

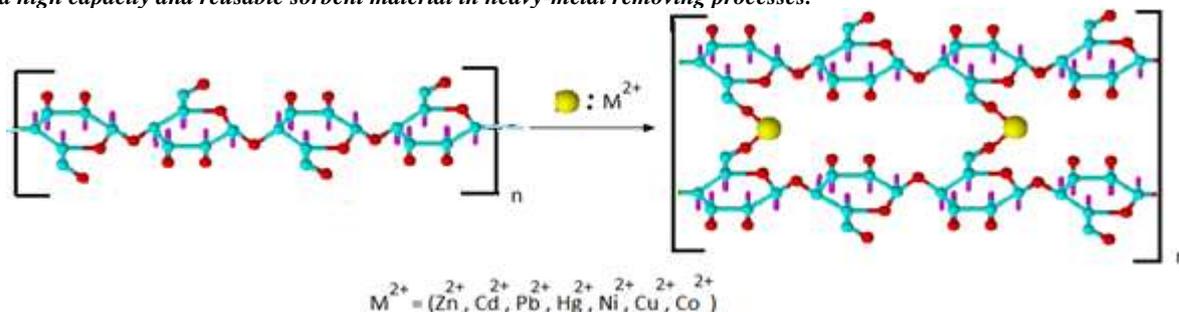
# Oxidized Vegetable Sponge (*Luffacylindrica*) as a Reusable Novel Heavy Metal Ions Adsorbent

Aloulou Fadhel<sup>1</sup>, Sabrine Alila<sup>2</sup>, Seffen Mongi<sup>3</sup>

<sup>1,3</sup> LabEM-LR11ES34: Laboratory of Energy and Materials, University of Sousse, Tunisia

<sup>2</sup>LMSE: Laboratoire Sciences des Matériaux et Environnement, University of Sfax, Tunisia

**Abstract:** *The use of biomass as an effective adsorbent follows meadow treatments and chemical treatments is profitable because of the low cost, high abundance, easy availability and high adsorption capacity. The vegetable sponge (*Luffacylindrica*) is one of the biomass renewable. The Luffa sponge is a rigid porous material, has been characterized by FTIR and NMR and used as an adsorbent for the removal of heavy metals from aqueous solutions. It showed an efficient adsorption, exceeding 96% toward  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$  and  $Ni^{2+}$  when their concentration was lower than 10 ppm and ranged from 90% to 60% for a metal concentration higher than 10 ppm. Over 98% of the adsorbed metal ion was recovered using EDTA as a desorbing solution, and the subsequent washing allowed the luffa sponge to be reused repeatedly without noticeable loss of adsorption capacity. It was concluded that the Luffa sponge oxidized may be used as a high capacity and reusable sorbent material in heavy-metal removing processes.*



**Keywords:** Green Chemistry, Heavy Metal, Fibers, Cellulose, Adsorption

## 1. Introduction

One of the main environmental issues today is related to water contamination by effluents and potentially toxic metals and their cumulative effects on biota [1].

The industries that release tailings into rivers and sewers without proper treatment are responsible for the majority of soil and water contamination with potentially toxic metals, threatening biodiversity.

Conventional methods for the removal of heavy metals from water are based on different approaches, such as adsorption, membrane, ion exchange and reverse osmosis, which are commonly applied to the treatment of industrial effluents [2].

Due to these rules, industries should provide proper treatment of waste before discharging it, determining the specific treatment for each residue.

One of the processes for the removal of toxic metals in liquid residues is adsorption, whose efficacy is directly related to the type of adsorbent employed [3].

Through the application of physicochemical models, adsorption interactions between the adsorbed species and the adsorbent material are studied. The relationship between the amount of a metal ion adsorbed in the solid phase ( $\Phi$ ) and its concentration in solution is quantified by an isotherm ( $\theta/C$  ratio) which allows us to know the type of adsorption.

Different adsorption models are used to quantify the effect, such as the Langmuir and Freundlich models [4].

The Langmuir isotherm model assumes that all the forces that act on the adsorption are similar in nature to those that involve a chemical reaction, and that the adsorption comes to be a single layer of molecules on the surface of solid particles [5].

The Freundlich model is an empiric equation that considers a multilayer structure; it does not predict the saturation of the surface and it refers to the adsorbent surface as heterogeneous. It is applied to characterize the multiple types of adsorptive sites, which possess different adsorptive characteristics [6].

Adsorption with activated charcoal, for example, is cited by the Environmental Protection Agency as one of the best technologies for the control of pollutants. However, its utilization is restricted due to its high cost [7].

Nevertheless, low cost materials like biomass are used on the adsorption of metals, including algae, microorganisms, compound materials and lignocelluloses, such as sugar cane bagasse, peanut, soybean and cotton crust. The use of biomass as adsorbent material is in agreement with the sustainability principle and the Green Chemistry.

The main concern of Green Chemistry is the development of new non-pollutants and non-environmental damaging technologies and processes. The application of Green

Chemistry principles leads to regulation and control in order to avoid unnecessary remediation. Besides the environmental benefits, such thinking also considerably reduces economic impact, due to decreased spending on decontamination and the payment of indemnities. The use of bioadsorbents based on renewable resources as a low cost adsorbent for heavy metal ions has received increasing attention [8,9]. Functional groups, such as carboxylate, hydroxyl, sulfate, amide, and amino groups appended on the bioadsorbents were responsible for metal binding [10].

However, in contaminated environments or in productive systems in which the minimization of residues is not yet possible, remediation aimed at lowering the impact of the contaminants is a necessity. The vegetable sponge (*Luffacylindrica*) is a natural, low cost, non-toxic, biodegradable and abundant material. Its growth rate is about 8,000 units per hectare in tropical countries such as Tunisia, and production can reach 100,000 dozens per year in a single production region.

Since the sponge has lignocellulosic material in its structure, it also contains lignin, cellulose and hemicellulose, all of them with adsorptive sites, like carbonyl, carboxyl, amine and hydroxyl groups, capable of adsorbing metal ions by interactions such as ionic exchange or complexation. On average, the natural sponge has 82.5% total cellulose and 11.6% lignin [11]. This factor combined with the porosity of the vegetable sponge has attracted studies on the processes of adsorption.

Diverse studies have explored the use of *Luffa cylindrica* as an adsorbent for removal of cationic surfactants [12], acetaminophen [13], dyes [14], textile dyes and phenol [15].

In relation to potentially toxic metals, it was verified that *Luffa* sponge can be used in the removal of copper ions from natural waters [16]. The use of natural sponge was investigated for the adsorption of lead (Pb) and it was verified that maximum capacity of Pb adsorption was 9.20 mg g<sup>-1</sup>; in the percolation of a lab effluent, more than 98% of the lead was adsorbed, presenting a concentration (0.17 mg L<sup>-1</sup>) below the maximum limit allowed by Tunisian law (0.5 mg L<sup>-1</sup>) [17].

In a series of a paper devoted to the possibility of using the modified cellulose fibers as a sorbent for the removal of dissolved organic pollutant, adsorption breakthrough curves were established under different operating condition such as concentration, flow rate and the column length. The main advantage of this substrate lies in its relative facile regeneration without a significant loss of its adsorption capacity [18].

