Adsorption of Pb(II) from Water by Olive Waste Cake: Equilibrium, Isotherm and Kinetics Studies

Mohamed Sulyman[1*], Ali Alzitrini[2], Younes El-Ghanoudi[1], Salem Abu Zariba[3]
1: Department of Chemistry, Tajoura Nuclear Research Center, Tripoli-Libya
2: Ministry of Education- Tripoli-Libya
3: Department of Chemistry, The Libyan Academy, Tripoli- Libya
* Coressboinding author: mohsuly.2020@gmail.com

ABSTRACT

Today, adsorption is an effective approach for adsorption of contaminates such as heavy metals from water using different sources of low cost agricultural wastes. In this study, treated olive cakes with potassium carbonate (K_2CO_3) have been used as a low cost and eco-friendly adsorbent for the adsorptive uptake of lead Pb(II) ions from its aqueous solution using batch mode system. The characterization study of adsorbent was performed using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) techniques. The Influence of various important parameters such as contact time , initial ion concentrations, and adsorbent dose, were investigated. The atomic absorption was used to analyze the remaining metal ions concentrations. According to data obtained during the experimental section the following results were obtained: 1) contact time of 120 min, initial Pb(II) concentration of 150 mg/l, adsorbent dose of 0.5 g, room temperature, agitiation rate of 250 rpm, and working solution of 50 ml; 2) The maximum adsorption capacity of treated-olive cake for Pb(II) ions was found to be 23.64 mg/g; 3) The adsorption equilibrium was achieved within 120 min; 4) Solution pH was kept constant at the neutral value of pH during the whole adsorption process; 5) Total cost of the adsorbent derived from olive-waste cake including raw material, transportation, filter paper, chemicals (K_2CO_3 and acetone), electricity was estimated to be 0.85 US$/kg).

Keywords: Adsorption, equilibrium, heavy metals, olive cake, batch mode, kinetics, agricultural waste.

1. Introduction

Water resources are defined as the sources which produce the water for our different types of uses and also those sources that give the huge benefit to the life of the humans. Basically, the function of the water resources is to overcome the desires or the requirement of the water for the agricultural or household purposes. A clean and reliable water supply is critical for domestic use, food and energy production, transportation, recreation, and maintenance of natural ecosystems [1-3]. Technological advancements directed towards increase in the comfort of human life have greatly increased industrialization and urbanization. One of the unintended consequences of this is the generation of a large volumes of wastewater every day, containing hazardous materials that have harmful effects to both human and aquatic life [1-6].

It was reported that million of tons of chemicals such as heavy metals, toxic sludge, solvents, dyes, chemicals, oil, acids and alkalis, salts, surfactants, industrial wastes and etc. were discharged into the natural water streams every year [1]. In 2014, about 2531.67 million tons of wastewater were discharged by the mining operations in China [5]. Heavy metals (HMs) are among the most common pollutants in wastewater, and they are defined as metallic elements with a density of more than 6.0 g/cm^3 when compared to water. Heavy metals are also toxic substances at trace concentrations and create hazardous to the environment, due to their accumulation through the food chain, toxic effects, highly soluble in aquatic settings, making them easily absorbed by biological organisms [3, 6-9], which undergo transformations and have great environmental, public health, and economic impacts [10].

There are many heavy metals have been classified as toxic pollutants in their mixed or elemental formssuch as Lead (Pb), Chromium (Cr), Cadmium (Cd), Selenium (Se), Zinc (Zn), Copper (Cu), Arsenic (As), Cobalt (Co), Nikel (Ni), Mercury (Hg) [6, 8, 11]. Among the sources of release of heavy metals into the aquatic environment are oil and gas, refining ores, sludge disposal, metal plating, plastic, pharmaceutical, storage-manusacturing battery, paper and pulp, mining operations, electroplating, paints, alloys, pesticides and preservatives, fly ash from incinerators, automobile industry, agricultural activities, chemical spills, printing, textile and pigments, fuels, photographic industries and explosive manufacturing, cosmetics, stabilizer, galvanizing, glass operations, iron and steel manufacturing units, cement plants and municipal wastewater [7, 8, 11].

Adsorption process is offering advantages over conventional processes such as low space requirements for batch and continuously packed bed units, zero water pollution, absence of odor emissions, low cost of the adsorbent, and simplicity of design and ease of operation, and production of high-quality treated effluent in many cases and less investment in terms of both initial cost and operational cost [12].

Agricultural products and by-products/wastes, as well as forestry residues are inexpensive materials in comparison to the commercial AC. They have proved very efficient for pollutants removal from water because the main components of these materials are cellulose, hemicelluloses, and lignin which contain various functional groups like hydroxyl and carboxyl groups. These functional groups can act as binding sites, which offer advantages of these wastes. They can also be easily modified by one step chemical activation for improving the adsorption capacities [13-16]. Agricultural and food production creates a great amount of wastes, and to many, food processing is considered as a big polluter. It is estimated that about 38% of food wastes are produced by the agri-food industry [17, 18].

A one ton of olive fruit can reportedly generate 0.35 ton of olive-cake waste. From an industry perspective, that is a great amount of solid waste generated by the olive mill, waste that accumulates around the processing mill of olive fruits [19]. In Libya, olive cakes are produced from oil mills near the coast areas since suitable for the olive trees to grow, which is the biggest agricultural wastes. Olive cake solid wastes are of nonuse, and being accumulated each year. Sometimes, olive cakes are presented as animal feed after being mixed with minerals. According to the survey conducted by the author on the Libyan coast from Alzawia to Zliten, which is about 200 km, on three years period (2018, 2019 and 2020) included 25 olive mills, has pointed out 90-98 tons of olive-waste cake are generated from one oil mill annually. The author are also estimated that the olive stones which is presented in the solid waste-cake is about 50-52 wt%. Figure (1) shows the accumulated of high amount of olive-waste cake around the olive mill.

Fig. 1: The accumulated of large amount of olive cake around the olive mill [by researcher camera].

2. Materail and Methods

2.1. Materails

In this study, olive-waste cake was used as an alternative adsorbent for the elimination of pollutant from its aqueous solution. Lead nitrate {$Pb(NO_3)_2$}, from Merck was used for the preparation of stock solution of Pb(II) ions. Potasuim carbonate K_2CO_3 from Merck was used as a chemical agent for the treatment of olive-waste cake, acetone as solvent to remove any oil from the olive-waste cake provided from POCH, Poland, distilled water obtained from chemical department at Nuclear research center in Tripoli.

2.2. Instrumentations

The list of instruments and tools which were used in this study are presented in Table (1).

Table 1: The list of instruments used in the present study

Instrument	Manufacture/ type
Electronic weight balance	Sartorius, 1000±0.0001g
Digital shaker (batch mode)	GFL 3005 model, Germany
Infrared Spectroscopy (FT-IR)	Tensor 27 Bruker, USA- at the range of 450 – 4000 cm-1
Mechanical mill	Two places. Each one has three stainless steel ball, Germany
Sieve plats	Ranging 0.125 – 1.0 mm
Filter paper	Whatman 40, circles, 125 mm Ø
pH meter	740 Inolab WTW with a SenTix 20 pH model double electrode
Themogravimetric (TGA)	TA instrument (SDT Q500)
X-ray fluorescence spectroscopy (XRF)	Bruker 1kw WD-XRF model S8 Tiger spectrometer
Scanning electron microscope	Quanta FEG, USA 10kV
Atomic adsorption	AA240FS (VARIAN)

2.3. Preparation of Adsorbent

In this study, olive-waste cake was used as an available and very cheap biosorbent material for the uptake removal of lead Pb(II) ions from their aqueous solution. The raw olive-waste cake was obtained from oil mill process at Zliten, Libya. The biomass was washed completely with warm water and soap. This washing without soap was repeated three times with distilled water followed with acetone to remove oil, impurities and other undesirable materials. After that, the olive cake was activated chemically by being soaked in (0.5 M K_2CO_3) solution for 24 h. It was subsequently washed many times with distilled water and dried at room temperature for 5 days, and in the oven at 105^{o}C until constant weight was reached. Finally, the dried material was crushed and blended using a mechanical mill, and passed through the 0.1 mm sieve plate to produce powder adsorbent material of uniform size and stored in plastic bags for further use.

