Adsorption of Nickel (II) Ion Aqueous Solution by using *Leucaena leucocephala* Pod

Nor Shafika Buniran, and Noor Harliza Abd Razak

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*-Removal of nickel is focused since the presence of nickel in wastewater or aqueous solution becomes harmful to human health and environment at a high level of nickel uptake. The adsorptive removal of Ni (II) metal ion was studied using chemically modified *Leucaena leucocephala* pod adsorbent which is an economic agricultural waste. The characterization of *Leucaena leucocephala* pod adsorbent was evaluated by Thermogravimetric Analysis (TGA), X-ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR). The effects of pH, contact time and adsorbent dose on the percentage removal and adsorption capacity of Ni (II) metal ion have been investigated. The results show that the point zero charges (pHpzc) of the adsorbent was identified at pH 6. The maximum percentage removal of Ni (II) ions on *Leucaena leucocephala* pod was 89.7% at pH 8. The adsorption amount of Ni (II) metal increased with time and reached equilibrium after 160 minutes. 0.25 g of adsorbent dosage was the most optimum and economical for the adsorption of Ni (II) heavy metal. Hydroxyl, ether and C-O-C groups were the major components that help in the adsorption of Ni (II) ion as identified by the FT-IR analysis. The modified *Leucaena leucocephala* adsorbent was proven as one of a potential and promising biosorbent for efficient adsorption and removal of Ni (II) ions from aqueous solution and also industrial wastewater.**

***Keywords*- Nickel, *Leucaena leucocephala*, pHpzc, pH, Dosage, Contact time**

1.0 INTRODUCTION

Nowadays, the discharge of the industrial effluents becomes a major environmental problem because the discharge is mainly contained toxic heavy metals, organic and also inorganic materials. The pollution of water bodies and the land is mainly caused by the unmethodical dumping of wastes either directly or indirectly into the river water due to the massive growth of the industrial sector [1]. Generally, the characteristics or properties of heavy metals found in the industrial effluent are cannot be decomposed by bacteria and are soluble in aqueous solution. There is an estimated that the total waste generation by Malaysia consists of 61% of agricultural waste, 26% of hazardous waste, 12% of municipal solid waste and 1% of electronic waste [2].

Presence of nickel in wastewater or aqueous solution becomes harmful to human health and environment at a high level of nickel uptake. Nickel is one of the highest priority toxic metal exists in water that should be properly removed. Nickel (II) metal concentration of 0.0001mg/L will fatal and can cause a serious case of pollution and illness to the human body. Nickel sources are mainly come from natural sources and also anthropogenic activity, and is widely distributed into the environment in either from mobile or stationary sources, which present in water bodies, oil, biological matter, and environment [3]. Generally, tobacco, stainless steel kitchen utensils, dental or inexpensive jewelry, contributed to the environmental sources of nickel, while the examples of natural sources of nickel are vegetation, volcanic eruptions, forest blazes. Nickel is essential to the human body at trace amount, however, at above 250 mg of nickel uptake is toxic to the human body. More bizarre symptoms that may occur are dermatitis, respiratory problems, also cancer [4].

Different methods for the Ni (II) removals, for example, chemical methods such as coagulation, electro floatation, and electrokinetic coagulation are hard to dispose and cause various problems with the disposal. Other methods such as membrane separation, and ion exchange are very costly to implement for heavy metals removal. Therefore, it is necessary to search for a possible replacement method that can control or prevent all the related problems caused by the

use of the chemicals and physical methods, which is the biosorption method. According to [5], biosorption is defined as a physiochemical methods to accumulate heavy metals from industrial wastewater and aqueous solution. There are many merits of using biosorption as a method to remove heavy metals such as it is economically efficient and attractive because of the use of biomass which is abundant in nature and inexpensive. Biosorption also gives a high energy saving or recovery for a more effective industrial effluent treatment system. The biomass help in the evacuation of substantial heavy metals, in which the metals stick on to the outside surface of the biomass. Biosorption also offers low operating cost, no need for the additional nutrient requirements and also minimization of biological and chemical sludge. The previous studies have conducted a various experiment for the removal of heavy metals by using various types of different bio-adsorbent such as sawdust [6], rice husk [7], rice straw [8], sea-weed [9], tea waste [10], etc. out of the wide and variety types of adsorbents.

Leucaena leucocephala pod is chosen since it seems like a good adsorbent and can be used as one of the candidates for the heavy metals removal in water. *Leucaena leucocephala,* which is biomass in agricultural waste are cheap, environment-friendly biomass and are readily abundantly available. Mansur, Ahmad, Megat, & Ismail, (2015) studied that *Leucaena leucocephala* pod consists of several functional groups which are hydroxyl, carbonyl, alcohols, carboxylic acids, ester, ethers, and C-O-C functional groups, and concluded that an abundant amount of hydroxyl, C-O-C and ether groups presence helps in the adsorption process by providing an active sites for the adsorption process. *Leucaena leucocephala* pods are used in the removal of heavy metals especially nickel (II) because of the ability is strongly attributed to the hydroxyl, amino, and ether functional groups found in the *Leucaena leucocephala* [11]. *Leucaena leucocephala* green pods mainly consist of 21.6% cellulose, 14.6% lignin, and 9.4% hemicellulose [12]

Therefore, the purpose of this study was to characterize the properties of *Leucaena leucocephala* pods by using FTIR, TGA, XRF, and Zeta potential. The study focused on the effect of pH, contact time and dosage in the removal of Nickel (II) by using *Leucaena leucocephala* pods biosorbent.

2. METHODOLOGY

2.1 Preparation of the *Leucaena leucocephala* Pod Biosorbent.

Leucaena leucocephala seed pods samples were collected from roadside around Shah Alam, Selangor. Then, the *Leucaena leucocephala* seed pods were rinsed thoroughly with distilled water to remove the dirt and undesirable materials. The seed pods were then dried in an oven at 353 K (80 ˚C) for 72 h until reached consistent weight. The seeds were then removed from the pods and ground into smaller particles size of 400µm.

2.2 Modification of *Leucaena leucocephala* pod.

2.2.1 Removal of Chlorophyll Content.

200 mL of distilled water in the 250 mL beaker was boiled until it reached 100˚C. 100 g of dried *Leucaena leucocephala* biomass of 400 µm was then placed into the beaker. The mixture was agitated at 220 rpm and at 290˚C for 10 minutes. It was filtered after cooling and the residue was dried in an oven overnight to a consistent weight at 105˚C.