The work of Sabrina Alila and all focuses on the use of chemically modified starch nanocrystals as sorbents for the removal of aromatic organic compounds from water. Best to our knowledge, such sorbent issued from biopolymer have never been reported. The viability of application of the modified nanocrystals for the removal aromatic organic contaminants in continuous mode was confirmed using a fixed bed column filled with modified anocrystals [19-20]. The surface modification is one method to boost the

adsorption capacity of the biosorbent and to extend its application to a wide range of organic pollutants [21-22-23-24].

In the present work, we modified *Luffa* sponge fibers using a new approach in the form of an material, submitted to a surface-modification with oxidation. The ensuing adsorbent exhibits a high porosity and a high specific surface along with a good mechanical stability. The structure of the modified *Luffa* sponge fibers was confirmed using FTIR, <sup>13</sup>C NMR spectroscopy. The adsorption equilibrium and the kinetics of heavy metals ions in aqueous solutions with *Luffa* sponge fibers were also investigated.

## 2. Material and Methods

### 2.1 Materials

*Luffa* sponge fibers used in this study were a bleached soda pulp from the Tunisian annual esparto (*luffa* sponge); they were highly porous and a specific surface area in a dry state of 3m<sup>2</sup>g<sup>-1</sup>. Their morphology was determined by averaging the length and width of 7380 fibers characterized with optical microscopy. The mean fiber length and width were found to be 2 mm and 25 μm, respectively, thus corresponding to an aspect ratio of 80. The carboxylic content of the original fibers was 45 μmol.g<sup>-1</sup>. Chemicals used to oxidize *luffa* sponge fibers, namely, TEMPO(2,2,6,6-tetramethyl-1-piperidinyloxy radical). Sodium bromide (NaBr), and 12% sodium hypochlorite solution, were of laboratory grade and used without further purification.

All chemicals used in this study were of analytical grade and supplied by Sigma–Aldrich. Stock solutions of 50 mg/L were prepared by dissolving appropriate amounts of Zn(II), Ni(II), Cu(II), Co(II), Pb(II), Hg(II) and Cd(II) nitrate salts in deionized water. Adjustment of pH was accomplished using 0.1 M NaOH or 0.1 M HNO<sub>3</sub>, and disodium salt of ethylenediaminetetraacetic acid (EDTA) were used in sorption experiments.

### 2.2 Oxidation procedure of *Luffa* sponge fibers

Oxidation of *Luffa* sponge fibers was carried out the following conditions. *Luffa* sponge (2,5 g) were dispersed in distilled water (1000 ml) to inflate. TEMPO (25 mg) and NaBr (250 mg) were added to suspension, and the pH was adjusted to 10 by addition of a 0.5 mol L<sup>-1</sup>NaOH solution. A 12% sodium hypochlorite solution was added the suspension over 30 min, and the resulting suspension was then stirred for 2h. The pH of the suspension was continuously adjusted to 10 by addition of the NaOH solution. The oxidation was stopped by adding 100 ml of ethanol, and oxidized fibers were filtered and washed two times with a 1 mol L<sup>-1</sup> NaOH solution to remove the traces of residual lignin. The recovered fibers were washed with distilled water until the pH of filtrate was close to 7. *Luffa* fibers oxidation by TEMPO is described in our previous work (Sabrina.Alila, Fadhel.Aloulou and all. Langmuir 2007).

## 2.3 Carboxyl content

The content of carboxylic moieties in the oxidized fibers was evaluated by using techniques conductometric titration of 1% luffa fibers suspension with  $10^{-3}$  molL<sup>-1</sup> HCl). Conductivity measurements were carried out in a thermostatic bath,  $\pm 0,1^{\circ}\text{C}$ , using a platinum electrode is described in our previous work (Sabrine.Alila, Fadhel.Aloulou and all. Langmuir 2007).

## 2.4 Characterization of the Luffa sponge oxidized

### 2.4.1 FTIR analysis

The FTIR spectra were obtained from KBr pellets with a Perkin-Elmer BX II spectrophotometer used in transmission mode with a resolution of  $2\text{ cm}^{-1}$  in the range of  $400\text{--}4000\text{ cm}^{-1}$ .

### 2.4.2 CP/MAS <sup>13</sup>C solid state NMR

Cross polarization/magic angle spinning (CP/MAS) <sup>13</sup>C solid state NMR experiments were performed with Bruker 300 spectrometer operating at a <sup>13</sup>C frequency of 75 MHz. The spinning speed was set at 300 Hz. The contact time for CP was 1 ms and the delay time for acquisition was 5 s. Chemical shifts were referred to tetramethyl silane (TMS).

## 2.5 Adsorption experiments

The Luffa sponge oxidized were added to a flask containing 20 ml of metal solution, and the flask placed in a thermostated water bath shaker operated at 150 rpm at the desired temperature for 3 h. In all the experiments, the amount of Luffa sponge oxidized sorbents was kept at around 200 mg. To obtain the equilibrium data, the initial concentration of the metal solutions was varied, while the amount of the adsorbent was kept constant. The initial pH values of the solutions had been previously adjusted with diluted HCl (0.01 M) using a pH meter. The concentration of the residual metal remaining in the aqueous solution was then analyzed, after suitable dilution, by atomic absorption using a Perkin-Elmer 560 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The amount of adsorption,  $q$  ( $\text{mg g}^{-1}$ ) was calculated as follows : ( $q_e = (C_0 - C_e) \cdot V/m$ ) where  $C_0$  (mg/l) and  $C_e$  (mg/l) are the initial and final metal concentrations of the solution, respectively,  $V$  (ml) is the volume of the metal solution, and  $m$  (g) the weight of the Luffa sponge oxidized. Each Luffa sponge oxidized pellet has a weight of about 0.2 g and exhibited a hydrophilic property. It was immediately wetted with the solution without any change in its volume.

## 2.6 Regeneration of the Luffa sponge fibers

The regeneration of the Luffa sponge oxidized adsorbent was accomplished using EDTA as a desorbing agent. The Luffa sponge oxidized were soaked in a 50 ml of  $10^{-3}\text{M}$  solution of EDTA at pH 5, and kept under shaking for 3 h. The desorption cycle was repeated twice, and then the Luffa

sponge fibers l was washed with water several times and subjected to another cycle of adsorption.

