husk (*Sclerocarya birrea*) biomass as a low cost biosorbent for removal of Pb (II) and Cu (II) from aqueous solution. *Industrial and Engineering Chemistry*, **27**, 126–132 (2015).
40. Pap S., Radonić J., Trifunović S., Adamović D., Mihajlović I., Vojinović Miloradov M. and Sekuli M. T., Evaluation of the adsorption potential of eco-friendly activated carbon prepared from cherry kernels for the removal of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> from aqueous wastes. *Journal of Environmental Management*, **184**, 297–306 (2016).
41. Bartzak P., Norman M., Klapiszewski Ł., Karwan' ska N., Kawalec M., Baczyn' ska M., Wysokowski M., Zdarta J., Ciesielczyk F. and Jesionowski T., Removal of nickel (II) and lead (II) ions from aqueous solution using peat as a low-cost adsorbent: A kinetic and equilibrium study. *Arabian Journal of Chemistry*, **11**, 8, 1209-1222 (2018).
42. Hamouda A. S., Ahmed S. A., Mohamed N. M. and M. Khalil M. H., Adsorption of Chromium(VI) from Aqueous Solution by Glycine Modified Cross-linked Chitosan Resin. *Egyptian Journal of Chemistry*, **61**(5), 799 - 812 (2018).
43. Al-Bizreh W.Y., Al-mostafa R. and AL-Joubbeh M., Adsorption of Nicotine on Calcinated and Modified Compressed Coffee Residue CACS and Its Surface Properties. *Egyptian Journal of Chemistry*, **61**(6), 1083 - 1096 (2018).
44. Madbouly M. D. and Al-Anwar A., Tamarixaphylla Biomass as an Efficient Adsorbent for Removal of Pb(II) Ions from Aqueous Solution: Kinetic and Applicability for Different Isotherm Models. *Egyptian Journal of Chemistry*, **61**(1), 101-119 (2018).
45. Foo K.Y. and Hameed B.H., Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, **156**, 2–10 (2010).
46. Bhatnagara A., Minocha A.K. and Sillanpää M., Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as Biosorbent. *Biochemical Engineering Journal*, **48**, 181–186 (2010).
47. Deng S., Yu G., Xie S., Yu Q., Huang J., Kuwaki Y. and Iseki M., Enhanced adsorption of arsenate on the aminated fibers: sorption behavior and uptake mechanism. *Langmuir*, **24**, 10961–10967 (2008).  
*Egypt.J.Chem.* **62**, No. 5 (2019)
48. Ning-chuan F., Xue-yi G. and Sha L., Enhanced Cu (II) adsorption by orange peel modified with sodium hydroxide. *Transactions of nonferrous metals society of china*, **20**, 146–152 (2010).
49. Bediako J. K., Reddy D. H. K., Song M.H., Wei W., Lin S. and Yun Y.S., Preparation, characterization and lead adsorption study of tripolyphosphate-modified waste Lyocell fibers. *Journal of Environmental Chemical Engineering*, **5**, 412–421 (2017).
50. Bediako J. K., Wei W., Kim S. and Yun Y.S., Removal of heavy metals from aqueous phases using chemically modified waste Lyocell fiber. *Journal of Hazardous Materials*, **299**, 550–561 (2015).
51. Chand P., Bafana A. and Pakade Y. B., Xanthate modified apple pomace as an adsorbent for removal of Cd (II), Ni (II) and Pb (II), and its application to real industrial wastewater. *International Biodeterioration & Biodegradation*, **97**, 60–66 (2015).
52. Bla'zquez G., Calero M., Ronda A., Tenorio G., Marti'n-Lara M.A., Study of kinetics in the biosorption of lead onto native and chemically treated olive stone. *Journal of Industrial and Eng. Chemistry*, **20**, 2754–2760 (2014).
53. Velazquez-Jimenez L. H., Pavlick A. and Rangel-Mendez J. R., Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water. *Industrial Crops and Products*, **43**, 200–206 (2013).
54. Liang S., Guo X. and Tian Q., Adsorption of Pb<sup>2+</sup> and Zn<sup>2+</sup> from aqueous solutions by sulfured orange peel. *Desalination*, **275**, 212–216 (2011).