2.4. Characterization of the Adsorbent

2.4.1. Bulk Density

For bulk density, a glass cylinder 25 ml was filled to a specified volume with each material and dried in an oven at 65 ^{o}C for 7 hr. The cylinder was tapped for few minutes to compact the material and the bulk density estimated and presented as g/ml using the following Equation. The procedure was similar to that used by Sulyman et al., (2018) [20].

$$\text{Bulk density} = \text{weight of dry adsorbent (g)} / \text{final volume (ml)} \quad . . . . (1)$$

2.4.2. FTIR Analysis of Adsorbent

Fourier-transform Infrared Spectroscopy (FTIR) is a widely accepted technique for the identification of functional groups [21]. Also makes possible to investigate the interaction between chemical substances like heavy metal ions and molecules of dyes and the active sites on the solid surface of adsorbent [22]. Tensor 27 Bruker model of Fourier transform infrared (FTIR) Spectroscopy, was used in this study to obtain the IR spectra of the olive cake adsorbent in the form of raw material. Samples were analyzed in spectral range of 500-4000 cm^1, with test parameters of 2 cm^{-1} resolution; 64 is the number of scans, and 4 mm is for spectral beam diameter.

2.4.3. Water Uptake

The swelling test were carried out at room temperature in liquid media using disttiled water. The system was carried out as follows: three separate samples of exactly 1.0 g of olive cake were kept into empty tea bags, then they were soaked in disttiled water using container glasses of 100 ml. After a given time, the samples were carefully taken off the liquid. The mass of the samples was measured during 250 min. The extent of swelling was calculated as the percentage of olive cake mass increment after a set time immersion in the water by the following Equation [23].

$$\text{Water uptake (\%)} = (m_f - m_i / m_i) \times 100 \quad . . . . (2)$$

Where: m_f is the wet weight of samples (g), m_i is the initial dry weight of the sample (g)

2.4.4. Surface morphology of adsorbent

Scanning electron microscopy (SEM) is also an initial tool for characterizing the surface morphology and fundamental physical properties of the adsorbents [24, 25]. The surface morphology of olive cake sample was researched by using a Zeiss EVO 40 scanning electron microscope (SEM), which enabled examining the phase distribution in the modified adsorbent. The SEM power was 10 kV.

2.4.5. Thermogravimetric Analysis

Thermal analysis (TGA) is good analysis technique to examine decomposition characteristics of the raw material and its activated carbon [26]. However, in order to determine the remaining amount of combustible material remaining in the sample TGA take place. For this analysis, a fixed amount 10 mg of the sample was performed by heating the sample under nitrogen flow rate of 100 ml/min using a furnace of a temperature range of 30-800 ^oC.

2.5. Preparation of Lead Pb(II) Ions Solution

Stock solution of lead Pb(II) (1000 mg/l) was prepared by dissolving lead nitrate $\{Pb(NO_3)_2\}$ in few distilled water (about 100 ml) and diluting quantitatively to 1.0 L using distilled water. Then required initial concentrations of Pb(II) standards solutions in the range of (50 to 250 mg/l) were prepared by adequate dilution of the stock solution with distilled water. Three drops of concentrated nitric acid were added during the preparation of stock solution:

2.6. Batch Adsorption Process

Adsorption experiments were carried out in 250 ml beakers containing using batch mode technique. In order to optimize the experimental conditions, the batch adsorption experiments were performed for different important parameters such as initial concentrations of adsorbate (50-200 mg/l), contact time (30-120 min), adsorbent mass (0.3-1.0g). At the beginning, fixed amount of biomass (0.1g) was contacting with 50 ml of a given concentration of adsorbate for 60 min at room temperature. In each case, a parameter was varied while others were kept constant. At the end of the adsorption time, the residual concentration of adsorbate in the solution was analyzed by Atomic Absorption "AA" technique after separation of solid phase from the mixture by filter paper. Each experiment was repeated three times under the same conditions and the average results were estimated. In each case, the agitiation rate, particle size of adsorbent, volume solution were kept constant at 250 rpm, 0.1 mm and 50 ml, respectively during the whole adsorption process. The experiments were coducted at pH 7 as most natural water resources have pH in the range 6-8. The adsorption capacity (qe) and adsorption effiecincy at equilibrium were calculated from the Equation (3) and (4), respectively [20].

$$\text{Adsorption capacity } q_e = (C_o\text{-}C_e) \text{ x } (V/M) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\text{Adsorption \%} = (C_o\text{-}C_e / C_o) \text{ x } 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where: C_o and C_e (mg/l) are the initial and final adsorbate concentration, respectively. V is the volume of the solution (L), M is the amount of adsorbent (g).

2.7. Isotherm Studies

The analysis and study the equilibrium data is very important in view to develop a model equation which can accurately represent the results and could be used for the design purposes [27, 20].

- *Langmuir adsorption isotherm*

Langmuir isotherm model represents the simplest in all known isotherm models for monolayer adsorption. Langmuir isotherm model is developed by assuming that the force of interaction between the adsorbed molecules are negligible, fixed number of accessible sites are available on the adsorbent surface in which these sites are energetically equivalent and once an adsorbate molecule occupies a site, no further adsorption takes place [28, 29]. In other words, the Longmuir presumes a specific homogeneous type of the adsorption. The linear form of the Langmuir adsorption is given as [30]:

$$C_e / q_e = 1/(q_{max}\, b) + C_e / q_{max} \quad \ldots\ldots\ldots\ldots\ldots(5)$$

where q_e is the adsorption capacity in the equilibrium state (mg/g), C_e is the equilibrium concentration of dye (mg/l), q_{max} is the maximum adsorption capacity corresponding to complete monolayer adsorption (mg/g), and b is the Langmuir isotherm constant (equilibrium constant l/mg). The slope and the intercept of linear plots of C_e/q_e vs. C_e help calculate the constant parameters of q_{max} (mg/g), and b (l/mg). The affinity between the liquid phase (solution of dyes/or heavy metal) and solid phase (adsorbent) can be predicted with the Langmuir parameter b from the dimensionless separation factor $R_{L,}$ Eq. 6: [30, 20].

$$R_L = 1 / (1 + b\, C_o) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where C_o is the initial dye concentration, b is Langmuir isotherm constant. The adsorption process as a function of R_L may be described as follows [20]:

$R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, and $R_L = 0$ irreversible.

- *Freundlich adsorption isotherm*

Freundlich isotherm model is widely used for many years, and this is mainly applied to describe characteristics for the hetrogeneouse surface. The model assumes that adsorption takes place on a heterogeneous surface, and can be used for non-ideal adsorption [31]. The linear form of Freundlich is given as [32]:

$$\ln q_e = 1/n\, (\ln C_e) + \ln K_f \quad \ldots\ldots\ldots(7)$$

where K_f, and n are Freundlich constants with "n" giving an indication of the facility with which adsorption process takes place, K_f (L/mg) is the adsorption capacity of the adsorbents.