## 2.7 Continuous adsorption

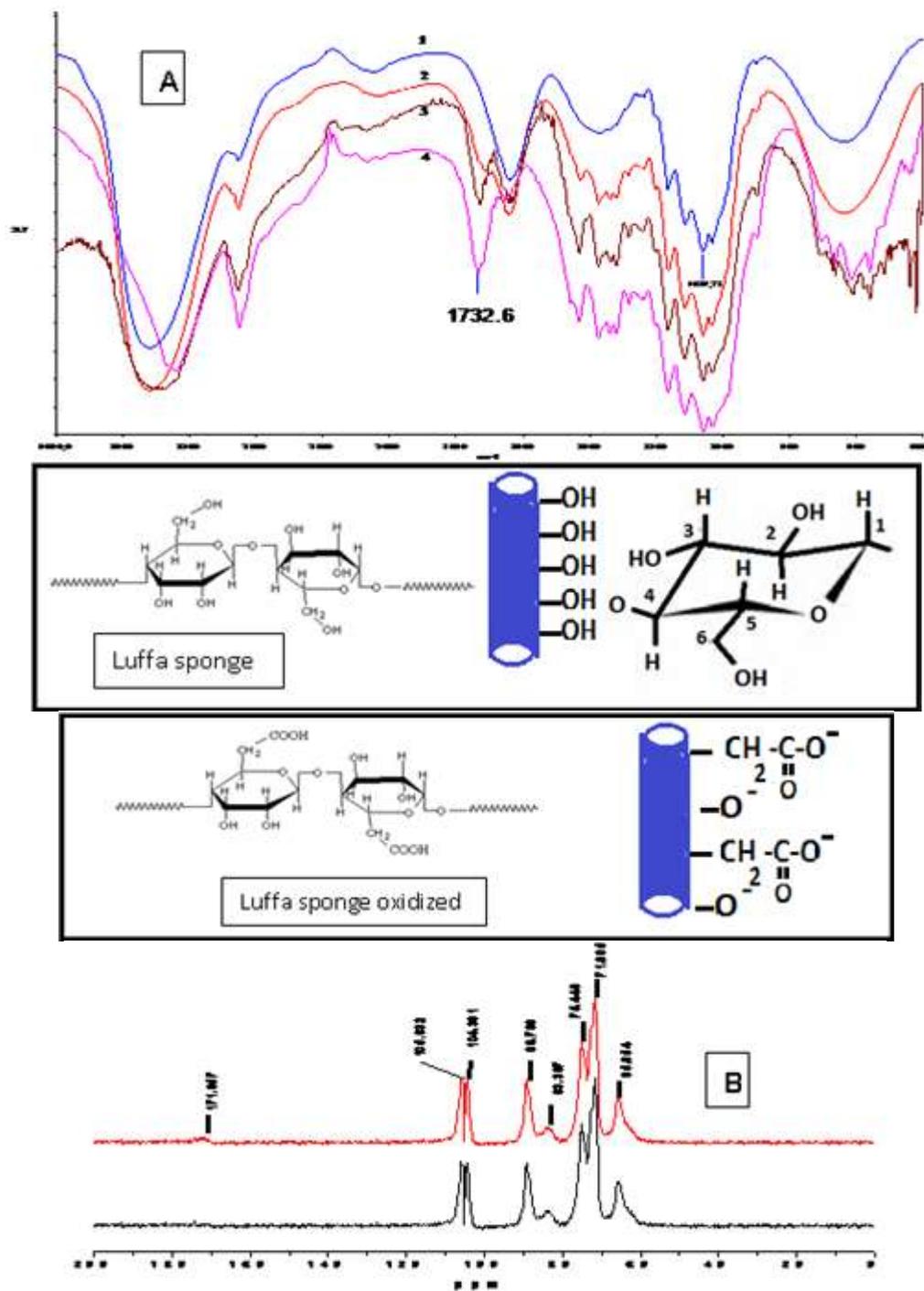
Continuous adsorption experiments were carried out under isothermal conditions using a packed column filled with pellets of the Luffa sponge oxidized. The packed column employed was a glass jacketed column of 10 mm in diameter and 15 cm long, packed with about 0.5 g of pellets of the Luffa sponge oxidized. The metal solution was percolated through the column from the bottom to the top, using a precision peristaltic pump. Effluent samples were collected at regular intervals and the concentrations monitored using atomic absorption.

## 3. Results and Discussion

### 3.1 Characterization of Luffa sponge oxidized

The Luffa sponge oxidized was confirmed by the FTIR spectra. **Figure 1A** shows the FTIR spectra of luffa sponge, and Luffa sponge oxidized. In the spectra of luffa sponge, and Luffa sponge oxidized (**Fig. 1A:1,2,3,4**), the spectra exhibit typical peaks for many functional groups of cellulose. The broad band at  $3338\text{ cm}^{-1}$  is attributed to the presence of free and hydrogen bonded OH stretching vibration and the other one at  $670\text{ cm}^{-1}$  is attributed to the OH out-of-plane bending vibration. The band at  $2900\text{ cm}^{-1}$  is due to the C-H asymmetric and symmetric tensile vibration. Bands corresponding to C-H bending vibrations were observed at  $1280$  and  $1337\text{ cm}^{-1}$ . The peak at  $1636\text{ cm}^{-1}$  originates from the bending mode of the absorbed water. The strong absorption at  $1056\text{ cm}^{-1}$  relates to C-O and C-O-C stretching vibrations, and the  $1160\text{ cm}^{-1}$  peak relates to the C-O antisymmetric bridge stretching vibration. The peak at  $1429\text{ cm}^{-1}$  corresponds to the CH<sub>2</sub> bending vibration. The IR spectrum of Luffa sponge oxidized (**Fig.1A:2,3,4**), displays two new absorption peaks at  $1732,6\text{ cm}^{-1}$  ( $\nu\text{C-O}$ ) and  $1440\text{ cm}^{-1}$  ( $\nu\text{C-O}$ ), indicate the presence of  $-\text{COOH}$  group in Luffa sponge oxidized.

The NMR spectra of luffa sponge, and Luffa sponge oxidized are shown in Fig. 1B. In the spectrum of Luffa sponge oxidized (**Fig. 1B**), all signals, i.e. those at 104.7 ppm (C-1), 89.8 ppm (C-4 of crystalline cellulose), 74.7 ppm (C-5), 72 ppm (C-2 and C-3), and 69.5 ppm (C-6 of crystalline cellulose) (Liu et al., 2010), are attributed to six carbon atoms of the glucose unit. However, there is no signal of C-4 and C-6 of amorphous cellulose in the spectrum, suggesting the complete disruption of the cellulose amorphous structure during the acid hydrolysis of cotton. Notably, two more intense signals appear in the spectrum of Luffa sponge oxidized (**Fig. 1B**) in addition to those of Luffa sponge oxidized, due to carbon atoms of carboxylic groups (C-7 and C-10) at 173.8 ppm and methylene groups (C-8 and C-9) at 30.1 ppm.



**Figure 1:** FTIR spectra (A) and solid-state CP/MAS <sup>13</sup>C NMR spectra (B) of luffa sponge (a), and Luffa sponge oxidized (b)

### 3.2 Adsorption behavior of Luffa sponge oxidized

To assess how the oxidation improved the adsorption performance of the Luffa sponge based sorbent, the adsorption efficiency and capacity of the pristine Luffa sponge, Luffa sponge oxidized toward Pb, Hg, Cu, Cd and Zn were compared. The data showed a huge enhancement in the adsorption efficiency and Luffa sponge oxidized exhibited the highest adsorption efficiency followed by the Luffa sponge oxidized. At an initial concentration of 50 ppm Pb(II), the adsorption efficiency grew from 20%, to 95% in presence of Luffa sponge, Luffa sponge oxidized, respectively. The increase in the carboxyl content from 540  $\mu\text{mol g}^{-1}$  for pristine Luffa sponge, to 7.5  $\text{mmol g}^{-1}$  for Luffa sponge oxidized was most likely at the origin of this

improvement. Indeed, in adsorbents bearing ionizable groups, the metal adsorption is mainly driven by ion exchange process and, accordingly, the higher the ionic group content, the better the adsorption capacity. However, although the content in carboxyl groups is quite high in Luffa sponge, its adsorption efficiency is lower than that of Luffa sponge oxidized. The increase in the adsorption rate for Luffa sponge oxidized compared to that Luffa sponge is presumably due to the presence of carboxyl groups. Given the presence of the carboxylic acid groups in Luffa sponge oxidized, more efficient binding of bivalent metal via chelating coordination is expected to occur for carboxylic acid groups. This enhances the adsorption efficiency of the adsorbent, and accordingly the adsorption rate is increased.

