*Applied Chemical Engineering (2023) Volume 6 Issue 3*
doi: 10.24294/ace.v6i3.2239

ORIGINAL RESEARCH ARTICLE

# Extraction and modification of cellulose from Artocarpus heterophyllus for biosorption of lead ion from aqueous solution as cost effective biosorbent

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## ABSTRACT

The heavy metals found in contaminated waters are dangerous for the environment and human health, so it is necessary to seek and apply techniques to remove these pollutants, using adsorption techniques with natural biopolymers as cost effective biosorbent. Since large amounts of Jackfruit (Artocarpus heterophyllus fruit) waste part are abandoned after the pulp used around Tepi areas, the possibility of developing value-added products from them is interesting innovation. In this work, cellulose fiber was extracted from Artocarpus heterophyllus fruit waste part and modified with Isopropyl alcohol groups to produce which were then used as Lead metal ion adsorbents. The modified cellulose was characterized by several techniques including Fourier transform infrared spectra (FTIR), scanning electron microscope (SEM), and thermogravimetric analysis (TGA). This modified cellulose was used as adsorbents for adsorption studies of heavy metal ions ($Pb^{2+}$) within batch adsorption systems. A solution of lead ion ($Pb^{2+}$) was used as artificial wastewater for the purpose of studying biosorption efficiencies. The biosorption efficiencies of modified cellulose were studied by using four adsorption parameters. The optimum biosorption of modified cellulose at 25 °C, were found to be 94.2%, 76.12%, 82.54%, and 90.13%, of $Pb^{2+}$ for the adsorption parameter; biosorbent dosage, contact time, Pb (II) concentration, and pH respectively. The biosorption kinetics behaviour of modified cellulose for $Pb^{2+}$ fitted well with a pseudo-second-order model with correlation coefficient of 0.9975. The biosorption isotherm behaviour was well described using the Langmuir biosorption isotherm model with higher correlation coefficient of 0.9935. The reusability and desorption study of modified cellulose shows that it can be reused 2 to 4 times and after 5th cycles the desorption was significantly decreased. This study showed that the modified cellulosic adsorbents made from (Artocarpus heterophyllus fruit) were able to efficiently adsorb metal ions from aqueous solution.

***Keywords:*** biosorption; isotherm; cellulose; lead; Jackfruit

**ARTICLE INFO**

Received: 12 June 2023
Accepted: 13 September 2023
Available online: 8 November 2023



## 1. Introduction

Water is one of the fundamental for life, in this manner, without water this world too nothing. Any natural water contains dissolved chemicals, a few of which are vital for human supplements whereas others can be destructive to human wellbeing. This basic compartment of the world can be contaminated by various human activities and natural features, like Agricultural activities, industrialization, small and large-scale sewage treatment processes, are among potentially contribute to contamination of water bodies[1]. The other Sources of water poisons broadly categorized into two; point source and non-point source. Point source contamination can be followed to particular

focuses of release and ascribed to a single, perceptible beginning. Non-point source contamination is from different scattered sources and non-point sources of contamination incorporate herbicides, insecticides, and fertilizer from agricultural fields, animal waste, textile industry, electroplating industries and toxic elements from abandoned mines[2]. Then, this contamination is carried by runoff into surface water bodies and groundwater. Nonpoint source contamination, which is the driving cause of water contamination within the world and it is ordinarily more difficult and expensive to control than point source pollution because of its low concentration, multiple sources, and much greater volume of water[2,3]. Among all the toxins, heavy metals contamination has gotten a great attention to environmental chemists due to their toxic nature. Heavy metals are usually present in trace amounts in natural waters but numerous of them are poisonous indeed at very low concentrations[4].

The main poisonous metals found in industrial products and wastewaters are Cr, Ni, Mn, Hg, Cd, Cu, Zn, and Pb. These metals are non-biodegradable and tend to accumulate in living organisms, producing various disorders[5]. From these heavy metal's bioaccumulation and biomagnification lead in plant and animals causes for the destruction of fatal brain, kidney diseases, circulatory, nervous and reproductive systems health problem directly or indirectly through food chain intake[6]. Lead is recorded a priority pollutant in drinking water and World Health Organization has set up as greatest admissible concentration for Pb (II) the maximum value of 0.01 mg/L in drinking water[7]. While lead poisoning can affect anyone, it's especially dangerous in children. It can damage children's nervous system, brain and other organs. Lead poisoning also lead to several health, and behavioral problems, including sudden brain damage and long-term intellectual deficits[8,9].

Researcher uses different number of evacuation framework to remove heavy metal and textile dyes through; chemical precipitation, coagulation/flocculation, ion exchange, filtration, evaporation, photocatalytic degradation, and Adsorption are the variety of treatment approaches available typically used to remove metal pollutants from an aqueous solution[6]. The most disadvantage of these approaches is: their powerless connection of adsorbent with metallic ion, low uptake capacity, low selectivity, and the major drawback is creation of high amount of sludge, as well as the difficulty of adsorbent and adsorbate recaptures[10]. Residual slurry, sawdust, microbial biomass, metal oxides nanoparticle and polymeric material are the countless adsorbents used for the heavy metal removal in aqueous solution[11]. Recently research is concerned with deployment of eco-friendly, biocompatible, biodegradables, naturally available and renewable raw materials such as biopolymer like starch, chitin, cellulose and its derivatives for adsorption of heavy metal from aqueous solution[12]. Therefore, the development of methods for handling pollutants into the environment, and water body that are relatively inexpensive and effective is still an aspect of research that attracts widespread attention throughout the world[13].

Generally, Biosorption is one of the most feasible methods that are generally employed for the elimination of heavy metals from water sources[14,15]. Mainly agricultural waste material as biosorbent is a promising substitution for existing ordinary removal systems due to their high accessibility and fulfils the requirements of environmental sustainability. Biosorption is preferable than other heavy metal expulsion procedure by providing flexible design, High quality treated discharge, regeneration of adsorbent and adsorbate, eco-friendly with high adsorption efficiency[16]. Among the several biopolymers, cellulose has a pronounced advantage in heavy metal removal from wastewater because of the presence of high number of hydroxyl groups presents in cellulose material which obtain great attention and modification of cellulose with non-toxic organic chemicals effectively increases the numbers of chelating sites which aids to remove heavy metal from wastewater[17]. Synthesis of Cellulose from agricultural wastes Artocarpus heterophyllus serves as double purposes. One is for environmental purpose; it converts unwanted, surplus agricultural wastes that disposed incorrectly by burning it, to useful value-added adsorbents, and another for economical purpose; using agricultural by products saves the high preparation cost of the prepared adsorbents[18,19]. By Considering, high adsorption efficiency, wide availability, high disposability and efficiency, and inexpensive methodology associated with

modified cellulosic adsorbents prepared from modifications of cellulose with any functionalizing modification, the current study, therefore, using Artocarpus heterophyllus as a new source of cellulose for developing modified cellulosic adsorbents to use as adsorbent and examine the removal efficiency heavy metal ion ($Pb^{2+}$ ions)[20]. A number of metal adsorption studies factor like solution pH, contact time, amount of dosage for adsorbent, and metal ion concentration, have been measured by using modified cellulose synthesized from waste Artocarpus heterophyllus part after the pulp used[21].

# 2. Materials and methods

## 2.1. Chemicals

Sodium Hydroxide (NaOH), sodium chlorite ($NaClO_2$, 80%), Lead nitrate ($Pb(NO_3)_2$), Glacial acetic acid ($CH_3COOH$, 98% AR), 1-Chloro isopropyl alcohol ($C_3H_7ClO$, 99.7% AR), Nitric acid ($HNO_3$ 69% AR), acetic acid (98% AR), Ethanol ($C_2H_6O$, 97% AR), and Potassium nitrate ($KNO_3$) all Chemicals were analytical grade.