2.8. Adsorption Kinetics Modeling in a Batch Experiment

Adsorption kinetics is dependent on the adsorbate-adsorbent interaction and conditions, which have been assessed for possible use in water pollution control [33]. The adsorption rate is a influence factor for a better choice of adsorbent, where the adsorbent should have a high adsorption efficiency and a fast adsorption rate. Existing adsorption investigation mostly used pseudo-first-order[34, 35], and pseudo-second-order models [34, 36] to understanding the behavior of adsorption kinetics of adsorbate by adsorbent [37]. The general kinetic rate equation can be written as Equation 8 [38].

$$dq_t/d_t = k_n\, (q_e - q_t)^n \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

n =1 ---→ first-order kinetics, and n =2 --→ second-order kinetics

- ***The pseudo first-order equation of Lagergren is generally expressed as follows:***

$$dq_t/d_t = k_1(q_e - q_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first-order adsorption (1/min). The linner form of pseudo first-order model is obtained given by integrating Eq. 10 for the boundary conditions t = 0-t and q_t =

0-q_t and given by equation 11 [39, 40]. Values of k_1 and q_e were calculated from the slope and intercept values of the straight line of plotting log (q_e-q_t) versus t, respectively.

$$\text{Log}\ (q_e - q_t) = \log\ (q_e) - (k_1/2.303)\ t \quad .....(10)$$

- ***The pseudo-second order equation is generally given as follows:***

$$dq_t/d_t = k_2(q_e - q_t)^2 \quad ....(11)$$

Where k_2 is the rate constant of pseudo second-order adsorption (g/mg min). Integrating Eq. 11 yields the linearized form as shown by Eq. 12 [39].

$$t/q_t = (1/k_2\ q_e^2\ ) + (1/q_e)\ t \quad ....(12)$$

Parameter values of k_2 and q_e were calculated from the slope and intercept values of the straight line of plotting t/q_t versus t.

3. Results and Discussion

3.1. Characterization of Adsorbent

- ***Physical Properties***

Table 2: Most physic-chemical characterization of treated olive cake

Parameter		Value
Bulk density, g/ml		0.65
Moisture content, %		6.5
Ash, %		1.2
Swelling, %		200
Elemental analysis (%)	Carbon content	50.0
	Hydrogen content	5.36
	Nitrogen content	0.70
	Oxygen content	30.77

- ***FTIR Analysis***

The FTIR spectra show the functional groups on the surface of the raw and modified adsorbent as shown in Fig 2-a and Fig 2-b, respectively. The broad band at 3330.63 cm-1 was due to (–OH) stretching of the hydroxyl groups [41-44]. The two bands at 2917.09 and 2850.39 cm−1 on adsorbent, were attributed to (-CH) stretch of (-CH3) and (-CH2) respectively [44, 42]. The absorbance peaks of olive cake at 1731.31 cm-1 is due to the presence of C=O stretching of carbonyl or most likely, a carboxylic group [41]. Furthermore, the figure indicated that the presence of a small peak at 1650 and 1606.57 cm-1 was due to the presence of C=O stretching of the amide group (I); the presence of nitrogen moiety is confirmed by Elemental Analysis (N = 0.7%). Furthermore, the figure indicated the presence of a small peak at 1513.48 cm-1 due to the presence of N-H bending types of bonds of amide (II) [45]. The bands appeared at 1035 cm-1 and 1162 cm-1 probably assigned to C-O stretching in alcohols. Finally, Peaks at 818.56 cm-1 and down to 565.79 cm-1 may indicated that aromatic units were still present within the material. Thus, the IR spectral study revealed that the adsorbent derived from olive cake contain mainly –OH, C=O, and –NH functional groups which were mainly responsible for the adsorption of adsorbates through chemical bondings [41]. After the treatment process of the adsorbent, some minor changes were observed at the position and intensity and a little shift of these peaks.

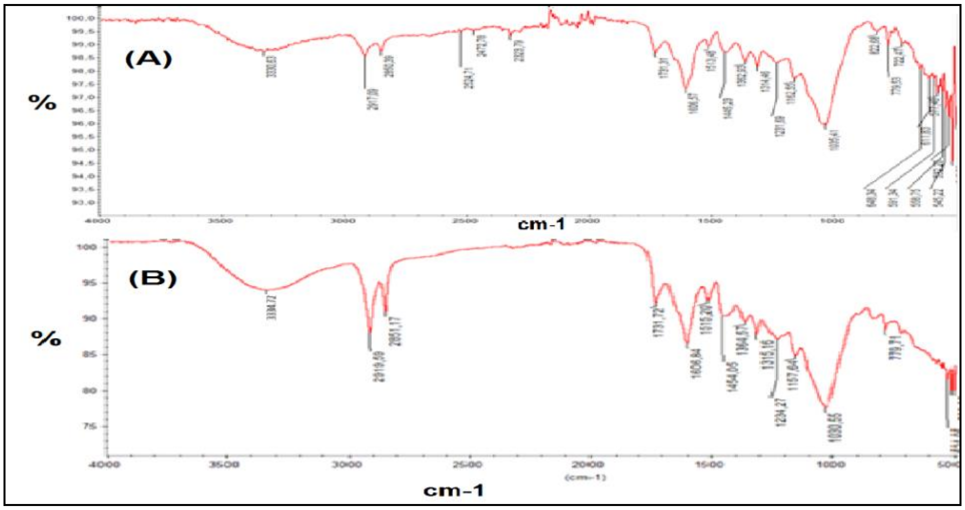

Fig. 2: FTIR analysis of olive cake-based bioadsorbent (a) and treated olive cake (b).

- ***Thermal Analysis- TGA***

Thermo-gravimetric analysis of the raw olive-waste cake was also performed by heating the sample up to 600 °C under nitrogen flow rate of 100 ml/min through a furnace of a temperature range of 30–800 °C. It can be observed from Figure (3.a) that there has been a very little drop in olive cake weight of approximately a total of 6.5% between initial temperature and 200 °C which could attribute to water elimination/desorption (moisture released) by the sample during heating which were physically adsorbed in olive cake. The second weight loss which started around 300°C due to the decomposition of lignocellulosic structure. Beyond this point, increasing temperature has led to a semi-sharp drop in weight to almost 65%, representing the degradation of the main components by dehydration, decarboxylation and decarbonizations [46, 41]. Therefore, at the oven drying temperature; that was 100 -105°C, there would be neither chemical nor structural modifications to occur by heating. Degradation of lignin and cellulose responsible probably for the adsorption of Pb(II) substances would be avoided. The derivative weight curve displayed two main endothermic peaks; one sharp peak at about 300 °C attributed to the degradation of cellulose, another peak as a shoulder at 450 °C attributed to degradation of lignin as indicated elsewhere [41].