Next, 100 g of dried biomass that has been free of silica content was transferred into a 1000mL beaker. 500 mL of 96% ethanol was added. The mixture was stirred at 300 rpm at 60 ˚C for 3 hours. It was then filtered after cooling and the residue was dried in an oven until reached consistent weight at 105˚C [13]. The removal of chlorophyll was essential in order to break the cell membrane, to soften the leaf cuticle and also to allow the biosorbent to react with any starch present that will help in the adsorption of Ni (II) ion. [13].

2.2.2 Removal of Lignin Content.

100 g of dried *Leucaena leucocephala* biomass that has been free of silica and chlorophyll contents was transferred into a 1000mL beaker. 500 mL of 0.1 N HCl solution was added. The mixture was agitated for 3 h at 323 K (50˚C) with a magnetic stirrer. Then, the residue was filtered and flushed thoroughly with distilled water until achieved pH 7 (neutral condition). It was then oven dried at 353 K (80˚C) for 48 h until reached consistent weight [14].

2.3 Batch adsorption experiment

Series of 250 mL conical flask along with 100 mL treatment solution at 50 ppm Ni (II) concentration was adopted under batch adsorption studies, which were carried out by batch method. The Inductively Coupled Plasma (ICP i-CAP 6300 Duo Analyzer) was used to measure the concentrations of nickel (II) ions. The percentage removal of nickel (II) metal ion can be determined and was calculated by following the equation:

$$\frac{C_0 - C}{C_0} \times 100\% \qquad (1)$$

Where C_0 is the initial concentration while C are the final concentration of nickel (II) ion (mg/L). The adsorption capacity nickel (II) ion by using *Leucaena leucocephala* pod adsorbent was measured using a mass balance equation (2) as stated by (Basu, Guha, & Ray, 2017).

$$q = \frac{(C_0 - C) \times V}{m} \qquad (2)$$

Where q is the amount of nickel (II) ion uptake (mg/L), m symbolizes the mass of biosorbent (g), and V represents the sample volume of nickel (II) solution (L).

2.3.1 Effect of pH.

The scope of pH under this study was from pH 2 to 12 conducted at a constant adsorbent dosage to determine the optimum pH in the biosorption of nickel (II) ions. 25 mL of Ni (II) solution of 50 ppm (50mg/L) was poured into a 100 mL of beaker. Either sodium hydroxide (0.1 M NaOH) or hydrochloric acid (0.1 N HCl) solutions were used to get the desired initial pH value of the Nickel (II) solution. Then, 0.25 g of *Leucaena leucocephala* adsorbent was added into the resulting solution that was poured into 250 mL conical flask. The mixture was placed into a shaker for 24h at room temperature (27 ˚C) with an unsettling rate of 120 rpm. Next, the solution was filtered to separate the residue with the solution. The filtrate was then analyzed using ICP i-CAP 6300 Duo Analyzer to determine the final concentration of Ni (II) metal ion [14].

2.3.2 Effect of Biosorbent Dose.

25 mL of 50 ppm of Ni (II) solution was poured into 250 mL conical flask at the optimum condition at pH 8. Biosorbent doses used in the experiment were from 0.01-1.0 g. The flasks containing the mixture were then placed into a shaker with a rotation speed of 120 rpm for 24 h. Next step, the solutions were filtered to separate the residue with the solution and diluted. ICP i-CAP 6300 Duo Analyzer was used to determine the final concentrations of Ni (II) after the adsorption process had occurred [14].

2.3.3 Effect of Contact Time.

The range of contact time considered under this study was 10, 20, 40, 60, 100, 120, 140, 160 and 180 minutes. A series of 250 mL conical flask each consist of 0.75 g of *Leucaena leucocephala* pod biosorbent and 100 mL of 50 ppm of Ni (II) was conducted in this experiment. The mixture was placed in a shaker at ambient temperature (27˚C) and at 120 rpm. The residues were filtered and the filtrates were analyzed using ICP i-CAP 6300 Duo Analyzer equipment to find the final concentration and to determine the adsorption capacity of the biosorbent to remove Ni (II) ion [14].

2.3.4 Determination of Point of Zero Charge (pHpzc) of *Leucaena leucocephala* pod adsorbent.

The pHpzc of *Leucaena leucocephala* pod was determined by pH titration method, in which 25 mL of 0.01 M KNO3 solution was poured in a series of six conical flasks from pH 2 to 12. 0.1 M NaOH or 0.1 M HCl solutions was used to adjust the solutions in order to obtain the desired pH of the solution. 0.1 g of *Leucaena leucocephala* pod adsorbent was then added in each flask and then agitated at 120 rpm in a shaker for 24 h. The initial (pHi) and final pH (pHf) of the solutions were analyzed using ICP i-CAP 6300 Duo Analyzer equipment and the difference in the initial and final pH of the solution (ΔpH) was calculated. The graph of pHi versus (pHi-pHf) was plotted. Based on the graph, the point of charge (pHpzc) was identified at the point at which the curve of pHi versus (pHi-pHf) crosses the x-axis.

2.4 Analysis of Equipment

2.4.1 Thermogravimetric Analysis (TGA) of *Leucaena leucocephala* adsorbent

Thermogravimetric analysis (TGA) which is one of an approach of thermal analysis that measured the mass of the sample as the temperature changes. TGA also used to determine thermal stability, to predict the composition of materials and can characterize the weight loss due to decomposition, oxidation, reduction and also sorption or desorption [15]. The model used was Mettler-Toledo (M) TGA851/1600. The sample of 10-20 mg is prepared for most applications, while 50-100mg is for measuring volatiles. TGA was basically conducted by using nitrogen gas. The temperature ranging from 0-1000˚C and the heating rate used in the TGA equipment was 10˚C/min [16]. First of all, the adsorbent was degassed at 200˚C in a nitrogen environment for a duration of 1 h.

2.4.2 Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared (FTIR) spectroscopy used was Perkin Elmer Spectrum One FT-IR Spectrometer, is the only analytical method that can provide the information on both ambient temperature operation and the ability to monitor the functional groups or binds presents such as carboxyl, hydroxyl, amino, ether, etc., which will characterize the molecular structure and the chemical reactions [17]. For this FTIR analysis, the wavelength used is from 500-4000 wavelength (cm-1).