## 2.2. Extraction of cellulose from Jackfruit

The natural product Jackfruit trees (Artocarpus heterophyllus) were collected from Ethiopian research institutes center, Tepi branch. The crude fiber was isolated from the internal parts of Jackfruit which was disposed after the pulp was utilized. A short time later the fiber was dried overnight in air oven at 80 °C, then the dried fiber was grounded using mechanical grinder. The extraction of cellulose was conducted according to the study of Jalija and Yahaya [22] with slight modification and briefly through taking 50 g grounded sample and dissolved in 1 L of 25% sodium Hydroxide (NaOH) at 100 °C for two hours on hot plate with magnetic stirrer. The brown liquor was decanted and the settled mixture filtered. The filtrate was rinsed with tap water for several times and with distilled water until the pH of the solution being nearly neutral. Afterward the filtered fiber was bleached with 12 g sodium chlorite ($NaClO_2$, 80%), 4 mL of glacial acetic acid ($CH_3COOH$, 98%), and 640 mL of distilled water (at ratio of, 3:1:160) at 80 °C for one hour on hot plate with magnetic stirrer of stirring speed 180 rpm. After that, the fiber was filtered and rinsed with tap water then with distilled water until the pH nearly neutral. The fiber was dried overnight in oven to remove the moisture in synthesized cellulose fiber.

## 2.3. Cellulose fiber modification

The extracted cellulose fiber needs modification for its low adsorption efficiency, due to it less functional group like hydroxyl group. The cellulose modification was performed according to the study of Daochalermwong et al.[23] with brief modification; first the cellulose fiber was grounded and sieved using 45 µ mesh to extend surface area of the cellulose powder. The extracted and sieved cellulose powder of 10 g was treated with NaOH (10% w/v) mixed with isopropyl alcohol (99.7%) employing proportion ratio of extracted cellulose/10% NaOH solution/isopropyl alcohol (1:4:20, w/v/v). The solution was stirred by magnetic hotplate stirrer for 45 minutes at 30 °C. Afterward 5 mL of sodium hypochlorite was added step wise into the solution, and the temperature were raised to 60 °C then left on hot plate magnetic stirrer for 1.5 hours with blending speed of 180 rpm. Then, the solution was neutralized by 90% of acetic acid (98% AR), and filtered. Finally, the modified cellulose was washed with ethanol (97%) solution (80% v/v), and kept in open dish to dry at room temperature until utilized as adsorbent.

## 2.4. Characterization of Extracted and modified cellulose

FTIR investigation was conducted using FTIR spectrophotometer (IR Affinity-IS, Shimaddzu, Japan). It gives information about the availability of organic and inorganic chemical functional groups that actively participate in metal ion binding. The FTIR characterization was carried out before loading of Pb (II) onto the neat cellulose, modified Cellulose and after biosorption of Pb (II). The spectrum was recorded on the

wavenumber range between 4000–400 $cm^{-1}$. The thermal stability of modified and unmodified cellulose was investigated by using Thermogravimetric analysis.

### 2.5. Preparation of stock solution

The stock solution of Lead ion ($Pb^{2+}$) of 1000 $mgL^{-1}$ solution, was prepared by dissolving 1.5986 g of Lead nitrate (Pb $(NO_3)_2$) in 1L distilled water. The Working standard solutions of Lead ion with diverse concentrations were prepared by diluting the stock solution appropriate dilution with distilled water. The pH of Lead ion solution was regulated to desired value using 0.1 M nitric acid ($HNO_3$) and sodium hydroxide (NaOH).

### 2.6. Batch adsorption studies

The biosorption of Lead ion ($Pb^{2+}$) on modified cellulose were conducted by batch biosorption tests and performed in 500 mL Erlenmeyer flasks. Throughout the studies, impact of pH on biosorption was investigated between pH range of 2–10 within the adjustment of 0.1 M $HNO_3$ and 0.1 M NaOH before the biosorption was conducted. The contact time optimization for biosorption with desired volume $Pb^{2+}$ solution and dosage of the biosorbent were investigated by hot plate magnetic stirrer, stirring speed of 180 rpm with time interval between 5–60 minutes. The starting metal concentration effect on biosorption was studied using metal ion concentration range 5–40 $mgL^{-1}$ and effect of biosorbent dosage were examined using dosage weight 100 to 250 $mgL^{-1}$. All the metal solutions were centrifuged after the required contact time was achieve and $Pb^{2+}$ ion concentrations in the supernatant solution before and after biosorption, remaining in solution was determined by using a flame atomic absorption spectrophotometer. The amount of adsorbed $Pb^{2+}$ ions per unit biosorbent (mg of metal ions par g of dry biosorbent) was calculated by using the following expression:

$$Qe = \frac{(\mathrm{Co} - \mathrm{Ce})\mathrm{V}}{M} \tag{1}$$

Where; $Qe$ is the amount of heavy metal ion adsorbed on biosorbent in mg. $g^{-1}$, V is the volume of solution in litters, Co is the initial metal ion concentration in $mgL^{-1}$, Ce is the equilibrium metal ion concentration in $mgL^{-1}$, and M is the dry weight of modified cellulose in grams.

The percent biosorption of metal ions was calculated as follows:

$$\%\mathrm{RE} = \frac{(\mathrm{Co} - \mathrm{Ce})}{\mathrm{Co}} \times 100 \tag{2}$$

where Co and Ce are initial and final concentration of metal ion respectively, RE is percent of removal efficiency.

### 2.7. Determination of pH point of zero charge (pzc)

To determine the $pH_{pzc}$ of modified cellulose, was conducted according to the study of Kuncoro et al.[24] and Viscusi et al.[25] with slight modification salt addition method was used in which a series of 6 mL Erlenmeyer flasks containing 0.05 g of modified cellulose were filled with 50 mL of 0.125 M $KNO_3$ and the initial pH was adjusted as 2, 4, 6, 8, 10, and 12 using 0.1 M $HNO_3$ and 0.1 M NaOH. The Erlenmeyer flasks were kept at room temperature in water bath and left for 48 h on a rotary shaker at 180 rpm; afterward the supernatant solution was filtered, and final pH was determined using a pH meter.

## 3. Result and discussion

### 3.1. Characteristics of biosorbent

#### 3.1.1. Analysis functional groups by FTIR

The FTIR spectroscopy strategy was utilized to better understand the nature of the functional groups that capable for the biosorption process. **Figure 1** shows the FTIR spectra of the neat cellulose modified cellulose

before and after biosorption of Pb (II). Hydroxyl (–OH), carbonyl (–C=O), and carboxylic (–COOH) groups were found in the modified cellulose. The peak around 3433 $cm^{-1}$ shifted to 3438.46 which were dominated by –OH stretching. The newly formed peak at 2927.41 $cm^{-1}$ characterized as mainly caused by C–H stretching vibrations. The peaks at 1633.4 $cm^{-1}$ and 1424 $cm^{-1}$ were moved to 1640.16 $cm^{-1}$ and 1457.92 $cm^{-1}$ respectively. This suggests the existence and increment of the corresponding –C=O and carboxylic –COOH groups, after modification of cellulose respectively[26,27].

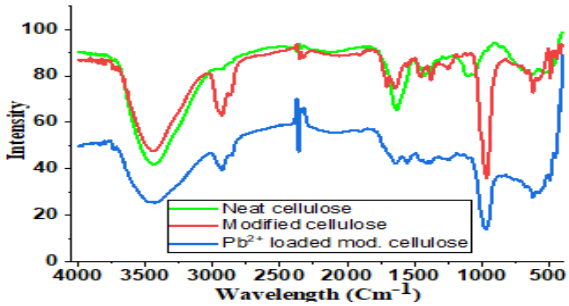


**Figure 1.** FTIR spectra of (green) unmodified cellulose, (red) modified cellulose, (blue) lead ion loaded modified cellulose.