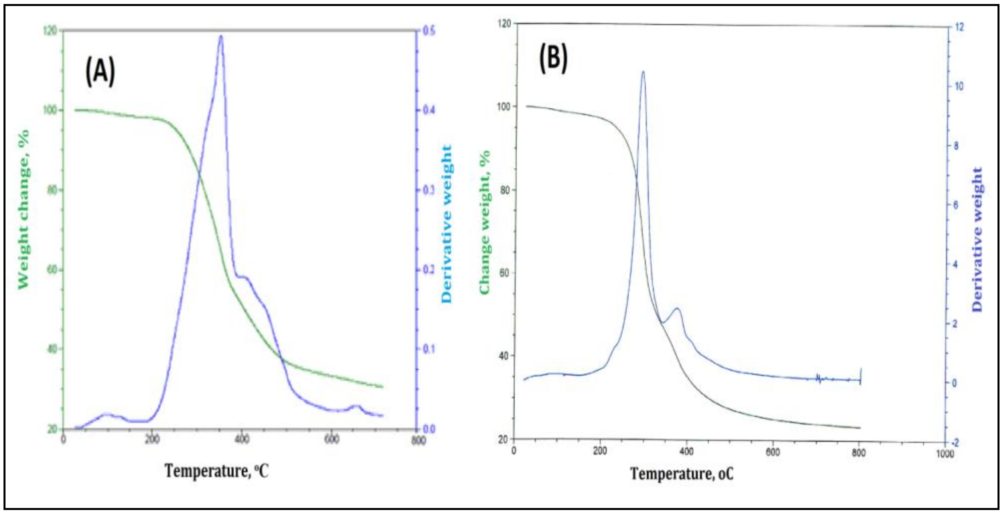

Fig. 3: Thermo-gravimetric analysis of olive cake-based bioadsorbent

- ***SEM Analysis***

Scanning electron microscope (SEM) is a useful technique to characterize the surface morphology of adsorbent [163]. The morphological images of adsorbent after and before treatment with K_2CO_3 are presented in Figure (4). The surface of adsorbent was irregular and rough. The images of SEM also showed some pores on the adsorbent surfac after treatment process figure (4-b). These conditions offered a good surface for the adsorption of pollutants such as lead ions. Similar results were obtained for *Carpinus betulus* sawdust which was used for the adsorption of basic red 46 [47].

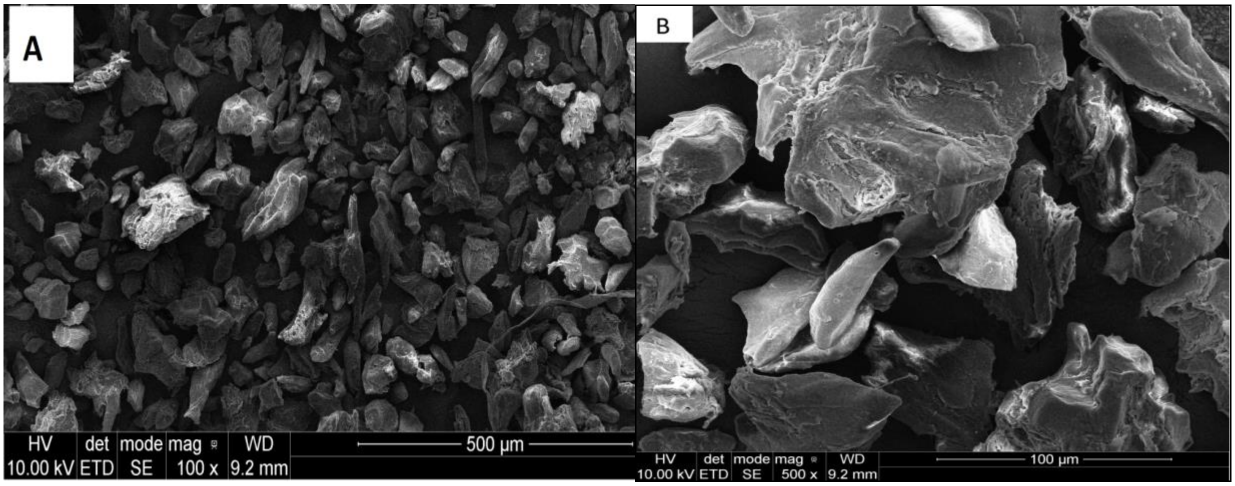

Fig. 4: SEM images of raw adsorbent (a), and treated adsorbent (b).

3.2. Optimization Studies for Pb(II) Ions onto Olive Cake

Table 3: Experimental range and levels of independent process variables involved in this study.

Independent variable	Unit	Levels			
		-2	-1	0	1
Adsorbent mass	g	0.3	0.5	0.75	1.0
Initial concentration	mg/l	50	100	150	200
Contact time	min	30	60	90	120

- **Equilibrium Optimization**

Tables 4 abstracted conditions for the adsorptive uptake of Pb(II) ions from its aqueous solution including initial concentration of lead, contact time and adsorbent dose, respectively. From table 4, it was clear that the Pb(II) concentration was a crucial factor during adsorption process, since it dictates the mass transfere resistance of the lead ion between the two phases (liquid phase and solid phase) [48]. However, it can be clearly observed that on changing the initial concentration of Pb(II) solutions from 50 mg/l to 200 mg/l, the adsorption capacity increased from 4.25 to 14.55 mg/g. This may be attributed to fact that for higher initial concentration, more efficient utilization of sorption sites was expected due to the great driving force of the concentration gradient in order to overcome all mass transfer resistance of HM ions between the aqueous and solid phases [48]. While, the percentage uptak for lead Pb(II) ions was decreased with increase in the initial concentration. It was decreased from 85.0 % to 72.75 % as the initial concentration increased from 50 mg/l to 200 mg/l. Besides, table 4.11 indicated that the removal effeiciency increased with increasing agitiation time, 69.80% for the solutions containing 200 mg/l of Pb (II) initially and then became almost stable representing the equlibiruim point within 120 min (85.34%). However, with the same adsorbent dose and contact time, there was a drop in the removal percentage with the increase in the initial Pb(II) concentration. At lower initial concentrations, sufficient adsorption sites were available for the adsorptive uptake of lead ions. Conversely, the numbers of Pb(II) ions at higher initial concentrations were relatively more as compared to the available adsorption sites. In this case, the availability of free adsorption sites dominates [28].

Table 4: Listed the adsorption capacity (mg/g) and removal efficiency (%) for Pb(II) at different Initial conc, (adsorbent dose 0.5g; contact time 120 min)

Initial conc. (mg/l)	Removal, (%) (average)	SD	Capacity mg/g (average)	SD
50	85.0	±1.047972	4.25	±1.3194710
100	80.9	±1.141976	8.09	±1.66421170
150	77.33	±2.109731	11.6	±1.641976502
200	72.75	±0.883194	14.55	±1.075512977
* SD is the Standrade deviation				

The time impact was determined in order to assess the pollutant uptake rate. The impact of adsorbent contact time was carried out by contacting a fixed amount of adsorbent (0.5g) using 150 mg/l of Pb(II) ions solution at an agitation rate of 250 rpm, room temperature. The efficiency of the adsorbent was evaluated using the time intervals of 30, 60, 90 and 120 min as shown in Table (5). A rapid uptake of Pb(II) ions within 90 thereafter equilibrium was reached. The results show that there was a fast adsorption at the beginning due to the available active sites being accessible on the surface of the adsorbents and after certain time the adsorption becomes slow because of saturation of the active sites [45].

Table 5: Listed the adsorption capacity (mg/g) and removal efficiency (%) for Pb(II) at different contact time, (adsorbent dose 0.5g; initial concentration 150 mg/l)

Contact time, (min)	Removal, (%) (average)	SD	Capacity mg/g (average)	SD
30	69.80	±1.209256	13.02	±0.944722
60	75.55	±0.686952	15.067	±1.774210
90	83.25	±2.273881	16.754	±2.050397
120	85.34	±0.854244	17.068	±1.07519730

The impact of adsorbent mass was carried out by contacting different amounts of adsorbent (0.3g – 1.0g) using 150 mg/l of Pb(II) ions solution at an agitation rate of 250 rpm, room temperature, for a period of time 120 min. Table 6 showd the variation of percentage removal versus amount olive cake for the Pb(II) ions. From the table it can be seen that with increase in adsorbent dose from 0.3 to 1.0 g the percentage removal of lead ions increased sharply from 70% to about 80% for contact time of 120 min. This can be attributed to the increase of the available adsorption active sites on the adsorbents surface with increase in amount of olive cake [50, 49]. However, it was seen that adsorption did not increase linearly with increase in adsorbent dose [50]. Thus the olive cake adsorbent was kept constant at 0.5/50 ml of solution lead ions in this study. In other site, the adsorption capacity was decreased from 23.45 mg/g to 7.75 mg/g as the adsorbent dose increasing from 0.3 to 1.0 g for 120 min. Similar outcome was observed and reported in many previous studies using other types of bioadsorbents derived from agricultural wastes [51-53].