2.4.3 X-Ray Fluoresence (XRF)

XRF analysis equipment was used to study the chemical composition of *Leucaena leucocephala* pod adsorbent, in which characteristic X-ray peak of different wavelengths represents different elements. The procedure was conducted by pelletizing the sample to 6 mm masks using wax as a folio with a powder to the proportion of 10 g to 3 g and then the sample was analyzed using Thermo-Fisher Scientific (Flash 2000 CHNS/O) Analyzer.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of *Leucaena leucocephala* pod adsorbent.

3.1.1 Point of Zero Charge (pHpzc)

The point of zero charges (pHpzc) is defined as the condition when the surface of the pH of the adsorbent suspension has a net charge of zero [18]. At this pHpzc, the charge of the positive and negative surface sites are equal. If the pH of solution is higher than pHpzc (pH>pHpzc), the surface charge will be deprotonated by OH- ions present in the solution while if the pH of the solution is lower than pHpzc (pH<pHpzc), basically the adsorbent surface will be protonated by the competition of H+ ions, (Putra et.al, 2017). Based on the experiment conducted to determine the pHpzc for *Leucaena leucocephala* pod adsorbent after been plotted in Figure 1, the observed pHpzc of the adsorbent was 6.00 [19].

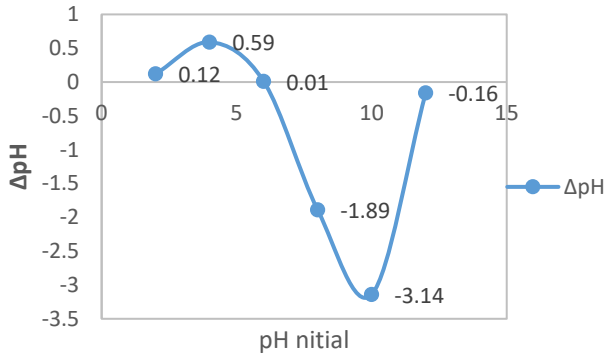


Figure 1: Point Zero Charge of *Leucaena leucocephala* pod adsorbent (pHpzc)

Villaescusa, (2009) stated that at (pH>pHpzc), the adsorbent surface is negatively charged and could only interact with positively charged metal, meanwhile at (pH<pHpzc), the adsorbent surface is basically positive and will interact with a negative type of metal. Therefore, from Figure 1, the pHpzc of *Leucaena leucocephala* pod adsorbent was at pH 6, in which when at pH lower than pHpzc, the adsorbent was positively charged and vice versa at pH solution more than pHpzc.

3.1.2 TGA Analysis

Figure 2 demonstrates the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of *Leucaena leucocephala* pod adsorbent samples of raw, modified and after adsorption of Ni (II) ions. These samples were firstly warmed under flowing air (nitrogen) up to a conclusive temperature of 996.1 ˚C. TGA is utilized to determine the weight reduction percentage of materials concerning the temperature of thermal degradation which can be determined through the TGA curves. On the other hand, DTG results will show the corresponding rate of weight reduction, in which the maximum curve of DTG is able to compare the thermal stability characteristics of different materials and also as a measure of thermal decomposition [20].

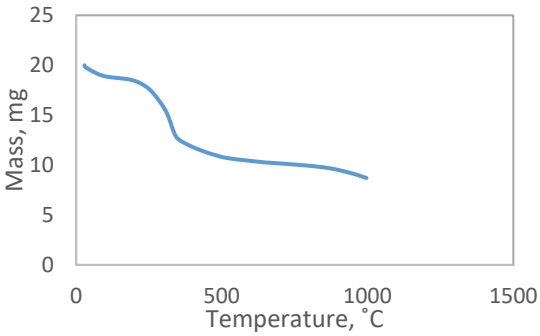
The weight losses of components can be determined in four stages in the TGA curves [21]. Basically, an initial weight loss of the samples will occur at a temperature below 100˚C, in which the change is contributed by the hydrophilic characteristic of the lignocellulosic components. The initial moisture content of the analyzed fibers component will affect the weight reduction as the temperature increases. From the observation of the previous study, the sharper weight loss is observed at a higher temperature. Basically, this is contributed by the presence of cellulose, hemicellulose, and lignin in the chemical composition of the biosorbent [22].

Figure 2 (a) (i) represented the TGA curve for raw *Leucaena leucocephala* pod adsorbent that shows about 5.44% of initial weight loss up to temperature rise of 61˚C was mainly caused by the evaporation of moisture content present in the raw sample. The second step at a temperature range from 61 ˚C to 318 ˚C, the process involved the degradation of hemicellulose, in which the maximum decline of the sample mass and residual weight of the biomass adsorbent after this stage was about 40 %. At temperature of 321 ˚C to 512 ˚C, about 22% of sample residue left that may be accounted for pyrolysis of cellulose. The decomposition of lignin occurred until 1000 ˚C that caused further weight loss of the biomass sample [23]. From the TGA analysis, it shows that the major components exist in raw *Leucaena leucocephala* pod was hemicellulose that is easily degraded, the second major component was cellulose and the lignin was the least that was the last to degrade due to its stability. Moreover, the difference between raw and modified *Leucaena leucocephala* pod adsorbent can be observed, in which the thermal stability of the modified sample increased due to the bleaching treatment.

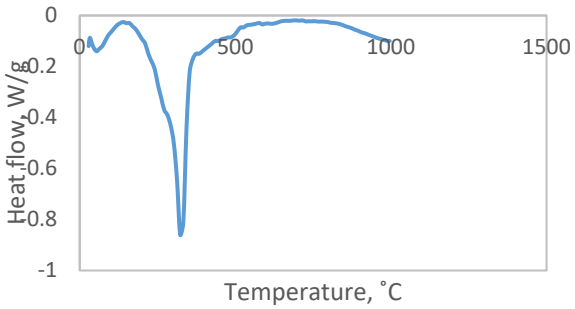
Figure 2 (b) (i) represented the TGA curve for modified *Leucaena leucocephala* pod adsorbent. The curve revealed that up to temperature rise of 55 ˚C, the initial weight loss was about 6.7% that may be caused by the evaporation of moisture content inside the sample. Next, at a temperature range of 55-351˚ C, the degradation of hemicellulose occurred [24]. This step showed that the maximum reduction in the sample mass and residual mass of the biomass after this phase was 59.49%. From the analysis, the hemicellulose present in the modified biomass adsorbent increased compared to raw *Leucaena leucocephala* pod biomass.