The FTIR spectra changed a lot after the biosorption of Pb (II). The wide intense peak around 3438.46 $cm^{-1}$ weakened and shifted to 3433.64 $cm^{-1}$, demonstrating that –OH played a role in the adsorption of Pb (II) by the modified cellulose. The peak of 2927.41 $cm^{-1}$ clearly expanded and moved to 2924.52 $cm^{-1}$, and the peak at 1640–1235 $cm^{-1}$ meaningfully debilitated and the intensity of the peak was decreased. This appearance resulted from the –C=O decreasing and the corresponding –C=O increasing due to the H ions in –COOH replaced by Pb (II). The important decrease of peak intensity was also observed for the bands of finger print after adsorption. All those changes can be attributed to the engagement of some chemical groups of modified cellulose during the biosorption[23]. Generally the results of the FTIR spectra demonstrated that the functional groups responsible for the binding of Pb (II) by the Modified cellulose might chiefly consists of –OH, and –COOH and this investigation agreeing with Kofa et al.[28].

### 3.1.2. Synthesis schematic and biosorption mechanism

The two main types of adsorption mechanisms between adsorbent and adsorbate are chemisorption and physisorption. In this study the effect of different parameter data was used to check the adsorption mechanism of Pb (II) onto modified cellulose from Artocarpus heterophyllus as shown on **Figure 2**. The result obtained from experimental data is in line with the finding of Kurniawan et al.[29], Jamshaid et al.[30] and Tsade et al.[31].

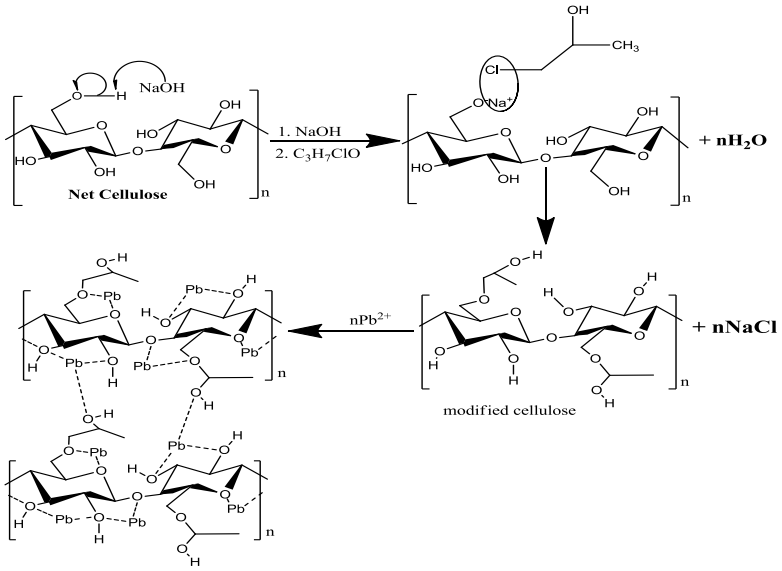


**Figure 2.** Hypothesis representation of Synthesis Schematic and biosorption mechanism of Lead ($Pb^{2+}$) by modified cellulose[29–31].

### 3.1.3. TGA analysis

The thermal properties of modified cellulose and unmodified cellulose were investigated and the results were shown in **Figure 3**. It shown that the decomposition temperature of unmodified cellulose was around 210 °C, and the modified cellulose samples was started the decomposition at about 185 °C, this result was due to the formation of cellulose esters, and may be some hydroxyl functional group, which was believed to lower the thermal stability of cellulose[32].

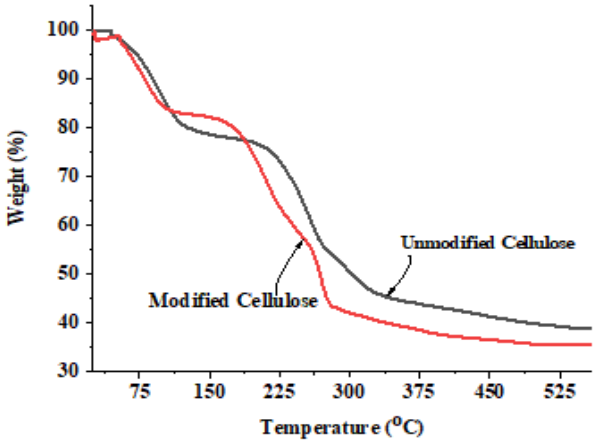


**Figure 3.** The thermograms of unmodified (black) and modified cellulose (red).

There were two stages of TGA curves of the cellulose samples depending on decomposition pattern, especially for the samples modified cellulose sample. The first stage for the temperature of 50 °C–108 °C the weight was decreased to 98% this may cause by loss of some volatile and moisture on both modified and unmodified cellulose. This result was agreed with previously reported research[33]. The second stage for the temperature of 110 °C–185 °C show the stability of modified cellulose, and 110 °C–210 °C which show the stability unmodified cellulose. After the second stage the decomposition of modified cellulose was faster the unmodified cellulose this may be come from the previous detachments of cellulose for modification make decomposition easier than that of unmodified cellulose[34].

### 3.1.4. Analysis of scanning electron microscopy (SEM) image

The morphology of modified cellulose Extracted from Artocarpus heterophyllus was analyzed using SEM with 10 µm scale and 1000 X resolution. As shown in **Figure 4a**, the SEM image of unmodified Cellulose highly aggregated, this may indicate that the existence of attachment between cellulose to cellulose and hemicellulose through the intermediate bond of lignin[35]. The second SEM image that shown on **Figure 4b** indicate that the reduction of size as a result of the treatment of cooking with sodium hydroxide, which remove the lignin that attaché the long chain of cellulose and modification of cellule was easily indicate from the wave number shift on FTIR. The modified cellulose structure was shown more irregular shape and change in size that proved the formation of modified cellulose from Artocarpus heterophyllus[15].

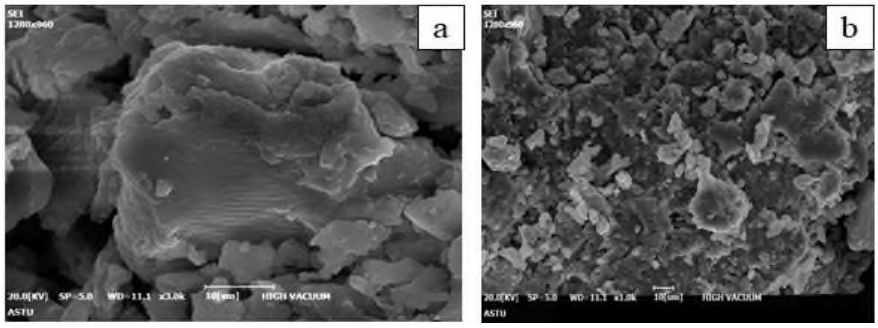


**Figure 4.** SEM image of **(a)** unmodified cellulose and **(b)** modified cellulose.

### 3.2. Effect of pH

The solution media is one of the variables for the elimination of metal ion aqueous, based on this concept the effect of pH on the elimination of $Pb^{2+}$ ion from solution is shown below in **Figure 5a**. As shown on the figure the highest percentage of removal for this study was obtained at pH 6 (90.13%) and the lowest biosorption was obtained at pH 2 (60.34%). The increasing in pH from 2 to 6 of the solution increases lead ion elimination to some extents because of decreasing for surface sites competition between lead metal ion and protons (hydrogen ion) as well as decrease in positive surface charge which results in lowering the repulsion between sorbent and metal ion this result closely similar with researcher [22].