Table 6: Listed the adsorption capacity (mg/g) and removal efficiency (%) for Pb(II) at different adsorbent dose, (initial concentration of 150; contact time 120 min)

Adsorbent dose, g	Removal, (%) (average)	*SD	Capacity mg/g (average)	*SD
0.3	70.13	±2.059402	23.45	±2.170733
0.5	72.75	±1.273162	14.55	±1.568128
0.75	77.31	±2.067104	10.2	±2.395519
1.0	79.55	±0.951488	7.75	±1.065173

3.3. Adsorption Isotherms

Langmuir and Freundlich *Isotherms*

The Langmuir and Freundlich adsorption isotherms study were performed by varying the initial concentration of Pb(II) from 50 to 200 mg/l, keeping all other conditions constant. The linear form of the Langmuir and Freundlich adsorption are given by Equation (5) and (7), respectively. Isotherm constants for the Langmuir and Freundlich models of Pb(II) obtained using olive cake are shown in Figure 5 and 6 and then listed in Table (7). Langmuir parameters were obtained from the slope and intercept of the straight line for Pb(II) ions adsporption by olive cake. The olive cake adsorption data fit well to both Langmuir and Freundlich models. Besides, the high value of correlation coefficient (R^2) from the Langmuir isotherm was found to be 0.996 for Pb(II) indicate a good agreement between the Langmuir constants and confirm the monolayer adsorption of metal ions by the adsorbent surface. The Langmuir constant q_{max}

representing the maximum adsorption capacity of adsorbent was estimated to be 23.64 mg/g. Simalir outcome has been observed for the adsorption of Pb(II) by sawdust and neem bark adsorbents [50-52, 54, 55], and adsorption of Pb(II) by olive stones. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor for the equilibrium parameter, R_L, which was used to predict whether an adsorption system was favorable or unfavorable. The separation factor was defined by Equation (6) and the R_L values were found to be from 0.4098 to 0.01479 at initial metal concentration from 50 to 200 mg/l , which confirmed favorable adsorption of Pb(II) ions onto olive cake. A similar result has been reported in previous studies [52, 49, 56].

Table 7: Equilibrium isotherm modeling of Pb(II) ions adsorption onto olive cake.

Eqiulibrium isothem constants					
Langmuir isotherm			Freundlich isotherm		
q_{max}	b	R^2	K_f	n	R^2
23.64 mg/g	0.0288	0.996	1.229	1.567	0.995

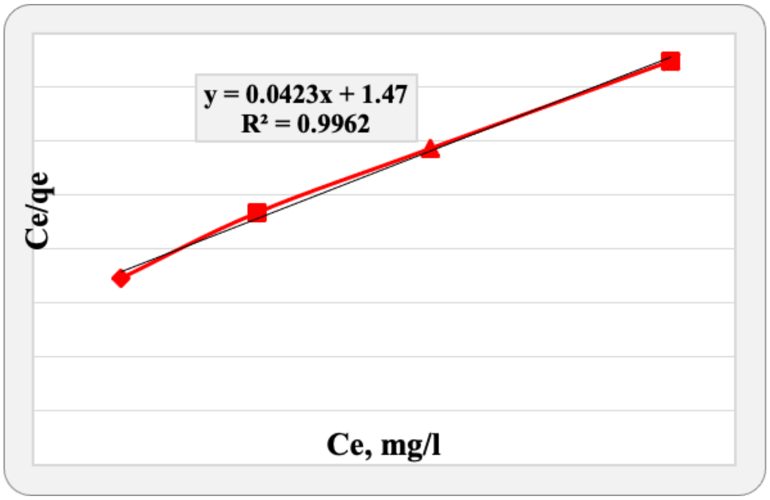

Fig. 5: Langmuir isotherm plot for the adsorption of Pb(II) onto olive cake

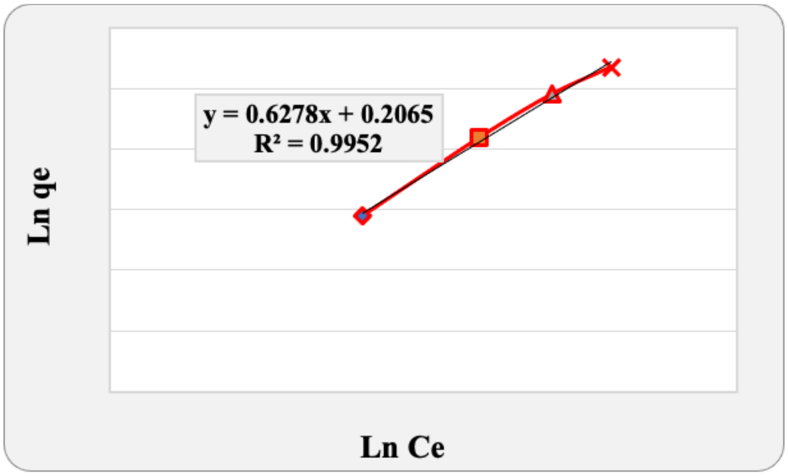

Fig. 6: Freundlich isotherm plot for the adsorption of Pb(II) onto olive cake.

3.4. Kinetic Modeling

Figurs 7 (a) and 7 (b) showed the plots of pseudo-first-order kinetic model and the pseudo-second-order model, respectively, for the adsorptive uptake of Pb(II) ions from its aqueous solution onto olive cake. According to the data obtained, the results suggested that the pseudo-frist-order model is less suitable to describe the adsorption system compared to the pseudo-second-order model. The correlation coefficent of second-order-kinetic model (0.999) was greater than for pseudo-first-order model (0.955). This confirmed that the rate limiting step was chemisorption, involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate [57, 58]. The kinetic parameters of both models were listed in Table (8). Other researchers have also observed a similar trend [52, 53].

Table 8: Illustrates Kinetic constants for the adsorption of Pb(II) onto olive cake bioadsorbent.

Kinetic constants					
Pseudo-first-order			Pseudo-second-order		
q_e	k_1	r^2	q_e	k_2	r^2
2.98	0.0258	0.956	18.72	0.00359	0.999

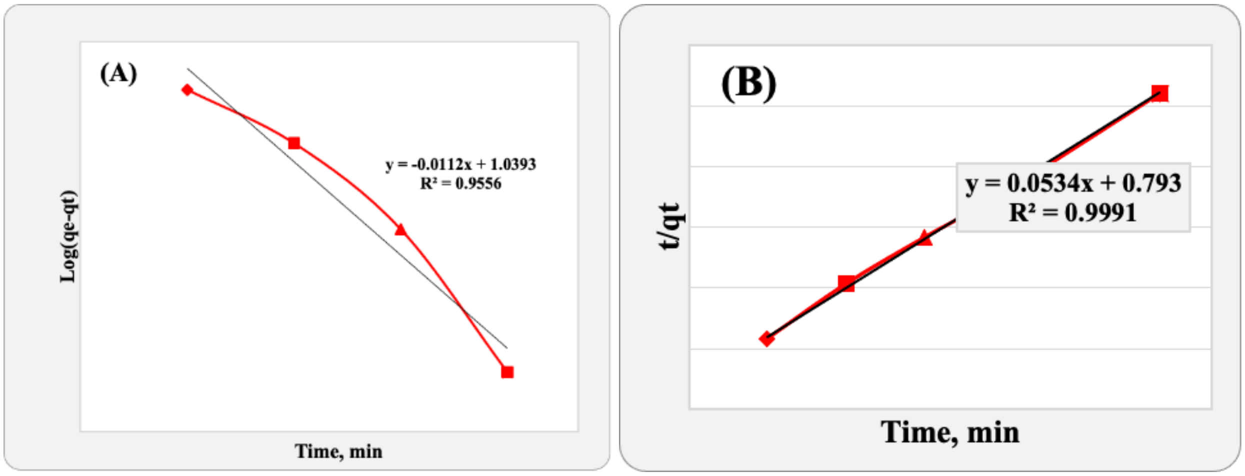

Fig. 7: Pseudo-first-order reaction of adsorption Pb(II) onto olive cake bioadsorbent (a) and Pseudo-second-order (b).