The change in the adsorbed amount of metal ions with time was studied to establish the equilibration time for maximum adsorption capacity and to assess the adsorption kinetics. For the metal studied (Pb), it was observed that the adsorption process was quite fast, approaching about 77% of the maximum adsorption capacity within the first 5 min of the process (Fig. 2).

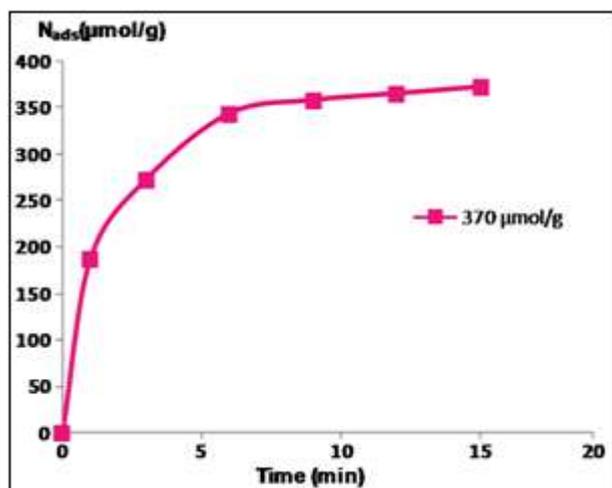


Figure 2: Effect of contact time on adsorption of metal ion  $Pb^{2+}$  by Luffa sponge oxidized

After this period, the adsorption rate decreased and saturation was reached within approximately 15 min. The evolution of the removal efficiency according to the initial concentration of metal ions is given in Fig. 4. When the initial concentration was lower than 10 ppm, the Luffa sponge oxidized exhibited a high adsorption performance with removal efficiency in the range of 90–95%, depending on the metal ions. Increasing the initial concentration of the metal above 10 ppm led to an increase in the adsorbed amount, but at the expense of the removal efficiency that oscillated between 95% and 77%. These two phenomena

might be explained by the fact that increasing the concentration of metal ions, while keeping the mass of the adsorbent constant, the probability of interaction between metal and the active site was favored. With a further increase in the metal ions concentration, less adsorption sites became accessible and the electrostatic and steric repulsion between the free and the bound metal ions reduced the extent of the adsorption. The adsorption capacity for the four ions ranged from 55 and 92  $mg\ g^{-1}$  (280 up to 540  $\mu\ mol\ g^{-1}$ ), depending on the metal and was ranked in the following order:  $Pb > Hg > Cd$ , which is the same as that of the ionic radius of the metal ions. This result demonstrates that, in addition to ion exchange process, the size of the cations also affected the adsorption capacity.

### 3.3 Effect of pH

One important factor in metal ion removal from aqueous solutions is the pH, which can affect the adsorbent surface charge and the degree of ionization. Figure 3 shows the effect of pH on the adsorption behavior. It was found that the adsorption capacities of  $Pb^{2+}$  and  $Cd^{2+}$  on Luffa sponge oxidized increased with increasing pH. When the pH values are lower ( $pH < pHPZC$ ), the concentration of protons competing with metal ions for the active sites is higher. Meanwhile, the adsorbent surface is positively charged and metal ions with positive charge have difficulty approaching the functional groups due to electrostatic repulsion. Thus adsorption capacities were found to be low at lower pH values. With the increase of pH ( $pH > pHPZC$ ), the concentration of protons decreases and the adsorbent surface charge becomes negative. Therefore, the electrostatic attraction increases between the metal ions and the adsorbent, which leads to a higher adsorption capacity. The optimum pH values which correspond to the maximum adsorption capacity of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  were observed at 5.5, 6, 5 and 6, respectively.

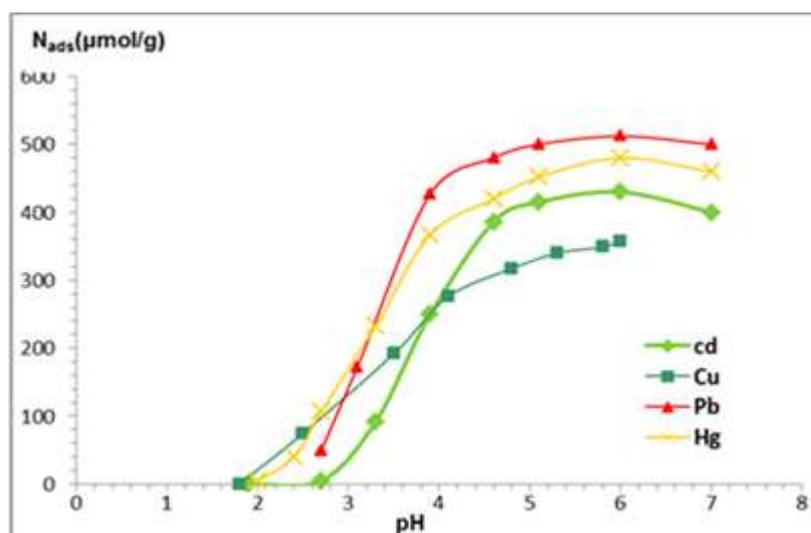


Figure 3: Effect of pH on adsorption of metal ions by Luffa sponge oxidized

### 3.4. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between the adsorbate and adsorbent, and the relationship between the concentrations of adsorbed and dissolved adsorbate at

equilibrium. For the adsorption isotherm studies, the initial metal ion concentrations were in the range of 10–200  $mg/L$  (Fig.4). Adsorption isotherms of metal ions by Luffa sponge oxidized.