### 3.3. Effect of metal ion concentration

The effect of initial metal ion concentration on the removal of Pb (II) ions from solution is shown in **Figure 5b** from the figure it can be seen that the highest removal percentage of Pb (II) was 82.54% at 90 mg/L concentration and afterwards with increase in the concentration of the ions there was no significant change because the occurrence of more unoccupied surface binding sites on the adsorbent fully saturated that could be responsible for removal efficiency of metal ion. On the other hand, on increasing metal concentration, equilibrium between metal ions and the adsorbent's active sites were probably established very soon thus efficiency may not bind to the adsorbent site due to the competitive effect of the metal ions for adsorptive sites[36].

### 3.4. Effect of contact time

The contact time effect of lead ion removal was studied by varying time range 5–40 minutes. The effect of contact time on the disinfecting of lead ion from solution is shown on **Figure 5c**. As point out on the figure it can be seen that the maximum removal efficiency was highest at 30 minutes with 76.12% removal efficiency and lowest at 5 minutes with 50.06% removal efficiency. From this study, as the time increment from 5 minutes to 30 minutes it was increased after the maximum adsorption, the efficiency of adsorption becomes linear, meaning the saturation point was at 30 minutes. The main concept in adsorption the rate of adsorption and desorption became equal at saturation points that means there is no adsorption site on adsorbent to be occupied by adsorbate[37].

### 3.5. Effect of biosorbent dosage

The biosorbent dosage impact on the removal rate was studied at equilibrium conditions as shown on **Figure 5d** Changing biosorbent measurement demonstrate that the amount of lead to adsorbed on biosorbent was varied, which means increasing the biosorbent dosage from 0.1–0.25 g, cause increments the biosorption efficiency from 72.87%–94.2% of lead ion. Increasing the amount of dosage (biosorbent) obviously increase the number of sites on biosorbent which leading to an increase in biosorption of lead ion modified cellulose. This works shows that similar trend with Jalali et al.[38] for the investigation of Copper, Cadmium and Nickel removal from aqueous solution using wheat stem biomass as biosorbent.

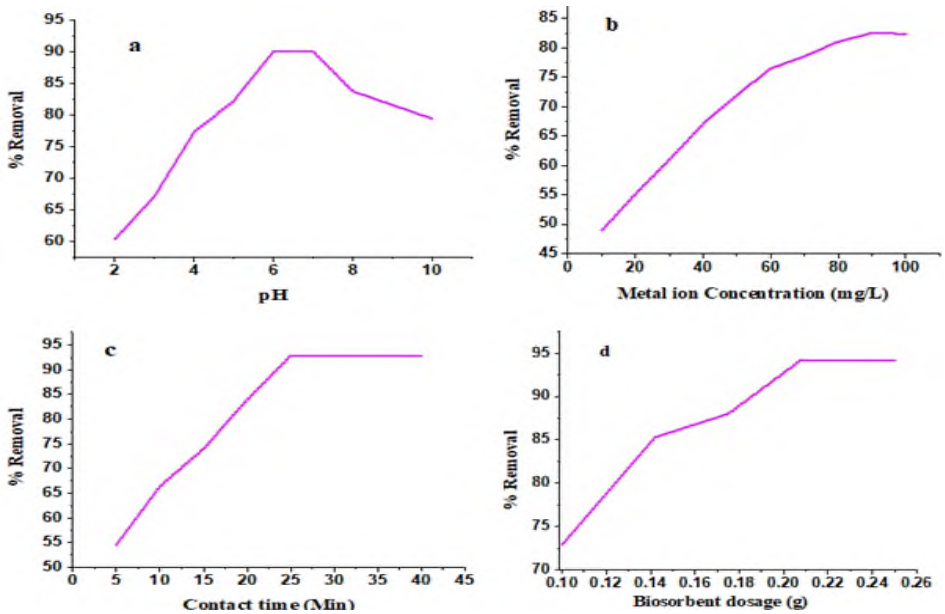


**Figure 5.** Effect of **(a)** pH, **(b)** initial ion concentration, **(c)** contact time, and **(d)** biosorbent dosage on the adsorption of Pb (II) by the modified cellulose.

### 3.6. Analysis of $pH_{pzc}$

Obviously point of zero charge ($pH_{pzc}$) is an imperative parameter to determine the net density of surface charge of biosorbent in solution[39]. According to the study of Rastuti et al.[40] the $pH_{pzc}$ was calculated from the plot of ΔpH Vs. $pH_{initial}$, the intersection points at which ΔpH = 0 specify by the value of $pH_{pzc}$ as shown in **Figure 6**. The point of zero charge was the pH at which the modified cellulose net surface charge was zero, the surface of the modified cellulose has a negative charge when pH > $pH_{pzc}$ and a positive charge at pH < $pH_{pzc}$. As indicated in **Figure 6**, it is realistic to say that the modified cellulose had more net negative charge than solution, which can contribute to reducing positive ions in aqueous solution[39,41]. Therefore, this suggested that higher %R of Pb (II) ions was detected at pH > 4.76 value, because, at solution pH > 4.76, the adsorbent surfaces are negative and thus react electrostatically with positively charged Pb (II) ions[35].

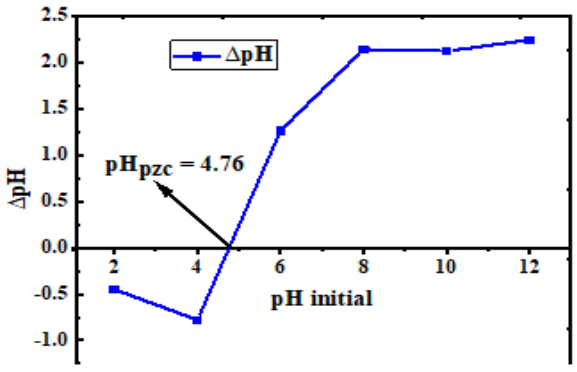


**Figure 6.** Point of zero charge plot of modified cellulose.

### 3.7. Adsorption isotherm study

Adsorption is one of well-known equilibrium separation process. There is different isotherm equation used for modelling the adsorption equilibrium, such as Langmuir, Freundlich, and Temkin.

#### 3.7.1. Langmuir adsorption isotherm

The Langmuir isotherm for the biosorption of Pb (II) by modified cellulose is shown in **Figure 7a**. The value of the coefficient of determination, $R^2$, for the Langmuir plot was found to be 0.9868. The Pb (II) ions therefore, showed a good fit of their equilibrium data for the Langmuir model which indicates a monolayer

adsorption[42]. The Maximum biosorption capacity $Q_{max}$ as calculated from the Langmuir plot was 8.92 mg/g. The values of the separation factors, RL, presented in **Table 1** (i.e., $0 < R_L < 1$) indicate that the adsorption process was a favourable one[22]. This isotherm is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is expressed by the equation below.

$$\frac{Ce}{qe} = \frac{1}{K_L Qo} + \frac{Ce}{Qo} \tag{3}$$

where $K_L$ (L/g) is a constant correlated to the adsorption/desorption energy, $Q_{max}$ (mg/g) is the maximum biosorption upon fully saturation of the adsorption, biosorbent surface[36]. $K_L$ was obtained from the graph of 1/qe against 1/Ce as a slope of the graph and $Q_{max}$ (mg/g) as the intercept.

To calculate the separation factor ($R_L$: dimensionless constant) was also calculated to test the favourability of biosorption. $R_L$ is calculated as the following using equation:

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

where $K_L$ is Langmuir isotherm constant and Co is the initial concentration of metal ion ($mgL^{-1}$). The value of $R_L$ shows the type of isotherm involved. Whereas: $R_L > 1$ Unfavourable; $R_L = 1$ Linear; $0 < R_L < 1$ Favourable; $R_L = 0$ Irreversible.