3.5. Elemental Analysis of Adsorbent

The study of elemental analysis including four elements Ca, Mg, Fe, Zr, and Pb were carried out using X-ray fluorescence spectroscopy (XRF) according to PN EN 15309:2010. The measurement was made in helium atmosphere. The analysis was also performed in a powder analysis vessel on a 4µm thick Prolene®film. The analysis was done for the solid phase (olive cake adsorbent) befor and after adsorption process for lead Pb(II) ions and the obtained results are listed in Table (9). From the table, it is clear that the Pb(II) was absent befor adsorption process of lead from its aqueous solution, and showed the value of 85 mg/kg after adsorption process. Also, the amount of Ca, Fe and Zr were highly decreased in the case of olive cake loaded with Pb(II). This confirmed that the Pb(II) has been adsorbed on the adsorbent surface.

Table 9: Illustrates elemental analysis for the adsorption of Pb(II) onto olive cake

Before adsorption			After adsorption		
Element	Unit	Amount	Element	Unit	Amount
Ca	%	0.38	Ca	%	0.01
Mg	%	0.20	Mg	%	Absent
Fe	mg/kg	89	Fe	mg/kg	86
Zr	%	0.15	Zr	%	0.12
Pb	mg/kg	Absent	Pb	mg/kg	85

3.6. Cost Analysis

In general, a cost comparison between commercial activated carbon which is widely used in wastewater treatment and several inexpensive adsorbents derived from agricultural by-products/wastes still needs a more and more attention from engineers and scientists because not much has been conducted in this trend. Since, the global activated carbon market accounted for $ 4.12 billion in the year of 2017 and is expected to reach $ 14.21 billion by the year of 2026 [59]. Researcher from Malaysia, Hameed and his co-workers (2008) have estimated the cost of coconut bunch waste (CBW) accumulates in the agro-industrial yards in , and reported that “such waste has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Hence, the utilization of these agriculture solid waste for wastewater treatment is most desirable. The cost of this waste as a dye sorbent is only associated with the transport and process expenses which are approximately US$ 50/ton whereas the average price of activated carbon used in Malaysia is US$ 1000–1100/ton. Thus the proposed CBW sorbent is more than 20 times cheaper than activated carbon” [60]. Although the adsorption capacity of CBW may be lower than commercial activated carbons, the adsorbent is renewable material, abundantly available and, therefore, low-cost adsorbent. The CBW would be an economical alternative for the commercially available activated carbon in removal of basic dye from aqueous solutions.

In this study, cost of treated olive waste-cake based adsorbent was estimated as follows: i) cost of raw material and transportation, cost of disttiled water, cost of electricity, cost of filter paper, and cost of chemicals such as K_2CO_3 and acetone. The cost analysis was estimated for 1.0 Kg. From the table, there was a difference between total cost of low-cost adsorbent from one to another depending on local currency of the country against the US dollar. Results have also observed that the cost of locally adsorbent obtained from the treated-olive cake was cheaper than commercial activated carbon. Although the adsorption capacity of OWC may be lower than commercial activated carbons, the adsorbent is renewable material, abundantly available and, therefore, low-cost adsorbent. However, from the economic point of view, olive-waste cake was efficient adsorbent and would be an economical alternative for the commercially available activated carbon in removing toxic substances from contaminanted water. Similar observiations have been reported for modified agrowaste based adsorbents [61] and for activated carbon derived from *gmelina aborea* leaves [62].

4. Conclussion

As expected, the application of low cost and eco-friendly adsorbents such as olive-waste cake in treatment of wastewater have significantly proven to improve quality of unclean waters. In order to achieve a superior and balanced treated water by the intended adsorbents, olive cake, parameters such as contact time, initial concentration of adsorbate, and adsorbent dose, must be considered. Based upon the experimental results of the current study, the following major conclusion were drawn:

1- The Langmuir isotherm and pseudo-second order kinetic model fit well to Pb(II) ions adsorption data.
2- The maximum adsorption capacity of olive cake for Pb(II) ions was found to be 23.64 mg/g.
3- The FTIR study revealed the involvement of hydroxyl, amino and carboxylic acid functional group in the adsorption of Pb(II) ions.
4- The results of this study show that olive cake can be successfully used as low cost and eco-friendly adsorbent for the adsorption of heavy metal like lead from water streams.
5- The adsorption equilibrium was achieved within 120 min for the removal of Pb(II) ions.
6- Solution pH was kept constant at the neutral value of pH during the whole adsorption process. Since there were sevral adsorbents derived from agricultural, by-products/wastes showed high adsorbent capacity at the neutral value of pH.
7- Total cost of olive cake adsorbent including raw material, transportation, filter paper, chemicals (K_2CO_3), electricity was estimated to be 0.85 US$/kg, which is very cheap compared to the commercial AC.

References

[1] **Gupta V. K., Carrott P. J. M., Carrott M. M. L. R., and Suhas. (2009)** Low-Cost Adsorbents: Growing Approach to Wastewater Treatment-A Review, *Critical Reviews in Environmental Science and Technology* 39: 783-842; Doi:10.1080/10643380801977610

[2] **Fadzil F., Ibrahim S., Hanafiah M. A.K.M. (2015)** Adsorption of Lead (II) onto Orange Acid Modified Rubber Leaf Powder: Batch and Column Studies, *Process Safety and Environment Protection*: 1-19. http://dx.doi.org/10.1016/j.psep.2015.12.001

[3] **Zwain H. M., Vakili M., and Dahlan I. (2014)** Waste Materail Adsorbent for Zinc Removal from Wastewater: A Comprehensive Review, *International Journal of Chemical Engineering*: 1-13. http://dx.doi..org/10.1155/2014/347912

[4] **Gupta V.K. and Ali I. (2013)** Environmental Water Advances in Treatment, Remediation and Recycling. Available at http://dx.doi.org/10.1016/B978-0-444-59399-3.00001-5

[5] **Eljiedi A. A. A., Kamari A., Sunardi and Is Fatimah (2019)** Lala Clam (*Orbicularia Orbiculata*) Shell as an Eco-Friendly Adsorbent for Cd(II), Cu(II) and Pb(II) Ions, *Arab Journal of Basic and Applied Sciences* 26(01): 462-475. https://doi.org/10.1080/25765299.2019.1674046

[6] **Barasikinaa J., and Chidamoio J. (2023)** Effect of Chemical Treated Okra Waste for Heavy Metal Adsorption from Natural Gas Production Wastewater, *Journal of Applied Science & Process Engineering* 10(2).