55. Liang S., Guo X., Feng N. and Tian Q., Isotherms, kinetics and thermodynamic studies of adsorption of Cu<sup>2+</sup> from aqueous solutions by Mg<sup>2+</sup>/K<sup>+</sup> type orange peel adsorbents. *Journal of Hazardous Materials*, **174**, 756–762 (2010).
56. Moghadam M. R., Nasirizadeh N., Dashti Z. and Babanezhad E., Removal of Fe (II) from aqueous solution using pomegranate peel carbon: equilibrium and kinetic studies. *International Journal of Industrial Chemistry*, **4**, 19-24 (2013).
57. Ahmed S. A., Batch and fixed-bed column techniques for removal of Cu (II) and Fe (III) using carbohydrate natural polymer modified complexing agents. *Carbohydrate Polymers*, **83**, 1470–1478 (2011).



## استخدام مخلفات البابونج النانومترية كمستخلص صلب طبيعي منخفض التكلفة لازالة السريعة لايونات بعض العناصر الثقيلة من عينات مياه طبيعية

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فى هذا البحث تم استعراض كيفية استخدام نفايات البابونج النانومترية (NCW) كمستخلص صلب انتقائي وذلك بغرض ازالة أيونات الفلزات الثقيلة. تم دراسة مجموعة متغيرات بما فى ذلك درجة الحموضة (6,0-1,0)، تركيز أيون الفلز (10-100 ميكرو لتر)، وزن المستخلص الصلب (10-1000 مللجم) وزمن الوصول لحالة الاتزان (0,5-90 دقيقة) وذلك من خلال استخدام تقنية الخلط بهدف تحسين السعة القصوى للمستخلص الصلب. وقد اتفقت النتائج العملية لهذه الدراسة مع كل من نموذج فروندليش ولانجمير ( $R^2 = 0.999$ ) هذا بالإضافة الى قيم سعة الاستخلاص والتي كانت 621,6 مللجم/جم (3 مللى مول /جم) لـ  $Pb(II)$ ، 163,9  $mgg^{-1}$  لـ  $Fe(III)$ ، و 2,58 مللى مول/جم للنحاس (II)، و 522,7 مللجم/جم (9,36 مللى مول/جم) لـ  $Fe(III)$ . ومن ناحية اخرى كانت قيم سعة الاستخلاص كدالة فى الزمن متفقتة مع نموذج النظام الثنائي الحركي حيث أكدت هذه النتائج على إمكانية الوصول السريع لايونات الفلز إلى سطح المستخلص الصلب، وذلك من خلال الوصول إلى الاتزان فى غضون 30 ثانية. تم عمل توصيف لسطح الـ NCW باستخدام أطياف FT-IR وتم وصف الصورة البلورية للمستخلص باستخدام انحراف الأشعة السينية (XRD). أيضا تم عمل توصيف للسطح مع حساب حجم الجسيمات للـ NCW وذلك باستخدام SEM و TEM، على التوالي. وعلى النطاق التطبيقي تم اضافة تركيزات معلومة لكل من  $Pb(II)$  و  $Cu(II)$  و  $Fe(III)$  فى عينات مياه طبيعية مثل المياه الجوفية (GW) ومياه الشرب (DTW) والمياه المعدنية (NDW) ومياه نهر النيل (NRW) ومياه البحر (SW) ومياه الصرف الصحى (WW) وذلك بغرض دراسة كفاءة الطريقة والمستخلص الصلب محل الدراسة فى ازالة هذه العناصر الثقيلة فى وجود عناصر أخرى. وقد أظهرت النتائج الحصول على نسب عالية من الاسترجاع بلغت  $\leq 98\%$ . فى النهاية يمكن القول بان استخدام مثل هذه المستخلصات الطبيعية من حيث رخص ثمنها من الناحية الاقتصادية، وفى نفس الوقت الحصول عليها فى الصورة النانومترية كان مشجعا لاستخدام مثل هذه المستخلصات (NCW) فى عمليات تخدم البيئة من خلال ازالة مجموعة من أيونات المعادن الثقيلة من عينات مياه طبيعية.