The cellulose was pyrolyzed from 351-547.74 ^{0}C. The cellulose content also increases compared to raw biomass sample due to the treatment process to modify the *Leucaena leucocephala* pod adsorbent. This can be seen from the mass decomposed for modified biomass sample was higher which was 11.06 mg compared to raw sample which was 6.45 mg. A further loss of weight continued until 1000 ^{0}C decomposing lignin [23]. The composition of lignin can be seen decreased from 10.77 mg to 6.52 mg. This result obtained shown that the amount of lignin present in the *Leucaena leucocephala* pod decreased after it was treated. As a result, a higher amount of Ni (II) metal ion can be adsorbed into the modified *Leucaena leucocephala* pod adsorbent.

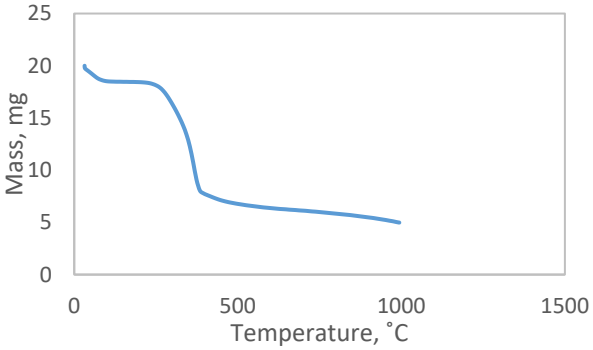
Moreover, based on our results, it was observed that the decomposition of cellulose and hemicellulose at the temperature between 140-550^{o}C which can be overlapped at these temperatures. The similar result was obtained by the previous study by (Burhenne, Messmer, Aicher, & Laborie, 2013) [25]. Usually, the decomposition of hemicellulose occurred at a temperature range of 225-325 ˚C while cellulose at 325-375˚C. Meanwhile, the decomposition of lignin occurred at a temperature between 512-1000˚C [26]. Therefore, it can be observed that the lignocellulosic material in the bio sorbent is important which serve as active sites for adsorption due to wide pore sizes and low surface area characteristics [27].



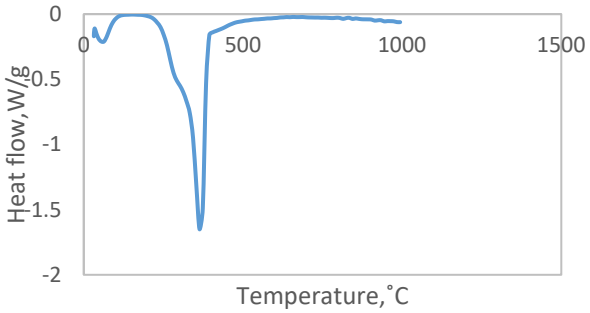
(a) (i)



(a) (ii)



(b) (i)



(b) (ii)

Figure 2: TGA curve (a) (i) and DTG curve (a) (ii) for raw *Leucaena leucocephala* pods, and TGA analysis (b) (i) and DTG curve (b) (ii) for modified LLP.

3.1.3 FT-IR Analysis

The FT-IR analysis was conducted to determine the functional groups present in the *Leucaena leucocephala* adsorbent and the possible interaction between the metals and these functional groups [11]. The FT-IR spectra of raw *Leucaena leucocephala* pod before and after Nickel (II) adsorption was shown in Figure 3.

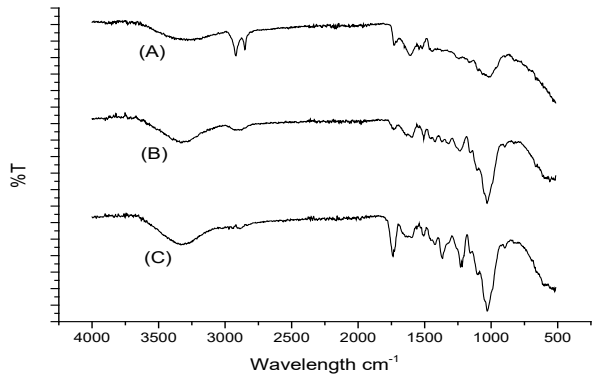


Figure 3: FT-IR spectra of raw, modified and after adsorption of Ni (II) ion for *Leucaena leucocephala* pod.

For *Leucaena leucocephala* pod adsorbent, the wide peak showed at 3327 cm^{-1} demonstrated the

stretching of hydroxyl (-OH) group. The characteristic of alkynyl C=C stretch is demonstrated at 2194 cm^{-1}. The peak at 1736 cm^{-1} was associated with the carbonyl group (C=O). The broad peak observed at 1594 cm^{-1} represent the aromatic C=C and amino bonding. C-O-stretch is detected by the peaks around 1000-1300 cm^{-1}. After Ni (II) was adsorbed on the *Leucaena leucocephala* pod adsorbent surface, a shift in wavenumber from 3327 to 3321 cm^{-1} was observed. The functional group that was responsible in the binding of Ni (II) ions was identified as hydroxyl group at this specific range of wavelength. Another functional group that could be helpful in adsorbing Ni (II) ions was C-O-C as there was a shift in wavenumber from 1232 to 1229 cm^{-1}. Based on this FT-IR study, it can be concluded that the major groups of hydroxyl, ether and C-O-C present on *Leucaena leucocephala* pod adsorbent provide active sites for Ni (II) to adsorb [11].

3.1.4 XRF

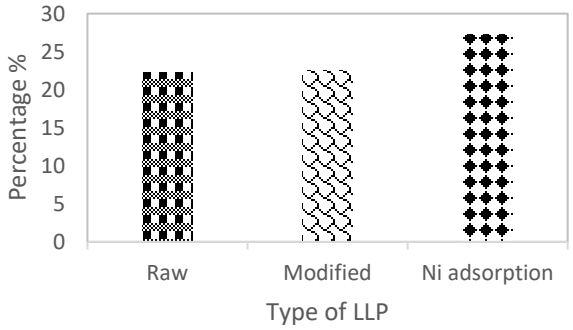


Figure 4: The percentage of Ni (II) component exist in raw, modified and after adsorption in *Leucaena leucocephala* pod biosorbent.