[7] **Nadeem R., Nasir M. H.,Hanif M. S. (2009)** Pb(II) Sorption by Acidically Modified *Cicer Arientinum* Biomass, *Chemical Engineering Journal* 150: 40-48; Doi:10.1016/j.cej.2008.12.001

[8] **Johnson T. A., Jain N., Joshi H. C., Prasad S. (2008)** Agricultural and Agro-processing Wastes as Low Cost Adsorbents for Metal Removal from Wastewater: A Review, *Journal of Scientific & Industrial Research* 67: 647-658

[9] **Jain C. K., Malik D. S., Yadav A. K. (2016)** Applicability of Plant Based Biosorbents in the Removal of Heavy Metals: A Review, *Environm. Process*; Doi:10.1007/s40710-016-0143-5

[10] **Naiya T. K., Bhattacharya A. K., Das S. K. (2008)** Adsorption of Pb(II) by Sawdust and Neem Bark from Aqueous Solutions, *Environmental Progress* 27(3): 313-328; Doi:10.1002/ep

[11] **Ghasemi M., Keshtkar A. R., Dabbagh R., Safdari S. J. (2011)** Biosorption of Uranium (VI) from Aqueous Solutions by Ca-Pretreated *Cystoseira Indica* Alga: Brekthrough Curves Studies and Modeling, *Journal of Hazardous Materails* 189: 141-149; Doi:10.1016/j.jhazmat.2011.02.011

[12] **Sulyman M., Namiesnik J., Gierak A. (2017)** Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review, *Pol. J. Environ. Stud.* 26 (2): 1-32; Doi: 10.15244/pjoes/66769.

[13] **Dawood S. and Sen T. K. (2014)** Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents, *J Chem Proc Eng*, 1: 104.

[14] **Garg V., Amita M., Kumar R., Gupta R. (2004)** Basic Dye (Methylene Blue) Removal from Simulated Wastewater by Adsorption Using Indian Rosewood Sawdust: A Timber Industry Waste, *Dyes and Pigments* 63(3): 243–250; Doi:10.1016/j.dyepig.2004.03.005

[15] **Adegoke K. A., and Bello O. S. (2015)** Dye Sequestration Using Agricultural Wastes as Adsorbents, *Water Resources and Industry*, 12: 8-24. https://doi.org/10.1016/j.wri.2015.09.002

[16] http://dx.doi.org/10.5772/53659 acailable online (accessed on October 2018)

[17] **Bharat Helkar, P.; Sahoo, A. (2016)** Review: Food Industry By-Products used as a Functional Food Ingredients. *Int. J. Waste Resour 6*(3). https://doi.org/10.4172/2252-5211.1000248

[18] **Szulc J., Błaszak B., Wenda-Piesik A., Gozdecka G., Żary-Sikorska E., Bąk M. and Bauza-Kaszewska J (2023)** Zero Waste Technology of Soybeans Processing, *Sustainability* **2023**, *15*, 14873. https://doi.org/10.3390/su152014873

[19] **Sulyman M. (2016**) Agricultural by-Products/Waste as Dye and Metal Ions Adsorbents: A Review, *Research Inventy: International Journal of Engineering And Science*, 6(6): 01-20.

[20] **Al-azabi K., Al-marog S., Abukrain A., Sulyman M. (2018)** Equilibrium, Isotherm Studies of Dye Adsorption onto Orange Peel Powder. *Chemistry Research Journal*, Vol. 3, No. 1, pp: 45-59.

[21] **Gupta N. K., Gupta A., Ramteke P., Sahoo H., Sengupta A. (2019)** Biosorption- A Green Method for the Preconcentration of Rare Earth Elements (REEs) from Waste Solutions: A Review, *Journal of Molecular Liquids*, 274: 148-164.

[22] **Ahmad T., Danish M., Rafatullah M., Ghazali A., Sulaiman O., Hashim R., Ibrahim M. N. (2012)** The Use of Date Palm as a Potential Adsorbent for Wastewater Treatment: A Review, *Environ Sci Pollut Res*, 19(5):1464-1484, DOI 10.1007/s11356-011-0709-8.

[23] **Hejna A., Sulyman M., Przybysz M., Saeb M., Klein M., Formela K. (2018)** On the Correlation of Lignocelluosic Filler Composition with the Performance Properties of Poly(ε-Caporolactone) Based Biocomposities, Waste and Biomass Valorization 11: 1467-1479. https://doi.org/10.1007/s12649-018-0485-5

[24] **Huang Y., Hu Y., Chen L., Yang T., Huang H., Shi R., Lu P., Zhong C. (2018)** Selective Biosorption of Thorium (IV) from Aqueous Solution by Ginkgo Leaf, PLOS ONE/ https://doi.org/10.1371/journal.open.0193659

[25] **Aljeboree A M., Alshirifi A. N., Alkaim A. F. (2017)** Kinetics and Equilibrium Study for the Adsorption of Textile Dyes on Cocnut Shell Activated Carbon, *Arabian Journal of Chemistry*, 10:S3381-S3393. http://dx.doi/10.1016/j.arabjc.2014.01.020

[26] **Gurten I. I., Ozmak M., Yagmur E., Aktas Z. (2012)** Preparation and Characterisation of Activated Carbon from Waste Tea Using K_2CO_3, *Biomass and Bioenergy* 3 7: 7 3-8 1; doi:10.1016/j.biombioe.2011.12.030

[27] **Maraie A. A., and Ibrahim H. G. (2015)** Biosorption of Copper (II) Ion from Wastewater onto Green Waste Tea: Isotherm and Kinetic Modeling Studies, *Der Chemica Sinica*, 6(7): 100-111.

[28] **Nadeem, M., Shabbir, M., Abdullah, A., Shah S., Mckay, G. (2009)** Sorption of Cadmium from Aqueous Solution by Surfactant-Modified Carbon Adsorbents. *Chem. Engi. J.* 148: 365-370.

[29] **Ho, Y.S.** Removal of Copper Ions from Aqueous Solution by Tree Fern, *Water Research*, **37**: 2323-2330, **2003**.

[30] **Langmuir I. (1918)** The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J. Am. Chem. Soc*. 40: 1361–1403.

[31] **Bharathi, K.S., and Ramesh S.P. (2012)** Equilibrium, Thermodynamic and Kinetic Studies on Adsorption of a Basic Dye by *Citrullus Lanatus Rind*, *Iranica Journal of Energy and Environment,* 3(1): 23-34.

[32] **Freundlich H.M.F. (1906)** Uber Die Adsorption in Losungen, *Z. Phys. Chem*. 57A: 385–470.

[33] **Bharathi K. S., and Ramesh S. T. (2013)** Removal of Dyes Using Agricultural Waste as Low-Cost Adsorbents: A Review. *Appl Water Sci,* 3: 773-790; DOI 10.1007/s13201-013-0117-y.

[34] **Babarinde A. and Onyiaocha G. O. (2016)** Equilibrium Sorption of Divalent Metal Ions onto Groundnut (*Arachis hypogaea*) Shell: Kinetics, Isotherm and Thermodynamics, *Chemistry International* 2(1): 37-46.

[35] **Lagergen S.(1898)** On the Theory of So Called Adsorption of Dissolved Substances. *Handlingar*, 24:1-39.

[36] **Ho Y. S., McKay G. (1999)** Pseudo-second Order Model for Adsorption Processes, *Process Bio Chem* 34: 451-465.

[37] **Salleh M. A., Mahmoud D. K., Abdul Karim W. A., Idris A. (2011)** Cationic and Anionic Dye Adsorption by Agricultural Solid Wastes: A Comprehensive Review, *Desalination*, 280(1-3): 1-13. https://doi.org/10.1016/j.desal.2011.07.019

[38] **Franca, A. S., Oliveria, L. S., and Ferreira, M. E. (2009)** Kinetics and Equilibrium Studies of Methylene Blue Adsorption by Spent Coffee Grounds, *Desalination,* 249**:** 267-272.