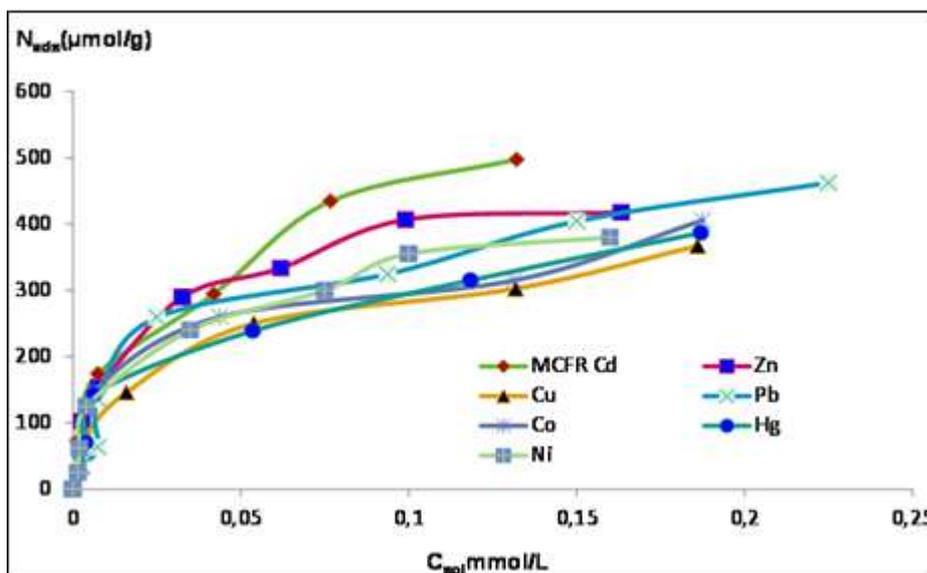


Figure 4: Adsorption isotherms of metal ions by Luffa sponge oxidized

The adsorption data have been subjected to different adsorption isotherms, namely the Freundlich and Langmuir.

### 3.4.1. Freundlich isotherm

The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of Cd(II) and Pb(II) adsorbed onto Luffa sponge oxidized at equilibrium,  $q_e$ , is

related to the concentration of Cd(II) and Pb(II) in the solution,  $C_e$ .

$$q_e = K_F C_e^{1/n}$$

This expression can be linearized to give:

$$\ln q_e = \ln K_F + (1/n) \ln C_e$$

Where  $K_F$  and  $n$  are the Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. A plot of  $\ln q_e$  versus  $\ln C_e$  would result in a straight line with a slope of  $(1/n)$  and intercept of  $\ln K_F$  and the constants are given in Table 1.

Table 1: Langmuir and Freundlich adsorption isotherm constants for  $Cd^{2+}$ ,  $Zn^{+2}$  and  $Cu^2$

Ions	Langmuir parameters			Freundlich parameters		
	$Q_{max}(mmol/g)$	$b(L/mmol)$	R	$1/n$	$K_F(mmol/g)$	R
$Cd^{2+}$	0,89	0,29	0,947	0,392	0,21	0,99
$Zn^{2+}$	0,73	0,38	0,823	0,358	0,19	0,983
$Cu^{2+}$	0,69	0,33	0,929	0,41	0,17	0,99

### 3.4.2. Langmuir isotherm

According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once a sorbet occupies a site, no further adsorption can take place at this site. Thus, the Langmuir model is given by the equation:

$$C_e/q_e = C_e/q_m + 1/bq_m$$

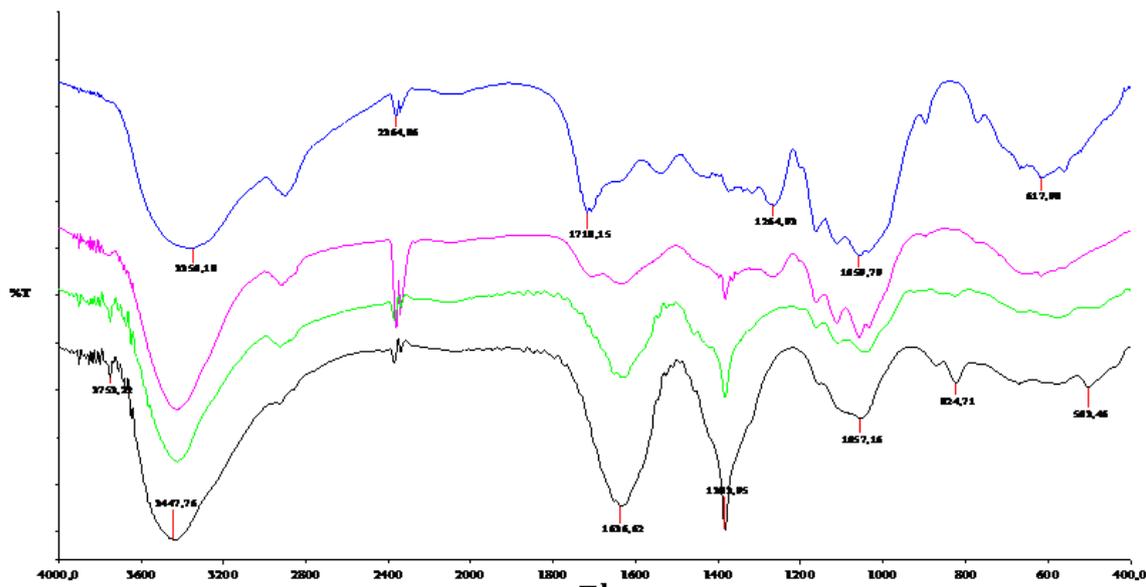
Where  $q_m$  and  $b$ , the Langmuir constants, are the saturated monolayer adsorption capacity and the adsorption equilibrium constant, respectively. A plot of  $C_e/q_e$  versus  $C_e$  would result in a straight line with a slope of  $(1/q_m)$  and intercept of  $1/bq_m$  and the calculated data are listed in Table 1. It is found that the maximum adsorption capacity of Cd(II), Hg(II) and Pb(II) are 497, 386 and 460  $\mu mol/g$ , respectively.

The bond energy ( $b$ ) of Cd(II), Hg(II) and Pb(II) are 0.002 and 0.003 L/mg, respectively. It can be concluded that Luffa sponge oxidized presents greater adsorption capacity and larger bond energy for Pb(II), Hg(II) and Cu(II). The Langmuir parameters given in Table 1 can be used to

predict the affinity between the sorbet and adsorbent and they indicate that adsorption of Cd(II), Hg(II) and Pb(II) is more favorable at higher initial metal ion concentrations than at lower ones. Based on the coefficient obtained, it can be concluded that the Langmuir equation gives a better fit to the experimental data than the Freundlich equation.

### 3.5 Adsorption mechanism

Figure 4 shows the FTIR spectra of Luffa sponge oxidized and cadmium-loaded Luffa sponge oxidized. The free carbonyl double bond stretching band at  $1718\text{ cm}^{-1}$  exhibited an evident shift to a lower frequency at  $1636\text{ cm}^{-1}$  for cadmium-loaded Luffa sponge oxidized, while the carboxyl C-O bond shifted from  $1205$  to around  $1415\text{ cm}^{-1}$ . The emergence of a new COOH band at  $1718\text{ cm}^{-1}$ ; in replacement of that at  $1636\text{ cm}^{-1}$  in the pristine Luffa sponge oxidized is indicative that upon adsorption of the metal ion, the proton of the second COOH of carboxylic acid had been transferred to the COO-group of the carboxylic acid unit (Deacon & Phillips, 1980). (Fig. 5).



**Figure 5:** FTIR spectra of Luffa sponge oxidized (a) and cadmium-loaded Luffa sponge oxidized (b: 30, 60 and 100).

The data in **Table 2** show that  $\Delta\nu$  after interaction with metal ions lied between 90 and 100  $\text{cm}^{-1}$ , which is smaller than the  $\Delta\nu$  for  $\text{Na}^+$ -carboxylate Luffa sponge oxidized ( $\Delta\nu$

= 250  $\text{cm}^{-1}$ ). This suggests that the carboxylic groups in the Luffa sponge oxidized were acting as a bidentate chelate coordinate to metal ions during the adsorption process.