**Table 1.** Isothermal parameters obtained from the Langmuir and Freundlich models for the adsorption of Pb (II) onto the modified cellulose.

| **Langmuir isotherm model** | | **Freundlich isotherm model** | | **Temkin isotherm model** | |
|---|---|---|---|---|---|
| **Parameter** | **Value** | **Parameter** | **Value** | **Parameter** | **Value** |
| $Q_{max}$ | 8.9198109 | 1/n | 2.423 | $B_T$ | 40.54 |
| $K_L$ | 0.05195088 | $K_f$ | 0.000870563 | $K_T$ | 0.1604571 |
| $R_L$ | 0.17619347 | $R^2$ | 0.91039 | | |
| $R^2$ | 0.99352 | | | $R^2$ | 0.62684 |

### 3.7.2. Freundlich adsorption isotherm model

The Freundlich isotherm plot for the biosorption reaction was displayed in **Figure 7b** as shown below. The coefficient value of $R^2$ was found to be 0.91039 which shows that the biosorption of Pb (II) ions onto the modified cellulose had a good fit for Freundlich isotherms since the values are close to unit. The value of 1/n was calculated from the slope of the Freundlich plot between lnqe and lnCe. The value of n was 0.413 $Lmg^{-1}$, this value of n doesn't lies between 1 and 10 and this indicates that the biosorption of modified cellulose was not advantageous adsorption for Freundlich isotherm model[23]. The Freundlich isotherm was also used to correlate the adsorption equilibrium data by using linearized form of the Freundlich equation as following:

$$\ln qe = \ln K_f + \frac{1}{n} \ln Ce \tag{5}$$

where "$K_f$" and "n" are Freundlich constants, 1/n and $K_f$ demonstrate the adsorption intensity and adsorption capacity separately. The affinity of adsorbate and adsorbent will be more in case of 1/n is higher and the surface will be more heterogeneous. The values of 1/n represent the relative distribution of energy sites and it depends on the nature of adsorption process. Linear plots were obtained by plotting lnqe Vs lnCe with slope 1/n (**Figure 7b**) at different Pb (II) ions concentrations. The n and $K_f$ ($Lmg^{-1}$) (adsorption capacity) were calculated from (**Figure 7b**). The "1/n" values show that the adsorbent is effective; surface is heterogeneous and possesses great affinity for metal ions and formation of monolayer biosorption[43]. The values of $K_f$, n and $R^2$ are presented in **Table 1**.

### 3.7.3. Temkin adsorption isotherm model

Temkin isotherm model was used to determine the interaction between adsorbent and the adsorbate. The way that we can validate whether the isotherm is chemisorption or physisorption process, we have to consider the value of $B_T$ from Temkin isotherm[34]. The Temkin isotherm was also used to correlate the adsorption equilibrium data by using linearized form of the Temkin equation as following:

$$Q_e = \left(\frac{R.T}{B_T} LnA_T\right) + \left(\frac{R.T}{B_T} LnC_e\right) \quad (6)$$

This equation can also express in the other forms as shown in the follows equation:

$$Q_e = B_1.\ln K_t + B_1.\ln C_e \quad (7)$$

where $K_t = A_T$ and $B_1 = RT/B_T$. The slope of $Q_e$ versus lnCe shown on **Figure 7c** was used to determine the value of $K_t$ (Temkin suitable equilibrium constant ($Lmol^{-1}$) for maximum energy bond) and the intercept was used to determine $B_1$ ($B_1$ was related to the adsorption part itself). $C_e$ was the concentration of solution at equilibrium ($mgL^{-1}$) and $Q_e$ represents the amount of adsorption equilibrium ($mgg^{-1}$).

According to the study of Neolaka et al.[44] the indication of whether the adsorption is via ion exchange or not, can determine by calculating the value of $B_T$ of Temkin isotherm; where the value was between 8 and 16 $kJmol^{-1}$ the biosorption was happened through ion exchange. If the value is less than $-40$ $kJmol^{-1}$, the biosorption follows physisorption process. From the **Table 1** that the value of $B_T$ on modified cellulose was indicated that the process was happened via chemisorption process because the value of $B_T$ was not less than $-40$ $kJmol^{-1}$[45].

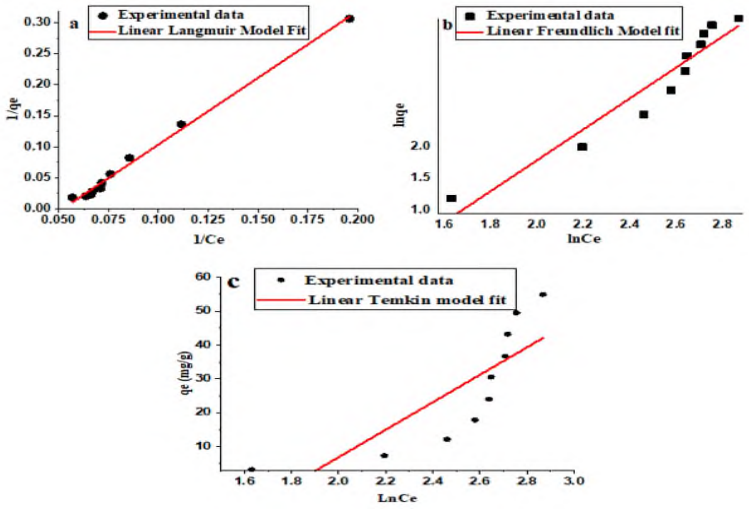


**Figure 7.** Isotherm plots of **(a)** Langmuir isotherm, **(b)** Freundlich isotherm and **(c)** Temkin isotherm model.

## 3.8. Biosorption kinetic studies

The forecast of biosorption rate is one of the most key factors for a biosorption since adsorption kinetics depends on the physical and chemical properties of the adsorbent, which affects the adsorption mechanism[46]. The investigation of adsorption mechanism of the biosorption constants of lead ion was measured using the pseudo-first-order kinetic model, and pseudo-second-order kinetic model equation[38]. Therefore; in order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order and pseudo-second-order models were applied to experimental data obtained from FAAS.

### 3.8.1. Pseudo-first-order

The pseudo-first-order kinetic model undertakes that the number of sites that solutes can occupy is proportional to the rate of adsorption[47] as indicated in **Figure 8a**. The pseudo-first-order kinetic model articulated below in equation (8):

$$\ln(qe - qt) = \ln qe - K_1 t \quad (8)$$

where qt and qe are adsorption capacities at time t and equilibrium ($mgg^{-1}$), t is contact time (min) and $K_1$ is pseudo-first-order rate constant ($min^{-1}$). The constants qe and $K_1$ $K_1$ can be calculated from the y-interception and slope of the straight line between ln (qe − qt) versus t, respectively.

### 3.8.2. Pseudo-second-order

The pseudo-second-order kinetic model includes chemisorption, where the removal of adsorbate from bulk liquid is due to the physiochemical interaction between adsorbent and adsorbate. The adsorption amount is also related to the availability of active sites on the adsorbent[24]. The pseudo-second-order kinetic model assumes that chemical adsorption can be the rate limiting stage involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate[48]. The pseudo-second-order kinetic equation is expressed as in Equation (9).

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \quad (9)$$

where $K_2$ ($gmg^{-1}$ min) is the rate constant of the second-order equation, $qt$ ($mgg^{-1}$) is the amount of biosorption at a time (min), and $qe$ is the amount of biosorption equilibrium ($mgg^{-1}$). Results show that the pseudo-second-order model was more appropriate for the adsorption of Pb (II) as justified from the correlation coefficient of adsorption using modified cellulose for pseudo-second-order kinetic model is closer to unity than for the pseudo-first-order kinetic model as shown in **Table 2**.

The linear plots of t/qe against $t$ for the pseudo-second-order model for the biosorption of Pb (II) ion onto modified cellulose is shown in **Figure 8b**. The rate constants ($K_2$) and the $R^2$ and the $qe$ values are given in **Table 2**. As shown on table the value indicates that pseudo-second order model fit biosorption lead metal on modified cellulose extracted from Artocarpus heterophyllus.

