

## Equilibrium and kinetics investigations for adsorption of aqueous lead ions using olive stone waste

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### ABSTRACT

Olive stone waste one of the biomass sorbents which was investigated to remove various aqueous metal ions especially heavy metals. This research aims to explore the data achieved from a batch studies of single bio-sorbent system for removal of lead metal ions  $Pb^{2+}$  by using Jordanian olive stone waste (OSW). The study investigated the effects of contact time, system pH, initial concentration of adsorbate, and adsorbent dose on removal of lead ions. Findings indicated that the suitable pH is of 6.8 for maximum removal of 82.5% of the initial concentration of 9 mg/L at temperature of  $25 \pm 1$  °C for adsorbent dose of 1-gram sorbent per 0.25 liters of solution. The equilibrium biosorption data have been analyzed to identify the biosorption isotherm and kinetics adsorption rates for the removal of lead ions by biosorbent (OSW) using commonly well-known adsorption isotherm models; Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich and Pseudo First Order, Pseudo Second Order, Elovich, and Intraparticle Diffusion models, respectively. Findings show that data were fitted well according to Freundlich isotherm adsorption model, while, the data were fitted the Pseudo First Order reaction in case of kinetics adsorption models' investigations. In conclusion, the adsorption rates in single system said that the processes are very fast and approved that the process is definitely adsorption and represented by Freundlich isotherm adsorption and pseudo second-order reaction models with high correlation coefficients equal approximately 1.

**Keywords:** adsorption isotherm, kinetics adsorption models, lead metal ions, olive stone waste.

### INTRODUCTION

All over the world, industrial aqueous contaminates are commonly pollutants discharging into environment harm the soil, water and air quality and causes serious environmental problems [Abdolalia et al., 2014; Abbas et al., 2013; Abdulaziz Ali Alghamdi et al., 2019]. Heavy metals such as chromium, nickel, cadmium, lead, and copper are highly toxic, non-biodegradable and most dangerous [Kawarada et al., 2005]. Discharging effluents of such harmful contaminates into surface waters create some health problems to all living things which is an important risk for the environment [Johnson et al., 2008]. Lead metal is essential in most industries as an ingredient in paint, coloring, batteries, fuel and others manufacturing processes [Rao et al., 2011]. Lead is harmful due to its effects such as carcinogenic, non-biodegradable in nature and toxicity toward

humans and animals. As a results toxic metals have to be treated and must identify the perfect methods of eliminating and defining the removal nature and mechanism [Bohli et al., 2013].

There are many methods and techniques used in removing such heavy metals contaminates from industrial wastewater. For example: precipitation [Bohli et al., 2013], ion exchange processes, coagulation and flocculation [Dragana et al., 2011], aeration and oxidation, filtrations, absorption, and adsorption [Ahmaruzza-man, 2011]. Numerous substances have the potential to be employed as bio-sorbents [Albayati and Doyle 2014; Albayati et al., 2014; Kumar et al., 2001; Mahdi et al., 2023; Saka et al., 2012]. A portion of these materials are produced using leftovers from agriculture. The olive stone that is produced during the olive processes is one of these wastes [Awad, 2024]. Olive stone waste is a biomass waste product that is produced in

large quantities in many countries during the extraction of olive oil [Gao et al., 2021]. This study employed olive stone waste as an adsorbent to extract lead metals that are harmful from liquid industrial waste. Olive stone waste is gathered in Jordan from different olive industries residuals sources, including olive oil mills.

Olive stone waste adsorbent was used to remove single aqueous lead ions  $Pb^{2+}$  [Abdolalia et al., 2014]. Investigations were done by implementing a set of experiments using the batch adsorption techniques to study the effects of solution pH, contact time, contaminants initial concentration, and adsorbent dose on removal of lead ions. These investigations were done in my previous research using batch techniques which was published in Results of Engineering Journal [Awad, 2024].

Activated carbons manufactured from different materials were used to remove heavy metals and other contaminants from liquid solution [Al-Ghouti and Da'ana, 2020; Kong and Adidharma, 2019; Firmansyah et al., 2024; Depci et al., 2012; Gao et al., 2009; Hegazi, 2013]. Cheaper adsorbents than activated carbons were also prepared from different agricultural waste such as olive stone wastes and tried to remove heavy metals [Mahmoud, 2016; Jeyakumar and Chandrasekaran, 2014; Goyal et al., 2001; Johns et al., 1999; Othman et al., 2019]. Following chemical treatment of the adsorbent surface, numerous investigators proposed olive stone waste as an adsorbent [Guerrero et al., 2015; Guo et al., 2014; Magriotis et al., 2014; Wang et al., 2015].

For the purpose of effective adsorption, the mechanism pathways overall and designing adsorption systems has to be realized and interpreted the adsorption isotherms correctly [El-Khaiary, 2008]. For continuing the study of lead ions removal nature and mechanism, the adsorption isotherm and reaction kinetics analysis were done based on the batch testing results. Data analysis aims to investigate and assessment the possible mechanisms that may be occurred and describe the removal processes. The equilibrium biosorption data usually used to study and identify the adsorption capacity of olive stone bio-sorbent by using commonly well-known adsorption isotherm models; Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich [Bohli et al., 2015; Babi'c et al., 2002], while, Pseudo First Order, Pseudo Second Order, Elovich, and Intraparticle diffusion models measure the reaction kinetics

rates [Basso et al., 2002; Brown et al., 2000]. Usually investigations have to be done at two stages, firstly; the batch testing and secondly the adsorption kinetics and isotherm analysis.