**Table 2:** Adsorption capacities of metal ions and of the corresponding carboxylate symmetric and asymmetric vibrational frequencies after interaction with metal ions

Metal ion	Adsorption capacity ( $\mu\text{mol g}^{-1}$ )	$\nu_{\text{as}}(\text{COO}^-)(\text{cm}^{-1})$	$\nu_{\text{sy}}(\text{COO}^-)(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$
Cd 30	149	1645	1373	272
Cd 60	298	1640	1379	261
Cd 100	497	1636,6	1383,9	252,7

This exchange took place during the interaction process to facilitate the bidental chelation of the metal ion by the two adjacent carboxylic groups, since metal cations in aqueous solution are found mainly as hexa-aqueo cations, the adsorption mechanism may be either by inner-sphere (IS) or by outer-sphere (OS) surface metal complex formation. In the IS mechanism, water ligands are substituted by carboxylate anions resulting in a quasi-covalent bond between the surface carboxylate and the cation. On the other hand, in the OS mechanism, water ligands remain between the surface functional groups and the adsorbed cations. Accordingly, the interaction is driven by electrostatic interactions between the carboxylate groups and the hexa-aqueo cation. In order to confirm whether the IS or OS mechanism is the operative process, the evolution of the adsorption at different ionic strength was studied. Results shown in **Table 3** indicate a steady decrease in the adsorption amount as the ionic strength went up (**Fig 6**), confirming that adsorption is driven by electrostatic interaction via the OS mechanism.

**Table 3:** Thermodynamic parameters for the adsorption of  $\text{Cd}^{2+}$  on Luffa spone oxidized

T(K)	$\Delta G^\circ$ ( $\text{KJ mol}^{-1}$ )	$\Delta H^\circ$ ( $\text{KJ mol}^{-1}$ )	$\Delta S^\circ$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
298	-8,5		
313	-10,6	59,5	225
328	-13,7		

However, the possible exchange process should not be ruled out when non-dissociated carboxyl groups are still present. The decrease in adsorption with ionic strength is the classical ionic strength effect, which is due to the competition between the adsorbing cations and those from the background electrolyte.

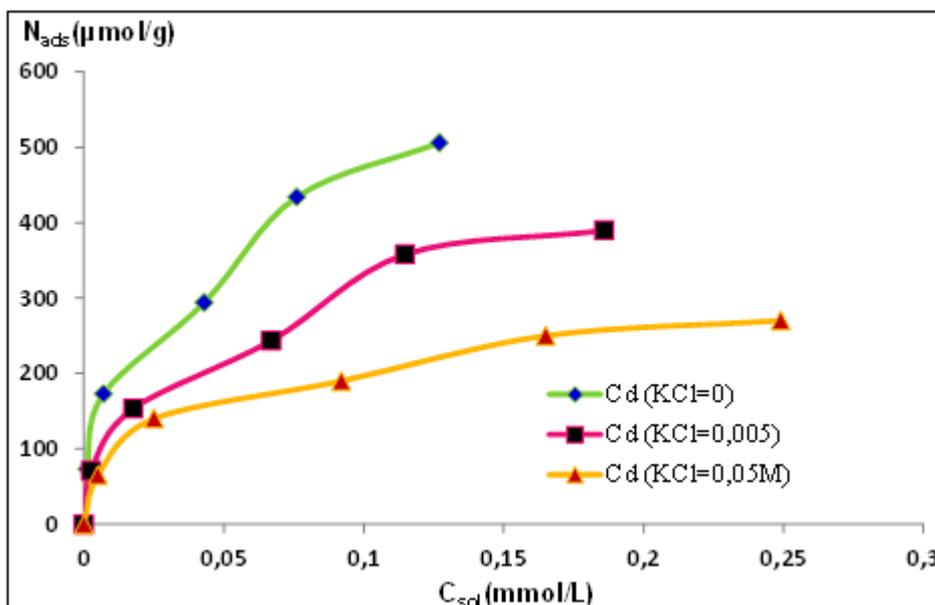
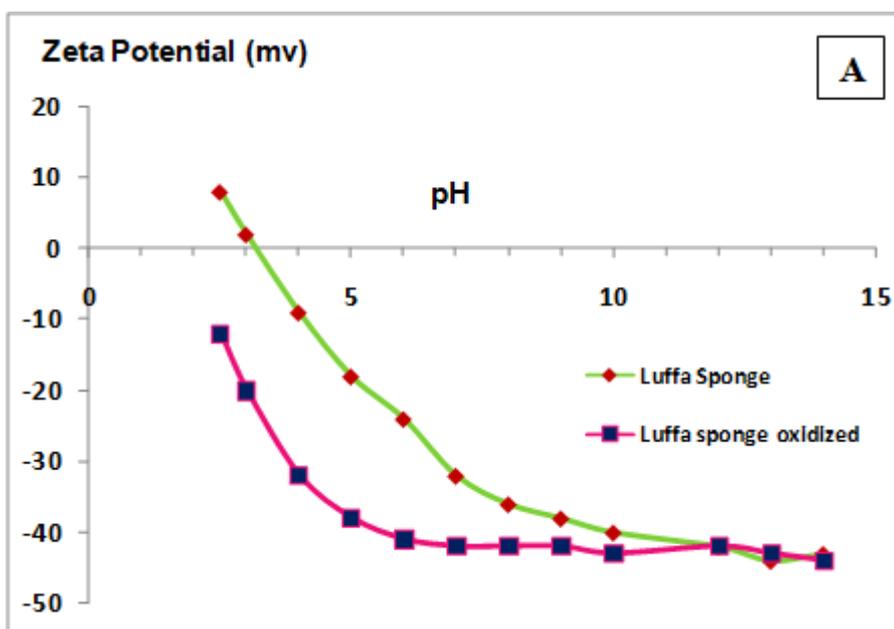


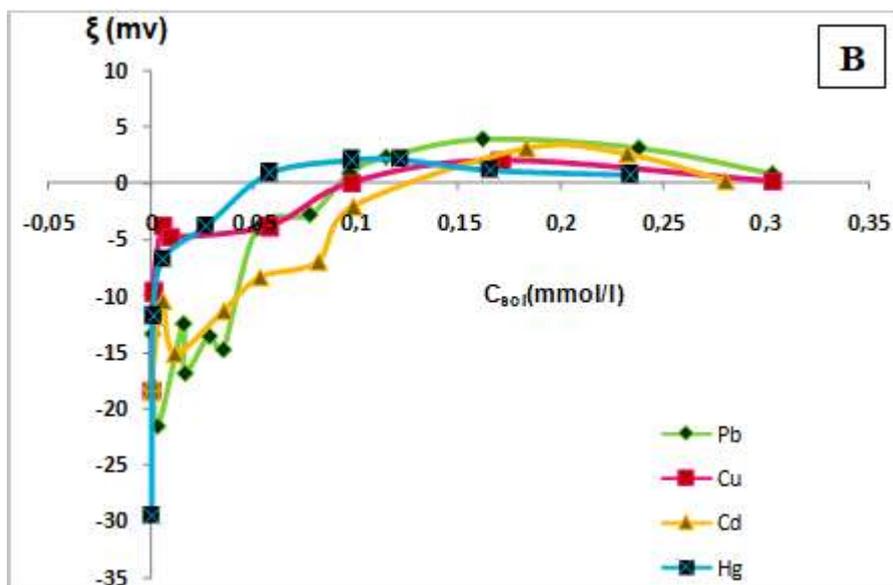
Figure 6: Cd adsorption data for 0,5 g/L (0 M ionic strength; 0.005 M ionic strength; 0.05 M ionic strength)

To further support the adsorption mechanism, a zeta-potential analysis of the Luffa sponge oxidized in the presence of metal ions was investigated.