**Table 2.** Kinetic parameters of pseudo first order and pseudo second order model for adsorption of Pb (II) onto the modified cellulose.

| **Pseudo-first-order** | | **Pseudo-second-order** | | **Intraparticle diffusion** | |
|---|---|---|---|---|---|
| **parameter** | **Value** | **parameter** | **Value** | **Parameter** | **Value** |
| $K_1$ | −0.0008175 | $K_2$ | 0.03445437 | $K_{id}$ | 0.5768 |
| qe (mg/g) | 3.57852248 | qe (mg/g) | 7.18752246 | $C_{id}$ | 3.1758 |
| $R^2$ | 0.90189 | $qe^2$ | 51.6604791 | $R^2$ | 0.9289 |
| | | $R^2$ | 0.9975 | | |

### 3.8.3. Intraparticle diffusion model

Diffusion mechanism from the solid/liquid interface to the interior of the solid particles plays an important role in shaping the metal ions adsorption overall rate[42]. During a solid/liquid adsorption process, the adsorbate passage from the bulk solution phase to the internal active sites on the modified cellulose and transfer is usually controlled by liquid phase external mass transfer (boundary-layer diffusion)[18]. To validate the diffusion process, the experimental data of lead ion biosorption by modified cellulose were studied using the intra-particle diffusion model represented by following Equation (10) shown below[38,18]:

$$qt = K_{id}\sqrt{t} + C_{id} \quad (10)$$

where qt was the amount of adsorbate adsorbed on biosorbent at a given time t (min), $C_{id}$ represent the intercept, and $K_{id}$ (mg/g $min^{1/2}$) the value of intraparticle diffusion rate constant. The values of $K_{id}$ and $C_{id}$ were determined from the plot of qt vs. $\sqrt{t}$ as shown on **Figure 8c**.

As shown on the **Figure 8c** the intraparticle diffusion model, have low correlation coefficient ($R^2$ = 0.7701) suggests that the adsorption process was not controlled by intraparticle diffusion. Due to the relatively smooth surface morphology of the prepared bio-adsorbents, it is possible to conclude that the intraparticle diffusion of lead into the adsorbent was unlikely[42].

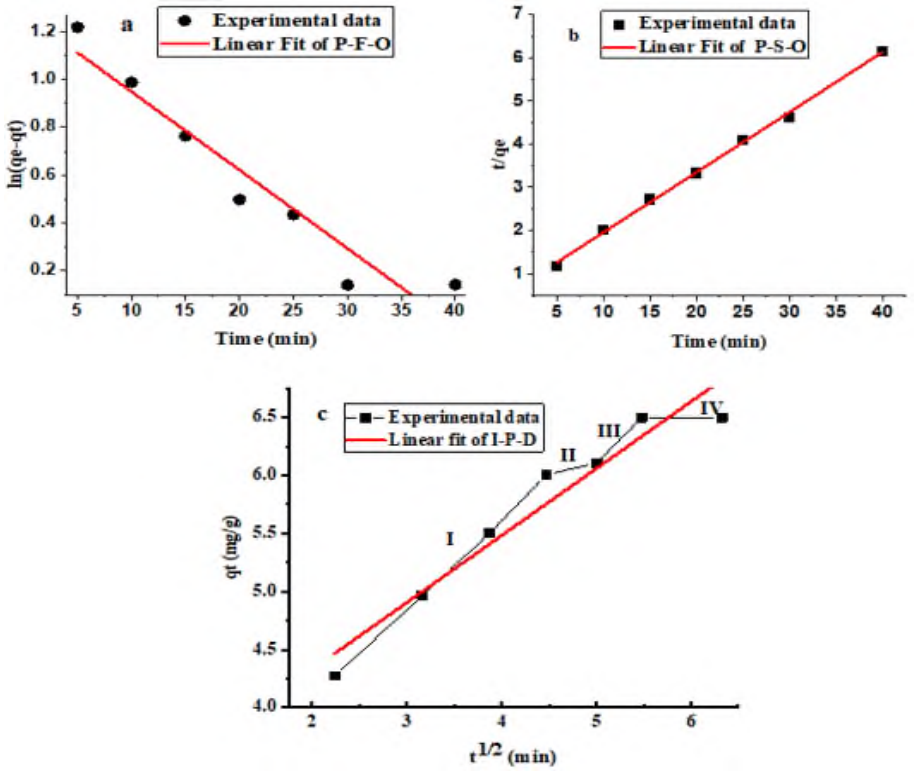


**Figure 8.** Plots of **(a)** pseudo first-order, **(b)** pseudo second order, and **(c)** Intraparticle diffusion kinetics model.

From **Figure 8c** intra-particle diffusion plot shows that the adsorption occurs in IV stage. The first, sharper region, fastest step, the plot is linear due to mass transfer which is attributed to the diffusion of Pb (II) is transported from the bulk solution to the modified cellulose surface. In this stage the rapid adsorption was very fast because of the strong interaction between the Pb (II) and the modified cellulose surface. On the second stage to third stage there was slow and reestablishments of biosorption of modified cellulose this may be caused by the competition between Lead ion and some other cation in solution. The fourth stage was pronounced the diffusion slowdown on very limited active site; followed by forming the final diffusion equilibrium of intra-particle diffusion and become stationary, because all the active sites of modified cellulose was occupied this result was similar with the study of Ali et al.[18].

## 3.9. Reusability of biosorbent

The reusability of biosorbent study is very critical parameters for real-world application of modified cellulose. The recovery of the modified cellulose was studied by adding 0.1 g of modified cellulose into 50 mL of 0.125M $HNO_3$ solution at 30 °C for 180 min. The desorption/adsorption ratios, defined as the amount of metal ion removed over the initial amount adsorbed, were presented in **Figure 9** corresponding to the different numbers of cycle. Evidently as shown on **Figure 9**, as the numbers of cycle increased, the desorption ratio decreased gradually after 4th cycle. It was found that 70.8% and 68.78% of Pb (II) was desorbed in the 5th and 6th recycle respectively. Therefore, the adsorbent modified cellulose demonstrated excellent recycling ability for the desorption of the Pb (II) up to the fourth cycles.