The result showed that there was a slight increase in the percentage of nickel in the surface of the raw LLP and modified LLP, which is 22.3% and 22.5% respectively. After adsorption occurred, the percentage of nickel in the LLP surface increased to 27.3%. This indicated that LLP adsorbent is capable of adsorbing Ni (II) ion in the adsorption process.

3.2 Effect of pH

Indisputably, solution pH which is one of the factors that governs sorption phenomenon by influencing the charge of the surface of the biosorbent and the level of ionization of the metal in the adsorption experiment. Other factors such as mobility and sequestration and metal specification also contributing to the adsorption process [28]. The best and ideal pH was observed to be pH 8. Figure 5 showed that the biosorption capacities were basically dependent on the pH of solution, in which at lesser pH value the adsorption capacities were low and increased gradually with an increase in the pH of the solution. The biosorption capacities were significantly increased from pH 2 to 4, then slightly increased from pH 4 to 8, and decreased as the pH reached pH 8 (Fig. 1). A sharp increase of Ni (II) adsorption occurs after pH 4, and the maximum uptake of Ni (II) is at pH 8. Figure 5 shows that the adsorption of Ni (II) ion onto *Leucaena leucocephala* pod adsorbent was dependent on the pH of the solution.

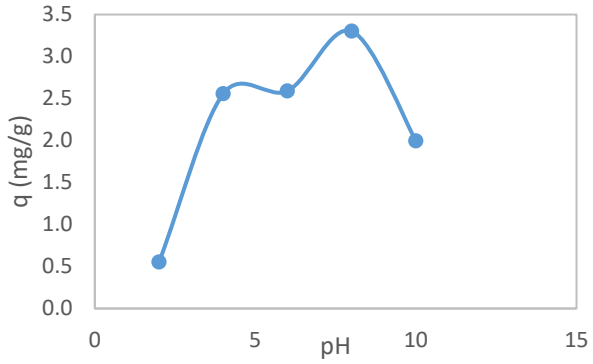


Figure 5: Effect of pH on biosorption of Ni (II) on *Leucaena leucocephala* pod adsorbent at room temperature (27 ± 0.5) and 0.25 g adsorbent dose.

The observed point of zero charges (pHpzc) of *Leucaena leucocephala* pod was 6.0. At pH < pHpzc, the adsorption capacities were low since the hydrogen ions occupied the surface of adsorbent with apparent prevalence over Ni (II). Meanwhile, at pH > pHpzc, the biosorption of Ni (II) would be higher since there are more vacant active sites available [29].

At the lower pH (pH <pHpzc~6.0), protons (H^+) possess aggressive race to occupy the adsorbent

surface and a higher competition occur at that region between Ni (II) ion and hydrogen ion which results in lower adsorption capacity and percentage removal of Ni (II) ions [14], [30]. Basically, similar results showed that at low pH which is an acidic condition, the percentage removal of Ni (II) ion is low and increases at higher pH values (alkali) has been reported by many studies [31], [32]. At lower pH values, the surface charge on the surface of the *Leucaena leucocephala* pod adsorbent is positive. The limited adsorption of Ni (II) ions was caused by an electrostatic repulsion that exists between the *Leucaena leucocephala* surface, which is positively charged and the cationic Ni (II) ions. Moreover, a declined uptake of Ni (II) ions also contributed by the higher concentration and competition of H^+ in the solution that will compete with Ni (II) ions for the adsorption sites [32]. The comparison of the Ni (II) concentration of the solution with and without the addition of adsorbent at different pH values are shown above (Fig.6).

The gradually increase in pH brought about a better Ni (II) adsorption capacities by reducing the electrostatic repulsion between the *Leucaena leucocephala* adsorbent and Ni (II), which decreased the competition for Ni (II) to occupy the adsorbent surface [11], [14]. At higher pH values (pH >pHpzc~6.0), the sorbent surface becomes negatively charged due to the deprotonation reaction. Thus, the adsorption capacities of Ni (II) metal ions is increased due to the strong electrostatic attraction between the metal ions and *Leucaena leucocephala* pod biosorbent surface.

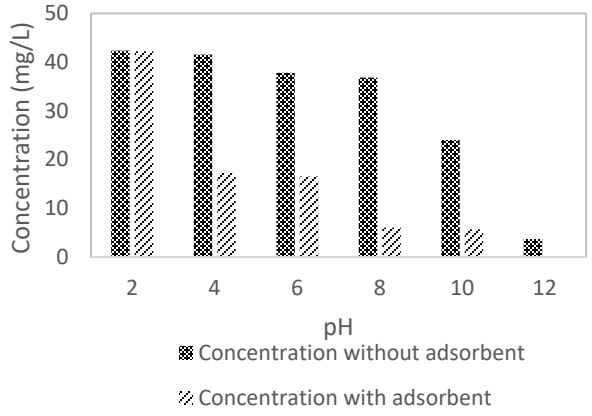


Figure 6: Effect of concentration of Ni (II) solution with and without the addition of adsorbent by using *Leucaena leucocephala* pod adsorbent at room temperature (27 ± 0.5) and 0.25 g adsorbent dose.

A slightly reduced in the concentration of Ni (II) solution occurs at pH 2 after the addition of adsorbent and the highest reduction of Ni (II) ion solution concentration was at pH 8. However, a slightly increased in the concentration of Ni (II) solution after adsorption occurs after pH 10 to 12.