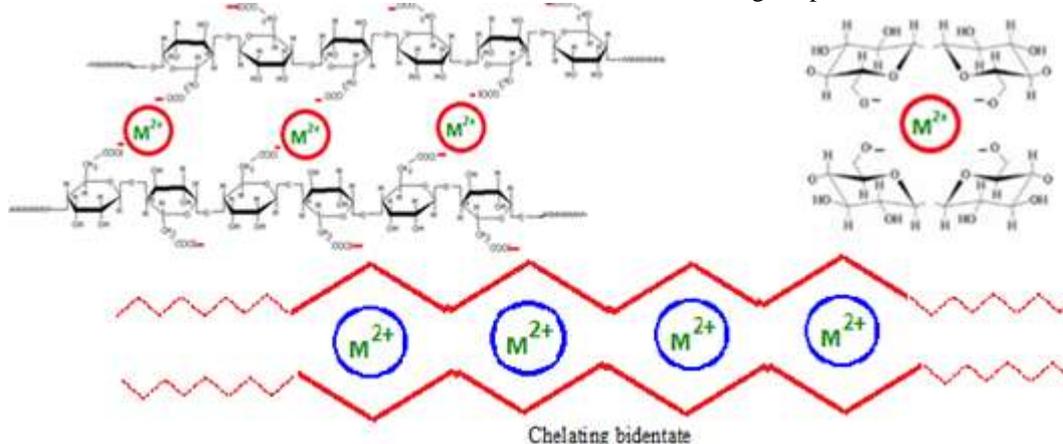
The change in the zeta-potential with pH for the pristine Luffa sponge oxidized (Fig. 7) reflected the change in surface charge according to the pH. The pristine Luffa sponge had a point of zero charge (PZC) around 3.5 and became negative above pH 4. The presence of carboxylic groups, with pKa around 4.5, was due to the oxidation pretreatment implemented on the fibers. The Luffa sponge oxidized exhibited a negative zeta potential over the whole pH range from 2,5 to 14, indicating that the surface was negatively charged in this domain. This evolution was due to the presence of carboxylic acid groups with pKa: COOH

with pKa= 4.8. Accordingly, one carboxylic acid was ionized above pH 2–3 and the two remaining carboxylic acids underwent ionization above pH 5–6. These ionized carboxylic groups constituted a binding site for the adsorption of metal ions via electrostatic interactions and/or ionic exchange mechanisms. At pH 5, the addition of Pb(II), Hg(II) or Cd(II) to the Luffa sponge oxidized led to a steady growth in the zeta-potential indicating a decrease in the density of negative charges. The same trend was noted for the two other metal ions tested. This result further confirmed that metal ions adsorption by the Luffa sponge oxidized was driven by electrostatic attraction between the negative charge on the material and the positive metal cations.





**Figure 7:** Change of the zeta-potential of (A) Luffa sponge-Luffa sponge oxidized vs pH, and (B) Luffa sponge oxidized vs metal ion concentration for  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  at pH 5.



The thermodynamic parameters, free energy of adsorption  $\Delta G^\circ$ , entropy  $\Delta S^\circ$ , and enthalpy  $\Delta H^\circ$  for the adsorption process by the Luffa sponge oxidized were determined using Van't Hoff equation:  $\ln K_c = \ln (q_e / C_e) = (\Delta S / R) - (\Delta H / RT)$  where  $K_c$  is the equilibrium distribution coefficients ( $K_c = q_e / C_e$ ),  $q_e$  and  $C_e$  the amounts adsorbed at equilibrium and the equilibrium concentration, respectively,  $R$  the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  the temperature (K). The enthalpy change was obtained by calculating the slope of a plot of  $\ln K_c$  vs  $1/T$ . The parameters obtained for Cd are listed in **Table 4**. The adsorption free energy ( $\Delta G^\circ$ ) was negative under all conditions, which reflects the spontaneity of the process.

**Table 4:** Change in the adsorption efficiency as a function of initial ionic strength

Metal ion	KCl ( $\text{mol L}^{-1}$ )	$Q_{ads}$ ( $\text{mg g}^{-1}$ )	Adsorption efficiency (%)
$Hg^{2+}$	0	350	35
	0,005	280	28
	0,05	180	18
$Cd^{2+}$	0	330	33
	0,005	260	26
	0,05	170	17
$Ni^{2+}$	0	380	38
	0,005	300	30
	0,05	200	20
$Cu^{2+}$	0	490	49
	0,005	260	26
	0,05	390	39
$Co^{2+}$	0	360	36
	0,005	290	29
	0,05	190	19
$Zn^{2+}$	0	440	44
	0,005	350	35
	0,05	230	23

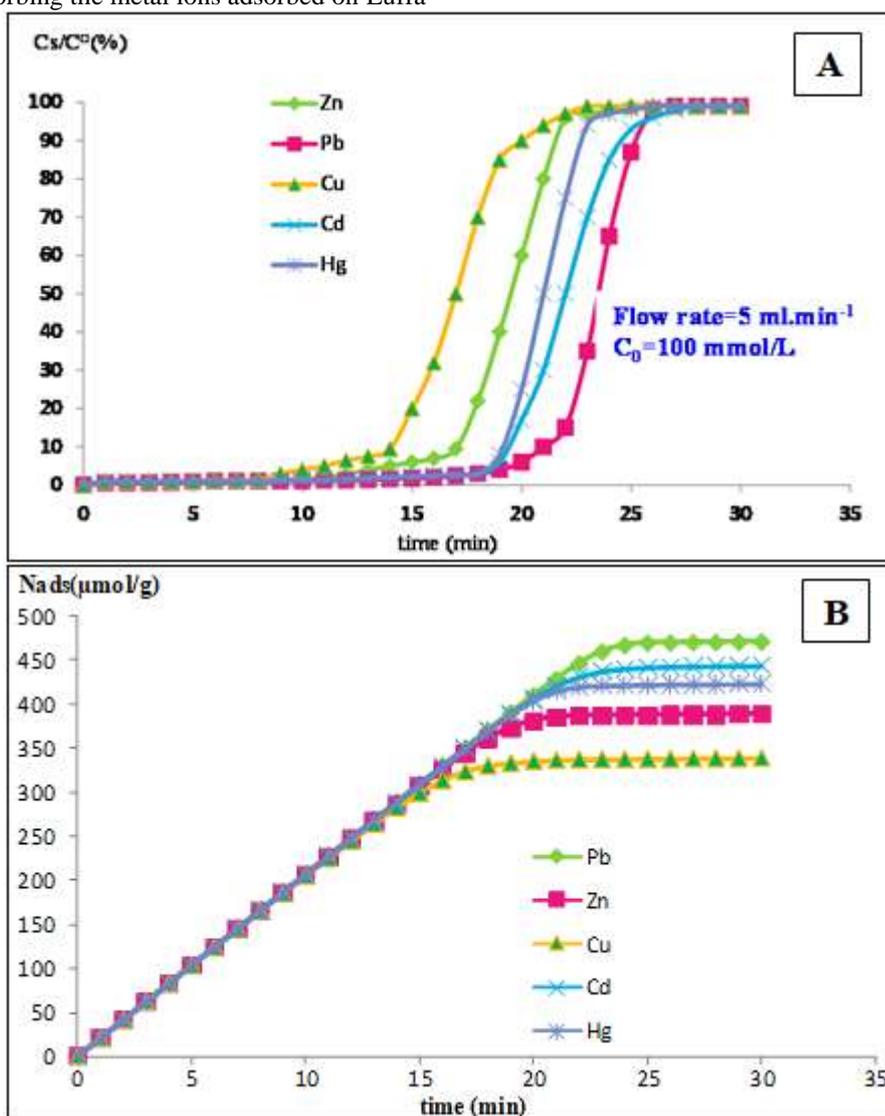
A positive enthalpy of adsorption was found, implying that the adsorption process was endothermic. The positive value