[39] **Prasad A. L. and Santhi T. (2012)** Adsorption of Hazardous Cationic Dyes from Aqueous Solutions onto Acacia Nilotica L. Leaves as an Eco-Friendly Adsorbent, *Sustain. Environ. Res.*, 22 (2), 113-122.

[40] **Hameed B. H., Salman J. M., and Ahmad A. L. (2009)** Adsorption Isotherm and Kinetic Modeling of 2,4-D Pesticide on Activated Carbon Derived from Date Stones, *Journal of Hazardous Materials*, 163: 121-126; Doi:10.1016/j.jhazmat.2008.06.069.

[41] **Sulyman M., Al-Marog S., Al-Azabi K., Abukrain A. (2016)** New Approach for In-House Treatment of Colored Wastewater Using Olive-Waste Cake as an Alternative Adsorbent, *IOSR Journal of Environmental Science, Toxicology and Food Technology,* 10(12): 19-31; Doi:10.9790/2402-1012041931

[42] **Kandaswamy S. B. and Srikrishna P. R. (2013)** Fixed-Bed Column Studieson Bio-sorption of Crystal Violet from Aqueous Solution by *Citrullus Lanatus and Cyperus Rotundus*, *Applied Water Science*; Doi:10.1007/s13201-01303-4.

[43] **Antonio Z., Roberto L., Franco M., Luigi P. (2013)** Spent Tea Leaves as Potential Low-Cost Adsorbent for the Removal of Azo Dyes from Wastewater, *Chemical Engineering Transactions* 32.

[44] **Thabede P. M., Shooto N. D., Naidoo E. B. (2020)** Removal of Methylene Blue Dye and Lead Ions from Aqueous Solution Using Activated Carbon from Black Cumin Seeds, *South African Journal of Chemical Engineering*. https://doi.org/10.1016/j.sajce.2020.04.002

[45] **Sulyman M. (2014)** Fixed-Bed Column Packed with Low-Cost Spent Tea Leaves for the Removal of Crystal Violet from Aqueous Solution, *5th Intenational Conference on Environmental Science and Technology, Gdansk-Poland.*

[46] **Abudaia J. A., Sulyman M. O., Elazaby K. Y., and Ben-Ali S.M.** (2013) Adsorption of Pb (II) and Cu (II) from Aqueous Solution onto Activated Carbon Prepared from Dates Stones

[47] **Deniz F. and Yildiz H. (2019)** Bioremediation Potential of a Widespread Industrial Biowaste as Renewable and Sustainable Biosorbent for Synthetic Dye Pollution, *International Journal of Phytoremediation* 21(3): 259-267. https://doi.org/10.1080/15226514.2018.1524451

[48] **Mokkapati R. P., Ratnakaram V. N., Mokkapati J. (2019)** Mass Transfer, Kinetic, Equilibrium, and Thermodynamic Study on Removal of Divalent Lead from Aqueous Solutions Using Agrowaste Biomaterails, Musa Acuminata, Casuarina Equisetifolia L., and Sorghum Bicolor, *Theoretical Foundations of Chemical Engineering* 53(4): 578-590.

[49] **Sadaf S. and Bhatti H. N. (2013)** Batch and Fixed Bed Column Studies for the Removal of Indosol Yellow BG Dye by Peanut Husk, *Journal of Taiwan Institute of Chemical Engineering*. http://dx.doi.org/10.1016/j.jtice.2013.05.004

[50] **Tangjuank S., Insuk N., Tontrakoon J., Udeye V. (2009)** Adsorption of Lead(II) and Cadmium(II) Ions from Aqueous Solutions by Adsorption on Activated Crbon Prepared from Cashew Nut Shells, *International Journal of Chemical and Molecular Engineering* 3(4).

[51] **Zhang L., Zeng Y., Cheng Z. (2016) Removal of Heavy Metal Ions Using Chitosan and Modified Chitosan: A Review**, *Journal of Molecular Liquids* 214: 175-191. https://doi.org/10.1016/j.molliq.2015.12.013

[52] **Naiya T.K., Bhattacharya A.K., Das S. K. (2008)** Adsoption of Pb(II) by Sawdust and Neem Bark from Aqueous Solutions, Environmental Progress 27(3); Doi:10.1002/ep

[53] **Ben Amar M., Walha K., Salvado V. (2020)** Evaluation of Olive Stones for Cd(II), Cu(II), Pb(II) and Cr(VI) Biosorption from Aqueous Solution: Equilibrium and Kinetics, *International Journal of Environmental Research*. https://doi.org/10.1007/s41742-020-00246-5

[54] **Yuvaraja G., Krishnaiah N., Subbaiah M. V., Krishnaiah A. (2014)** Biosorption of Pb(II) from Aqueous Solution by Solanum Melongena Leaf Powder as a Low-cost Biosorbent prepared from Agricultural Waste, *Colloids and Surfaces B: Biointerfaces* 114: 75-81. http://dx.doi.org/10.1016/j.colsurfb.2013.09.039

[55] **Albadarin A. B., Collins M. N., Naushad Mu., Shirazian S., Walker G., Mangwandi C. (2017)** Activated Lignin-Chitosan Extruded Blends for Efficient Adsorption of Methylene Blue, *Chemical Engineering Journal* 307: 264-272. http://dx.doi.org/10.1016/j.cej.2016.08.089

[56] **El Haddad M., Regti A., Laamari M. R., Slimani R., Mamouni R., El Antri S., Lazar S. (2013)** Calcined Mussel Shells as a New and Eco-friendly Biosorbent to Remove Textile Dyes from Aqueous Solutions. *Journal of Taiwan Institute of Chemical Engineering*. http://dx.doi.org/10.1016/j.jtice.2013.05.002

[57] **Sadaf S. and Bhatti H. N. (2013)** Batch and Fixed Bed Column Studies for the Removal of Indosol Yellow BG Dye by Peanut Husk, *Journal of Taiwan Institute of Chemical Engineering*. http://dx.doi.org/10.1016/j.jtice.2013.05.004

[58] **Lafi R., Ben Fradj A., Hafiane A., Hameed B. H. (2014)** Coffee Waste as Potential Adsorbent for the Removal of Basic Dyes from Aqueous Solution, *Korean J. Chem. Eng.*, 31(12): 2198-2206. doi:10.1007/s11814-014-01717.

[59] **Ahmad A. A., Din A.T. M., Yahaya N. K.EM., Khasri A., Ahmad M. A. (2020)** Adsorption of Basic Green 4 onto *Gasified Glyricidia* Sepium Woodchip Based Activated Carbon: Optimization, Characterization, Batch and Column Study, *Arabian Journal of Chemistry*. https://doi.org/10.1016/j.arabjc.2020.07.002

[60] **Hameed B.H., Mahmoud D.K., Ahmad A.L. (2008)** Equilibrium Modeling and Kinetic Studies on the Adsorption of Basic Dye by a Low-cost Adsorbent: Coconut (Cocos nucifera) Bunch Waste, *Journal of Hazardous Materials* 158: 65-72; doi:10.1016/j.jhazmat.2008.01.034

[61] **Ahmed M. J. K., Ahmaruzzaman M., Reza R. A. (2014)** Lignocellulosic Derived Modified Agricultural Waste: Development, Characterization and Implementation in Sequestering Pyridine from Aqueous Solutions, J. *Colloid Interface Sci*. 428: 222-243.

[62] **Belle O. S., Adegoke K. A., Fagbenro S. O., Lameed O. S. (2019)** Functionalized Coconut Husk for Rhodamine-B Dye Sequestration, *Applid Water Science* 9: 189. https://doi.org/10.1007/s13201-019-1051-4