The increase in pH solution increased the biosorption capacity but achieved a maximum value at pH 8. Meanwhile, at a pH higher than pH 8 the adsorption capacity reduced as shown in Figure 6. Similar results were reported by numerous researchers [11], [14], [31]. Ni (II) is in ionic form below pH 8 [33], at pH more prominent than 8, the development of dissolvable salt that will compete with the active sites might be the cause that will result in a reduction of the adsorption capacity of Ni (II) [34]. Besides, at higher pH, the binding site may not be initiated in essential or basic condition [35]. The removal of Ni (II) ions was not completely by adsorption since the nickel started to precipitate at above pH 8 due to a high number of OH^- ions present in the solution [36], [37]. Reduction of the concentration of Ni (II) free ion at pH higher than pHpzc might be caused of the formation of salt or formation of anionic hydroxide complexes which resulted in a decrease of the biosorption capacity [38]. Lataye & Kurwadkar, (2016) stated that the adsorption capacity was decreased due to the large amount of OH^- ions in the aqueous solution causing the deprotonation of the *Leucaena leucocephala* pod adsorbent surface, which implies above pH 6, the adsorbent surface was negatively charged resulted in decrease of the Ni (II) ions uptake, which is due to the pHpzc [32]. Accordingly, as can be seen from Figure 6, pH=8 was chosen as the optimal pH and at pH lower than the corresponding pHpzc (pHpzc~6.0) almost no sorption of Ni (II) metal ions can be seen.

3.3 Effect of Dosage

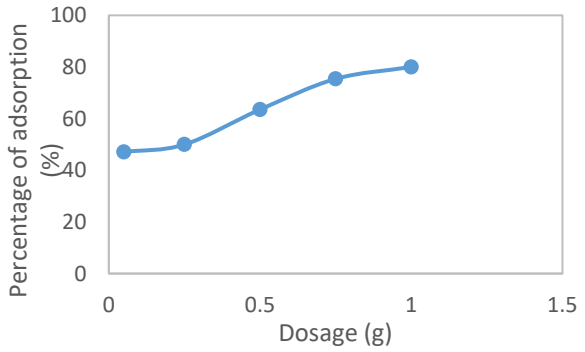


Figure 7: Effect of biosorbent dose on the biosorption of Ni (II) using *Leucaena leucocephala* pod at pH 8 and temperature of 313 K.

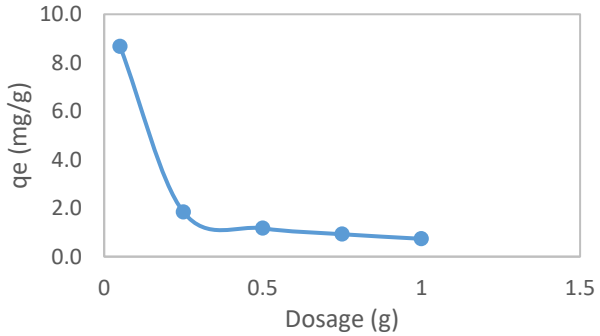


Figure 8: The effect of biosorbent dose on percentage of Ni (II) ions removal using *Leucaena leucocephala* pod.

Dosage of a biosorbent has a huge effect and decisive on the removal of the metals (nickel) under certain conditions [5]. The effect of dosage experiments showed that Ni (II) ion removal was increasing with an increasing amount of dosage. Results showed in Figure 7 and 8 for the adsorption of Ni (II) using different dosage demonstrated that the adsorption efficiency is highly dependent on the amount of the biosorbent added to the solution [39]. Figure 7 shows a positive trend whereby the higher is the uptake and percentage removal of the Ni (II) ions when the biosorbent dose present in the solution is higher. It was observed that the adsorption of Ni (II) ions increased from 47% to 80 % at a dosage of 0.1 to 1.0 g, respectively, and the highest yield was reached at 1 g of the adsorbent dose. This is because of the increased surface area, which gives increasingly the number of the vacant active site for the uptake of the Ni (II) metals ions [40], [41]. Besides, the adsorption efficiency is basically dependent on the amount of biosorbent added.

There was no huge increment in the evacuation of Ni (II) ion when there was a further increase in the biosorbent dose because the equilibrium was reached when all the Ni (II) metal ions have fully bounded to the *Leucaena leucocephala* biosorbent [34]. On the other hand, at much higher biosorbent dosage, a reduction in the biosorption capacity Ni (II) ions might be caused by aggregation, flocculation of the adsorbent particles, some biosorption sites remained unsaturated and also due to the saturation of biosorbent by adsorbate [14], [34], [42]. The aggregation occurred due to the particle interaction that led to the decreased in the surface area of the biosorbent which reduces the uptake of Ni (II) metal ions [11].

However, there was a reduction in the amount of Ni (II) ions adsorbed (mg/g) which is from 8.7 to 0.7 mg/g due to saturation of the adsorption sites. The sudden reduction of biosorption capacities minimizes significantly after 0.25 g biosorbent dose, afterward, since the difference is too small, the reduction uptake is negligible. Therefore, from the economical aspect of heavy metals removal perspective, biosorbent dose of 0.25 g was adopted for the subsequent studies as the optimum dosage [14]. Accordingly, 0.25 g of *Leucaena leucocephala* pod adsorbent was used in all subsequent experiments (Fig 8).

3.4 Effect of Contact Time

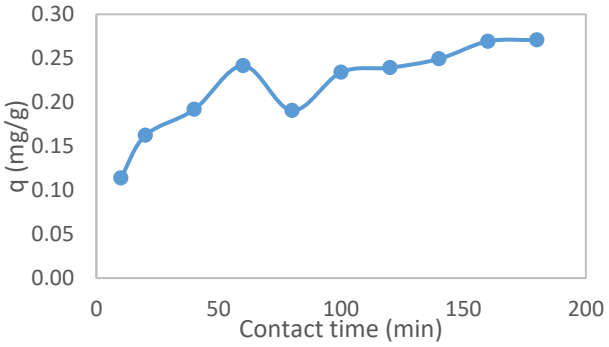


Figure 9: Effect of contact time on the adsorption of Ni (II) onto *Leucaena leucocephala* pod (Conditions: sorbate concentration 50 mg/L; pH=8; adsorbent dose 0.25 g; T=313K).

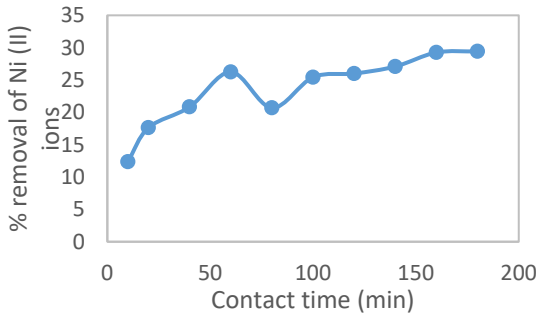


Figure 10: The effect of contact time on percentage of Ni (II) ions removal using *Leucaena leucocephala* pod.