of  $\Delta H^\circ$  might be explained by assuming that when metal ions were brought into contact of the surface, their solvating water molecules were stripped off. This dehydration process requires energy and presumably it exceeded the exothermicity of the metal ions attaching to the surface. The  $\Delta S^\circ$  was also positive indicating an increased randomness at the solid/solution interface during the adsorption process, even though the metal ions were immobilized on the adsorbate. This was due probably to the higher mobility gained by water molecules lost by the adsorbate ions, thus allowing the increase in the randomness in the system.

### 3.6. Regeneration of Luffa sponge fiber

For potential practical application, it is important to examine the possibility of desorbing the metal ions adsorbed on Luffa

sponge oxidized and reusing them (Liu & Bai, 2006). The effect of five adsorption–desorption consecutive cycles on the efficiency of the individual adsorption of Cd(II), Hg(II) and Pb(II) on luffa sponge fiber was studied. **Fig 8** shows the corresponding desorption efficiencies obtained at EDTA solution. For desorption conducted with EDTA solution, it was found that the Cd(II), Hg(II) and Pb(II) adsorbed on Luffa sponge oxidized were easily desorbed. The desorption efficiency reached about 99% after the first cycle. The desorbed Luffa sponge oxidized was highly effective for the read sorption of Cd(II), Hg(II) and Pb(II), and the adsorption ability of Luffa sponge oxidized was kept constant after several repetitions of the adsorption– desorption cycles. EDTA can form steady complex with metal ions.



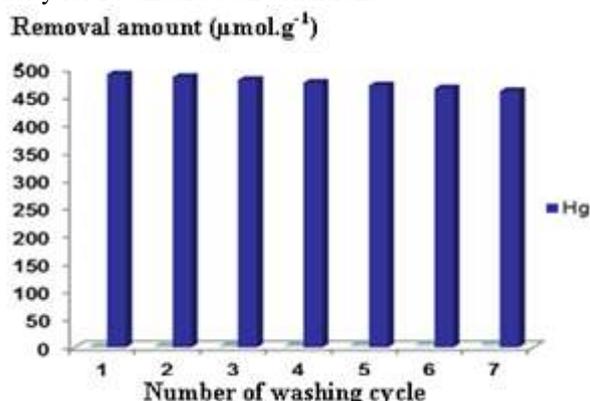
**Figure 8:** Removal rate during fixed bed column adsorption of  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  solution at (A) and the corresponding retained amount vs. time (B): Initial concentration:  $50 \text{ mg L}^{-1}$ ; flow rate is  $5 \text{ ml min}^{-1}$ ; pH = 5.5 and temperature  $25 \text{ }^\circ\text{C}$

### 3.7. Column studies

The results obtained from batch adsorption experiments showed the effective use of the Luffa sponge fiber to remove metal ions with effectiveness that might exceed 95%. To explore the adsorption capacity during continuous operation, a laboratory column filled with modified fibers was

designed. From the economic point of view, a fixed bed column is one of the most effective configurations for cyclic adsorption–desorption, allowing a more efficient use of the adsorbent. A test was conducted on  $50 \text{ mg L}^{-1}$  :  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  solution with a flow rate  $5 \text{ ml min}^{-1}$  and a glass column with 10 cm height (**Fig.9**). Removal rate during fixed bed column adsorption of  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,

$Cd^{2+}$  and  $Hg^{2+}$  solution: Initial concentration:  $50 \text{ mg L}^{-1}$ ; flow rate is  $5 \text{ ml min}^{-1}$ ; pH = 5.5 and temperature  $25^\circ\text{C}$ . The ratio ( $C_s/C_0$ ) of the effluent concentration  $C_s$  to the input concentration  $C_0$  was plotted a gain time to obtain the breakthrough curve at a constant flow rate. The breakthrough volume, defined as the point when the concentration of the effluent reaches 5% of the input concentration, was found to be around 400ml. The maximum uptake amount of the column before exhaustion was  $105 \text{ mgg}^{-1}$ , which is 30% lower than head sorption capacity for Pb under batch conditions.



**Figure 9:** Evolution of the maximum adsorption capacity under continuous flow as a function of the number washing cycle.

#### 4. Conclusion

In conclusion, Luffa sponge oxidized was synthesized and characterized by FTIR and element analysis. The capacity of Luffa sponge oxidized in adsorption Cu(II) and Pb(II) was investigated. The experimental data showed that the best adsorption performance of Luffa sponge oxidized for Cu(II) and Pb(II) ions was obtained in solution at  $\text{pH } 4.5 \pm 0.1$ . The adsorption process reached the adsorption equilibrium at about 1 h. The experimental adsorption isotherm data were well fitted with Langmuir model and the maximum adsorption capacity of Cd(II), Hg(II) and Pb(II) are 497, 386 and  $460 \text{ } \mu\text{mol/g}$ , respectively, in the solution of  $\text{pH } 4.5 \pm 0.1$ . The prepared Luffa sponge oxidized could be regenerated successfully without significantly affecting its adsorption efficiency. This study provides the relatively comprehensive data for the Luffa sponge fiber application to the removal of metal ion in the wastewater.

Luffa sponge oxidized seems to be an efficient and low cost alternative biosorbent to be considered for industrial wastewater treatment. Development of this technology for polluted effluents decontamination would likely increase seaweed demand and consequently increase the economies of countries that produce this good.

Building on the adsorption performance along with the ease of the regeneration of the sorbents, the Luffa sponge oxidized can be considered as an adsorbent for removal and recovery of dissolved organic pollutants from industrial effluents. Compared to conventional adsorbent such as activated carbon, the Luffa sponge oxidized exhibited several advantages, among which we can cite such as its availability from a renewable resource, its low energy

consumption which needn't be high neither for its production nor regeneration that can be easily conducted by a simple washing treatment.

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