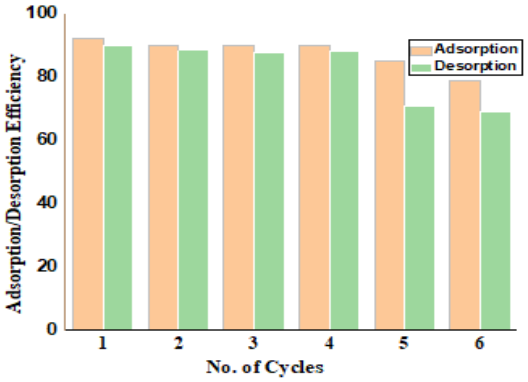


**Figure 9.** Adsorption/Desorption ratios of modified cellulose adsorbent at different cycles.

## 4. Conclusions

Successfully cellulose fiber was extracted from Artocarpus heterophyllus using alkali cooking method afterward the extracted cellulose was successfully modified with alcohol (Isopropyl alcohol) groups to use as biosorbent. The results of FT-IR showed that there was a change on the functional groups such as hydroxyl, carboxyl and carbonyl on the modified cellulose that enhance the adsorption effect. The SEM image was showed that there is significant change on structure and morphology of modified cellulose before and after modification which had a certain adsorption effect on heavy metal ions ($Pb^{2+}$). TGA analysis showed that the modified cellulose had less stable than neat cellulose (unmodified cellulose). This result may be happened in case of change in functional group on modified cellulose. From biosorption parameter (pH effect, metal ion conc. effect, contact time effect, and dosage effect) it was found that the modified cellulose had maximum biosorption for $Pb^{2+}$ within a given pH rage of 2–10 was 90.13% at the pH 6 and dosage from 0.1–0.25 g, was 94.23% at the dosage of 0.208 g; this result relatively shows the maximum result comparing with another researcher investigation. However, other parameter of biosorbents also possesses good biosorption efficiencies when compared to other biosorbents that have the same functional group, potentially due to the differences in the number of active sites per weight of the adsorbents. In the study of biosorption time, it was found that for $Pb^{2+}$ solutions the time required to reach equilibrium adsorption was shorter. In the kinetic model study, a pseudo-second-order model yielded a higher correlation coefficient ($R^2$ = 0.9975) than other kinetic model; this describe that well fit of pseudo-second-order model for biosorption behaviour of $Pb^{2+}$ onto modified cellulose. Additionally, the adsorption isotherm behaviour for adsorbate onto adsorbent was well described using the Langmuir isotherm model which shows the highest correlation coefficient ($R^2$ = 0.9935); since the adsorption behaviour of adsorbents involved monolayer chemisorption in this study. The reusability study data shows that modified cellulose can be recycled 2 to 4 times. From the results of this investigation, there is countless possibility for the growth of low-cost biosorbent materials like cellulose. This study showed that the cellulose fiber which extracted from Artocarpus heterophyllus and can be modified and can be used as heavy metal ion adsorbents.

## Author contributions

Conceptualization, DJ and DW; methodology, DJ; software, DJ and DW; validation, DJ, DW and GT; formal analysis, DJ, DW and GT; investigation, DJ, DW and GT; resources, DJ; data curation, DW and GT; writing original draft preparation, DJ; writing review and editing, DW and GT; visualization, supervision, DJ; project administration, DJ; funding acquisition, DJ, DW and GT. All authors have read and agreed to the published version of the manuscript.

## Acknowledgments

All the authors greatly acknowledge Mizan Tepi University (MTU).

## Data availability

Upon request the data used during the current study are available from the corresponding author.

## Declarations

All authors are declared that this work not published elsewhere.

## Informed consent

Informed consent was obtained from all of the authors of this article.

## Conflict of interest

The authors declare no conflict of interest.

## References


1. Furlan FL, Filho NC, Consolin MFB, et al. Use of agricultural and agroindustrial residues as alternative adsorbents of manganese and iron in aqueous solution. *Revista Ambiente & Água* 2018; 13(2): 1. doi: 10.4136/ambi-agua.2181
2. Viman OV, Oroian I, Fleşeriu A. Types of water pollution: Point source and nonpoint source. *AACL Bioflux* 2010; 3(5): 393–397.
3. Park M, Choi YS, Shin HJ, et al. A comparison study of runoff characteristics of non-point source pollution from three watersheds in South Korea. *Water* 2019; 11(5): 966. doi: 10.3390/w11050966
4. Akl M, Ismail MA, Hashem MA, Ali DA. Synthesis, spectroscopic characterization and adsorption studies of $Cu^{2+}$, $Hg^{2+}$ and $Pb^{2+}$ from environmental water samples. *Research Square* 2021; preprint.
5. Boudrahem F, Aissani-Benissad F, Soualah A. Adsorption of lead(II) from aqueous solution by using leaves of date trees as an adsorbent. *Journal of Chemical & Engineering Data* 2011; 56(5): 1804–1812. doi: 10.1021/je100770j
6. Verma A, Kumar S, Kumar S. Biosorption of lead ions from the aqueous solution by Sargassum filipendula: Equilibrium and kinetic studies. *Journal of Environmental Chemical Engineering* 2016; 4(4): 4587–4599. doi: 10.1016/j.jece.2016.10.026
7. Morosanu I, Teodosiu C, Paduraru C, Ibanescu D, Tofan L. Biosorption of lead ions from aqueous effluents by rapeseed biomass. *New Biotechnology* 2017; 39: 110–124. doi: 10.1016/j.nbt.2016.08.002
8. Neolaka YAB, Lawa Y, Naat J, et al. Indonesian Kesambi wood (Schleichera oleosa) activated with pyrolysis and $H_2SO_4$ combination methods to produce mesoporous activated carbon for Pb (II) adsorption from aqueous solution. *Environmental Technology & Innovation* 2021; 24: 101997. doi: 10.1016/j.eti.2021.101997
9. Darmokoesoemo H, Magdhalena, Putranto TWLC, Kusuma HS. Telescope snail (Telescopium sp) and mangrove crab (Scylla sp) as adsorbent for the removal of $Pb^{2+}$ from aqueous solutions. *RASAYAN Journal of Chemistry* 2016; 9(4): 680–685.
10. Marwani HM, Lodhi MU, Khan SB, Asiri AM. Cellulose-lanthanum hydroxide nanocomposite as a selective marker for detection of toxic copper. *Nanoscale Research Letters* 2014; 9(1): 466. doi: 10.1186/1556-276x-9-466
11. Hassan M, Liu Y, Naidu R, et al. Mesoporous biopolymer architecture enhanced the adsorption and selectivity of aqueous heavy-metal ions. *ACS Omega* 2021; 6(23): 15316–15331. doi: 10.1021/acsomega.1c01642
12. Ha HT, Huong NT, Dan LL, et al. Removal of heavy metal ion using polymer-functionalized activated carbon: Aspects of environmental economic and chemistry education. *Journal of Analytical Methods in Chemistry* 2020; 2020: 8887488. doi: 10.1155/2020/8887488
13. Neolaka YAB, Riwu AAP, Aigbe UO, et al. Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes. *Results in Chemistry* 2023; 5: 100711. doi: 10.1016/j.rechem.2022.10071
14. Khera RA, Iqbal M, Ahmad A, et al. Kinetics and equilibrium studies of copper, zinc, and nickel ions adsorptive removal on to Archontophoenix alexandrae: Conditions optimization by RSM. *Desalin Water Treat* 2020; 201: 289–300. doi: 10.5004/dwt.2020.25937
15. Rahaman H, Islam A, Islam M, et al. Biodegradable composite adsorbent of modified cellulose and chitosan to remove heavy metal ions from aqueous solution. *Current Research in Green and Sustainable Chemistry* 2021; 4: 100119. doi: 10.1016/j.crgsc.2021.100119
16. El Maghrabi AH, Marzouk MA, Elbably MA, Hassouna MEM. Biosorption of manganese by amended aspergillus versicolor from polluted water sources. *Nature Environment and Pollution Technology* 2020; 19(4): 1645–1656. doi: 10.46488/nept.2020.v19i04.032