The effect of contact time on nickel adsorption is shown in Figure 9 and 10, in which the adsorption capacity and percentage removal increases with the increase of contact time up to a certain minute and then decreases. Figure 9 demonstrated that the rate of nickel adsorption was very rapid amid the initial 60 min, and dropped at minute 70, and thereafter, the rate of adsorption slightly increased until minute 140. The adsorption capacity remained stable and reached equilibrium after 160 minutes of the experiment since the difference of the value is too small and there were no significant increments observed after 160 minutes. At adsorption equilibrium (160 min), the percentage removal for Ni (II) ions is 29%.

Initially, there was a large number of vacant active sites available and an abundance amount of nickel (II) ions were attracted rapidly on the biosorbents surface. The adsorption process occurred at a faster adsorption rate. The binding site was shortly reduced and become limited, in which the remaining vacant surface sites were difficult to be occupied by Ni (II) ions due to the formation of repulsive forces between the nickel on the biosorbent surface and the adsorbate [39]. Therefore, the optimum contact time for this study was determined at 160 minutes.

4.0 CONCLUSION

Leucaena leucocephala pod adsorbent was chemically treated and successfully functionalized with hydroxyl, ether and C-O-C groups. The effectiveness of the *Leucaena leucocephala pod* as a promising adsorbent is proven as the Ni (II) metal ion are removed. Based on the results, metal ion removal is dependent on the dosage, contact time and pH.

From the batch studies, it was found that the best optimum condition for *Leucaena leucocephala pod* adsorbent in Ni (II) removal is at pH 8 with 0.25 g of biosorbent and reached equilibrium at 160 min. From this study, it can be concluded that *Leucaena leucocephala pod* have the potential to remove nickel ion at its optimum conditions.

5.0 ACKNOWLEDGEMENT

A special thanks to my supervisor, Madam Noor Harliza Bt Abd Razak for her assistance and expertise throughout all aspects of my study and for her help in writing the manuscript. I also thank Universiti Teknologi Mara (UiTM) especially the lab assistance for providing me with the assistance in analyzing the results and equipment and materials required in the completion of this study.

References

[1] N. Sridhar, “Removal of Toxic Metals (Lead & Copper) From Automotive Industry Waste Water By Using Fruit Peels,” vol. 1, no. 2, pp. 188–192, 2014.

[2] U. P. Litter, “Waste Management,” pp. 2051–2057, 2000.

[3] M. Cempel and G. Nikel, “Nickel: A review of its sources and environmental toxicology,” *Polish J. Environ. Stud.*, vol. 15, no. 3, pp. 375–382, 2006.

[4] Y. Dai *et al.*, “Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review,” *Chemosphere*, vol. 211, pp. 235–253, 2018.

[5] M. A. Hossain, H. H. Ngo, W. S. Guo, and T. V Nguyen, “Removal of Copper from Water by Adsorption onto Banana Peel as Bioadsorbent,” pp. 227–234, 2012.

[6] B. Yasemin and T. E. Z. Zeki, “Removal of heavy metals from aqueous solution by sawdust adsorption,” vol. 19, pp. 160–166, 2007.

[7] I. Nhapi, N. Banadda, R. Murenzi, C. B. Sekomo, and U. G. Wali, “Removal of Heavy Metals from Industrial Wastewater Using Rice Husks,” *Open Environ. Eng. J.*, vol. 4, no.

April 2016, pp. 170–180, 2011.

[8] H. Amer, A. El-Gendy, and S. El-Haggar, "Removal of lead (II) from aqueous solutions using rice straw," *Water Sci. Technol.*, vol. 76, no. 5, pp. 1011–1021, 2017.

[9] D. Aderhold, C. J. Williams, and R. G. J. Edyvean, "The removal of heavy-metal ions by seaweeds and their derivatives," *Bioresour. Technol.*, vol. 58, no. 1, pp. 1–6, 1996.

[10] S. R. Singh and A. P. Singh, "Adsorption of Heavy Metals from Waste Waters," *Glob. J. Res. Eng.*, vol. 12, no. 1, pp. 3–7, 2012.

[11] N. F. Mansur, M. Ahmad, K. Megat, and M. Ismail, "Adsorption of Pb (II) Ions on Sulfuric Acid Treated Leucaena leucocephala Leaf Powder," no. November, 2015.

[12] S. K. Arora, R. S. Paroda, U. N. Joshi, M. L. Saini, and J. V. S. Haryana, "Forage Yield and Quality of s o m e L e u c a e n a Cultivars in the S e m i a r i d R e g i o n of Hisar," vol. 16, pp. 355–366, 1986.

[13] M. D. Putra, A. Darmawan, and I. Wahdini, "Extraction of chlorophyll from pandan leaves using ethanol and mass transfer study," vol. 82, pp. 921–931, 2017.

[14] M. Ngabura, S. Aslina, W. Azlina, W. A. Ghani, and M. Saedi, "Utilization of Renewable Durian Peels for Biosorption of Zinc from Wastewater Journal of Environmental Chemical Engineering Utilization of renewable durian peels for biosorption of zinc from wastewater," *J. Environ. Chem. Eng.*, vol. 6, no. 2, pp. 2528–2539, 2018.

[15] K. Mohomed, "Thermogravimetric Analysis (TGA) - Theory and Applications," *TA Instruments - Waters LLC*, p. 235 slides, 2016.

[16] M. Basu, A. K. Guha, and L. Ray, "Adsorption of Lead on Cucumber Peel," *J. Clean. Prod.*, vol. 151, pp. e55–e55, 2017.

[17] W. M. Doyle, "Principles and Applications of Fourier Transform Infra- red (FTIR) Process Analysis."

[18] A. Savran, "Removal of Cu (II), Zn (II) and Co (II) ions from aqueous solutions by adsorption onto natural bentonite," no. May, 2007.

[19] K. M. D. Lataye and V. M. S. Kurwadkar, "Adsorption of hexavalent chromium onto activated carbon derived from Leucaena leucocephala waste sawdust : kinetics , equilibrium and thermodynamics," *Int. J. Environ. Sci. Technol.*, vol. 13, no. 9, pp. 2107–2116, 2016.