17. Cichosz S, Masek A, Rylski A. Cellulose modification for improved compatibility with the polymer matrix: Mechanical characterization of the composite material. *Materials* 2020; 13(23): 5519. doi: 10.3390/ma13235519
18. Ali RM, Hamad HA, Hussein MM, Malash GF. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering* 2016; 91: 317–332. doi: 10.1016/j.ecoleng.2016.03.015
19. Kuncoro EP, Mitha Isnadina DR, Darmokoesoemo H, et al. Characterization and isotherm data for adsorption of $Cd^{2+}$ from aqueous solution by adsorbent from mixture of bagasse-bentonite. *Data in Brief* 2018; 16: 354–360. doi: 10.1016/j.dib.2017.11.060
20. Daneshfozoun S, Nazir M, Abdullah B, Abdullah M. Surface modification of celluloses extracted from oil palm empty fruit bunches for heavy metal sorption. *Chemical Engineering Transactions* 2014; 37: 679–684. doi: 10.3303/CET1437114
21. Mahalakshmi R, Preethi K, Kalaiselvi D, et al. Adsorption behaviour of chemically modified cellulose bearing benzothiazole chelating group towards lead ions from water bodies. *RASĀYAN Journal of Chemistry* 2019; 12(1): 245–250. doi: 10.31788/rjc.2019.1215001
22. Jalija DO, Yahaya MG. Removal of lead (II) ions from aqueous solution using calcium alginate beads. *Science World Journal* 2020; 15(4): 128–131.
23. Daochalermwong A, Chanka N, Songsrirote K, et al. Removal of heavy metal ions using modified celluloses prepared from pineapple leaf fiber. *ACS Omega* 2020; 5(10): 5285–5296. doi: 10.1021/acsomega.9b04326
24. Kuncoro EP, Isnadina DRM, Darmokoesoemo H, et al. Characterization, kinetic, and isotherm data for adsorption of $Pb^{2+}$ from aqueous solution by adsorbent from mixture of bagasse-bentonite. *Data in Brief* 2018; 16: 622–629. doi: 10.1016/j.dib.2017.11.098
25. Viscusi G, D'Amico F, Gorrasi G. In situ one-step fabrication of layered double hydroxide deposited on cellulose: Effect of modified cellulose on physical properties of polyurethane composites. *Polymers for Advanced Technologies* 2022; 33(7): 2300–2312. doi: 10.1002/pat.5684
26. Zeng G, He Y, Liang D, et al. Adsorption of heavy metal ions copper, cadmium and nickel by Microcystis aeruginosa. *International Journal of Environmental Research and Public Health* 2022; 19(21): 13867. doi: 10.3390/ijerph192113867
27. Thirumavalavan M, Lai YL, Lin LC, Lee JF. Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms. *Journal of Chemical & Engineering Data* 2009; 55(3): 1186–1192. doi: 10.1021/je900585t
28. Kofa GP, Nkoue Ndongo GR, Kameni Ngounou MB, et al. Grewia spp. biopolymer as low-cost biosorbent for hexavalent chromium removal. *Journal of Chemistry* 2019; 2019: 6505731. doi: 10.1155/2019/6505731
29. Kurniawan TW, Sulistyarti H, Rumhayati B, Sabarudin A. Cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) as adsorbents of heavy metal ions. *Journal of Chemistry* 2023; 2023:5037027. doi: 10.1155/2023/5037027
30. Jamshaid A, Hamid A, Muhammad N, et al. Cellulose-based materials for the removal of heavy metals from wastewater—An overview. *ChemBioEng Reviews* 2017; 4(4): 240–256. doi: 10.1002/cben.201700002
31. Tsade H, Anshebo ST, Sabir FK. Preparation and characterization of functionalized cellulose nanomaterials (CNMs) for Pb(II) ions removal from wastewater. *Journal of Chemistry* 2021; 2021: 5514853. doi: 10.1155/2021/5514853
32. Saravanan R, Ravikumar L. The use of new chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. *Journal of Water Resource and Protection* 2015; 7(6): 530–545. doi: 10.4236/jwarp.2015.76042
33. Miao J, Sun H, Yu Y, et al. Quaternary ammonium acetate: An efficient ionic liquid for the dissolution and regeneration of cellulose. *RSC Advance* 2014; 4(69): 36721. doi: 10.1039/c4ra06258b
34. Neolaka YAB, Supriyanto G, Kusuma HS. Adsorption performance of Cr(VI)-imprinted poly(4-VP-co-MMA) supported on activated Indonesia (Ende-Flores) natural zeolite structure for Cr(VI) removal from aqueous solution. *Journal of Environmental Chemical Engineering* 2018; 6(2): 3436–3443. doi: 10.1016/j.jece.2018.04.053
35. Villabona-Ortíz Á, Figueroa-Lopez KJ, Ortega-Toro R. Kinetics and adsorption equilibrium in the removal of azo-anionic dyes by modified cellulose. *Sustainability* 2022; 14(6): 3640. doi: 10.3390/su14063640
36. Yogeshwaran V, Priya AK. Biosorption of heavy metal ions from the aqueous solutions using porous Sargassum Wightii (SW)brown algae: batch adsorption, kinetic and thermodynamic studies. *Research Square* 2022; preprint.
37. Ibrahim LA, El-Sesy ME, ElSayed EE, et al. Simultaneous removal of metal ions from wastewater by a greener approach. *Water* 2022; 14(24): 4049. doi: 10.3390/w14244049
38. Jalali A, Mirnezami F, Lotfi M, et al. Biosorption of lead ion from aqueous environment using wheat stem biomass. *Desalin Water Treat* 2021; 233: 98–105. doi: 10.5004/dwt.2021.27518
39. Manzoor K, Ahmad M, Ahmad S, Ikram S. Synthesis, characterization, kinetics, and thermodynamics of edta-modified chitosan-carboxymethyl cellulose as Cu(II) ion adsorbent. *ACS Omega* 2019; 4(17): 17425–17437. doi: 10.1021/acsomega.9b02214
40. Rastuti U, Siswanta D, Pambudi W, et al. Synthesis, characterization and adsorption study of C-4-Phenacyloxy-phenylcalix [4]resorcinarene for Pb(II), Cd(II) and Cr(III) Ions. *Sains Malaysiana* 2018; 47(6): 1167–1179. doi: 10.17576/jsm-2018-4706-12

41. Neolaka YAB, Lawa Y, Naat J, et al. Evaluation of magnetic material IIP@GO-Fe3O4 based on Kesambi wood (Schleichera oleosa) as a potential adsorbent for the removal of Cr(VI) from aqueous solutions. *Reactive and Functional Polymers* 2021; 166: 105000. doi: 10.1016/j.reactfunctpolym.2021.105000
42. Jaihan W, Mohdee V, Sanongraj S, et al. Biosorption of lead (II) from aqueous solution using Cellulose-based Bio-adsorbents prepared from unripe papaya (Carica papaya) peel waste: Removal Efficiency, Thermodynamics, kinetics and isotherm analysis. *Arabian Journal of Chemistry* 2022; 15(7): 103883. doi: 10.1016/j.arabjc.2022.103883
43. Ali A. Removal of Mn(II) from water using chemically modified banana peels as efficient adsorbent. *Environmental Nanotechnology, Monitoring & Management* 2017; 7: 57–63. doi: 10.1016/j.enmm.2016.12.004
44. Neolaka YAB, Lawa Y, Naat J, et al. A Cr(VI)-imprinted-poly(4-VP-co-EGDMA) sorbent prepared using precipitation polymerization and its application for selective adsorptive removal and solid phase extraction of Cr(VI) ions from electroplating industrial wastewater. *Reactive and Functional Polymers* 2020; 147: 104451. doi: 10.1016/j.reactfunctpolym.2019.104451
45. Neolaka YAB, Lawa Y, Naat J, et al. Adsorption of methyl red from aqueous solution using Bali cow bones (Bos javanicus domesticus) hydrochar powder. *Results in Engineering* 2023; 17: 100824. doi: 10.1016/j.rineng.2022.100824
46. Sharma M, Singh J, Hazra S, Basu S. Adsorption of heavy metal ions by mesoporous ZnO and $TiO_2$@ZnO monoliths: Adsorption and kinetic studies. *Microchemical Journal* 2019; 145: 105–112. doi: 10.1016/j.microc.2018.10.026
47. Neolaka YAB, Lawa Y, Naat J, et al. Efficiency of activated natural zeolite-based magnetic composite (ANZ-Fe3O4) as a novel adsorbent for removal of Cr(VI) from wastewater. *Journal of Materials Research and Technology* 2022; 18: 2896–2909. doi: 10.1016/j.jmrt.2022.03.153
48. Zhang Y, Zhao J, Jiang Z, et al. Biosorption of Fe(II) and Mn(II) ions from aqueous solution by rice husk ash. *BioMed Research International* 2014; 2014: 973095. doi: 10.1155/2014/973095