[20] M. Hosur, A. Tcherbi-narteh, and S. Jeelani, "Extraction and characterization of lignin from different biomass resources," no. December, 2014.

[21] A. M. M.Boumediene, H.Benaissa, B.George, St.Molina, "CHARACTERIZATION OF TWO CELLULOSIC WASTE MATERIALS (ORANGE AND ALMOND PEELS) AND THEIR USE FOR THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS," 2015.

[22] N. Johar, I. Ahmad, and A. Dufresne, "Extraction , preparation and characterization of cellulose fibres and nanocrystals from rice husk," *Ind. Crop. Prod.*, vol. 37, no. 1, pp. 93–99, 2012.

[23] R. M. Ali, H. A. Hamad, M. M. Hussein, and G. F. Malash, "Potential of using green adsorbent of heavy metal removal from aqueous solutions : Adsorption kinetics , isotherm , thermodynamic , mechanism and economic analysis Potential of using green adsorbent of heavy metal removal from aqueous solutions : Adsorption kinetics , isotherm , thermodynamic , mechanism and economic analysis," *Ecol. Eng.*, vol. 91, no. January 2019, pp. 317–332, 2016.

[24] C. S. T. Araújo, I. L. S. Almeida, H. C. Rezende, and S. M. L. O. Marcionilio, "Elucidation of mechanism involved in adsorption of Pb (II) onto lobeira fruit (Solanum lycocarpum) using Langmuir , Freundlich and Temkin isotherms Elucidation of mechanism involved in adsorption of Pb (II) onto lobeira fruit (Solanum lycocarpum) using Langmuir , Freundlich and Temkin isotherms," *Microchem. J.*, vol. 137, no. November, pp. 348–354, 2017.

[25] L. Burhenne, J. Messmer, T. Aicher, and M. Laborie, "Journal of Analytical and Applied Pyrolysis The effect of the biomass components lignin , cellulose and hemicellulose on TGA and fixed bed pyrolysis," *J. Anal. Appl. Pyrolysis*, vol. 101, pp. 177–184, 2013.

[26] B. S. Kauldhar and S. K. Yadav, “Turning waste to wealth : A direct process for recovery of nano-silica and lignin from paddy straw agro-waste,” *J. Clean. Prod.*, vol. 194, pp. 158–166, 2018.

[27] E. D. Asuquo and A. D. Martin, “Journal of Environmental Chemical Engineering Sorption of cadmium (II) ion from aqueous solution onto sweet potato (Ipomoea batatas L .) peel adsorbent : Characterisation , kinetic and isotherm studies,” *Biochem. Pharmacol.*, vol. 4, no. 4, pp. 4207–4228, 2016.

[28] S. K. Das and A. R. Das, “A Study on the Adsorption Mechanism of Mercury on Aspergillus versicolor Biomass,” pp. 8281–8287, 2007.

[29] G. Urbain, “The Constitution and Fundamental Properties of Solids and Liquids,” vol. 252, 1916.

[30] R. S. J. and D. J. L. G. Annadurai, “Adsorption of Heavy Metals From Water Using Banana and Orange Peels,” *Water Sci. Technol.*, vol. 47, no. October, pp. 185–190, 2002.

[31] A. K. Patil, V. S. Shrivastava, and D. N. Mahavidyalaya, “Removal of Cu (II) Ions by Leucaena Leucocephala (Subabul) Seed Pods from Aqueous Solutions,” vol. 7, no. Ii, pp. 377–386, 2010.

[32] W. Muhammad, H. Wan, M. Hazim, and M. Amini, “Characterization of Activated Carbon Produced from Leucaena leucocephala Biomass as Heavy Metal Adsorbent : Adsorption of Cadmium from Aqueous Solution Characterization of Activated Carbon Produced from Leucaena leucocephala Biomass as Heavy Metal Adsorbe,” no. May, 2018.

[33] C. Paduraru, L. Tofan, C. Teodosiu, I. Bunia, N. Tudorachi, and O. Toma, “Biosorption of zinc (II) on rapeseed waste : Equilibrium studies and thermogravimetric investigations,” *Process Saf. Environ. Prot.*, vol. 94, no. Ii, pp. 18–28, 2014.

[34] R. M. Salim, A. Jalal, K. Chowdhury, R. Rayathulhan, K. Yunus, and Z. I. Sarkar, “Biosorption of Pb and Cu from aqueous solution using banana peel powder,” vol. 3994, no. October, 2015.

[35] A. Demirbas, “Agricultural based activated carbons for the removal of dyes from aqueous solutions : A review,” vol. 167, pp. 1–9, 2009.

[36] J. R. Memon, S. Q. Memon, M. I. Bhanger, G. Z. Memon, A. El-Turki, and G. C. Allen, “Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal,” *Colloids Surfaces B Biointerfaces*, vol. 66, no. 2, pp. 260–265, 2008.

[37] P. X. Sheng, Y. Ting, J. P. Chen, and L. Hong, “Sorption of lead , copper , cadmium , zinc , and nickel by marine algal biomass : characterization of biosorptive capacity and investigation of mechanisms,” vol. 275, pp. 131–141, 2004.

[38] B. S. Inbaraj and N. Sulochana, “Carbonised jackfruit peel as an adsorbent for the removal of Cd (II) from aqueous solution,” vol. 94, pp. 49–52, 2004.

[39] J. Anwar, U. Shafique, Waheed-uz-Zaman, M. Salman, A. Dar, and S. Anwar, “Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana,” *Bioresour. Technol.*, vol. 101, no. 6, pp. 1752–1755, 2010.

[40] Z. Abbasi, M. Alikarami, E. R. Nezhad, F. Moradi, and V. Moradi, “Adsorptive Removal of Co 2 + and Ni 2 + by Peels of Banana from Aqueous Solution,” *Univers. J. Chem.*, vol. 1, no. 3, pp. 90–95, 2013.

[41] A. Ali, K. Saeed, and F. Mabood, “Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent,” *Alexandria Eng. J.*, vol. 55, no. 3, pp. 2933–2942, 2016.

[42] M. Soleimani and Z. H. Siahpoosh, “Determination of Cu (II) in water and food samples by Na + -cloisite nanoclay as a new adsorbent : Equilibrium , kinetic and thermodynamic studies,” *J. Taiwan Inst. Chem. Eng.*, vol. 000, pp. 1–11, 2015.