## RESEARCH AIMS AND SIGNIFICANCE

This work aims to show the effects of initial metal concentration on the kinetics of lead adsorption by olive stone waste used as sorbent. By this work the adsorption performance will be investigated by using the most widely used adsorption isotherm models; Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherms. In addition, the reaction kinetics rates are investigated by using: Pseudo First Order, Pseudo Second Order, Elovich, and Intraparticle diffusion kinetics adsorption models. The novel approach of this work is to in match the nature of the adsorbent (OSW adsorbent) and the best pathway to remove contaminants (heavy metal – lead metal ions), and to improve the design parameters of removal processes. The batch testings' results will be analyzed to obtain and identify the research objectives.

## MATERIAL AND EQUIPMENT

### Lead metal ions solutions, effective adsorbent dose, and pH adjustment

The lead metal aqueous solutions were prepared by dissolve lead nitrate  $Pb(NO_3)_2$  in appropriate volumes of distilled water to prepare the following solutions with an initial concentration of (0.3, 2.7, 4.5, 9, 18 and 60) mg/l. The adsorbent dose of the tested solutions was prepared by added a one gram of olive stone waste in 0.25 liter of adsorbate prepared solutions previously, which achieve a (4 grams of adsorbent/liter of lead solutions). This adsorbent is the effective dose tested and achieved in batch testing. The pH was adjusted by adding  $HNO_3$  (0.1 M) solution.

### Bio-sorbent preparation

The olive oil extraction industries in Jordan produce huge quantities of an excess materials make up the olive residues [Alslaibi et al., 2013; Bohli et al., 2017]. Jordanian olive stone waste (OSW) was used as an adsorbent for removal of

toxic metals from aqueous solutions [Rahmani and Sasani, 2016; Esalah et al., 2000]. This agricultural biowaste were collected from different sites in Jordan, mixed, cleaned, washed and soak with diluted nitric acid for 3 hours and then washed with distilled water and finally dried at 104 °C [Albadarin et al., 2015; Begum et al., 2015]. The adsorbent after drying was formed in a spherical granular particle with a diameter of about 40 μ cm [Nworie et al., 2019; Rodríguez et al., 2014]. Adsorbent is kept separately away from moisture and air in special containers.

### Instruments of measurement

HACH DR2000 Bench Top Spectrophotometer manufactured by HACH Company (USA) was used to measure the concentrations of lead ions during the testing time. The solutions pH was always measured and by using a digital pH meter (AZ PH meter 86501, Taiwan). For the purposes of weighting of different materials were used in the experiments a digital balance manufactured by (HANNA, USA) was used.

### METHODOLOGY

This research was done based on batch investigations which studied the effects of process pH, contact time, adsorbent dose and adsorbate initial concentrations on removal efficiency. The removal of contaminants (lead metal ions) by olive stone waste (bio-sorbent) is described as adsorption process. The removal percentages (R%) and the metal uptakes ( $q_t$ ) of the lead metal ions solutions at all

initial concentrations of (0.3, 2.7, 4.5, 9, and 18) mg/L eliminated by olive stone waste at adsorbent dose (OSW) of 1gram in 0.25 liters of liquid solution  $Pb^{2+}$ , pH of 6.8, and temperature of  $25 \pm 1$  °C were calculated by using Equations 1 and 2 below, respectively [Marwa et al., 2020; Al-Meshragi et al., 2008]. The obtained biosorption capacity ( $q_t$ ) of olive stone waste, and the removal percentages of lead metal ions (%R) values at different initial concentrations versus time (t) are tabulated in Table 1 and shown in Figure 1.

$$\text{Removal percentage of lead} = \frac{(C_{\text{initial}} - C_{\text{final}})}{C_{\text{initial}}} \times 100 \quad (1)$$

$$\text{Metal uptake} = \frac{(C - C_0)V}{M_s} \quad (2)$$

where:  $C_0$  is the initial concentration of the lead ions in mg/L and  $C$  is the final or equilibrium concentration of the solution in mg/L,  $V$  is the adsorbate volume in liters and  $M_s$  is the adsorbent amount in grams.

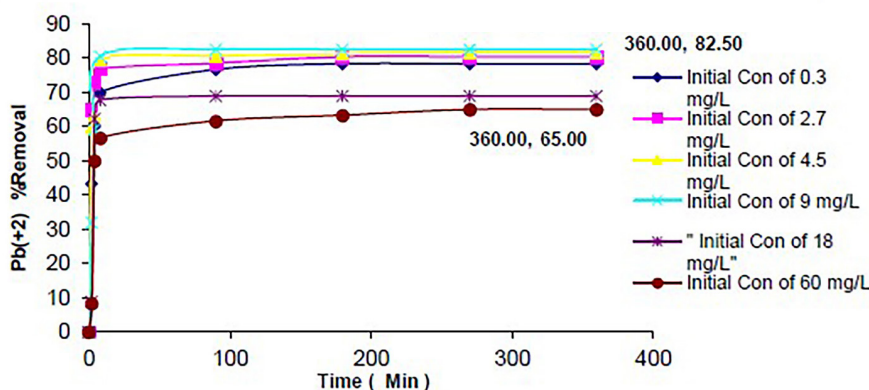
## RESULTS AND DISCUSSION

### Batch experiments

The previous experiments were designed to identify the optimal parameters of lead ions removal processes by using olive stone waste as done in the research by [Awad, 2024]. Firstly, the critical solution pH for the best highest removal efficiency of lead ions from liquid solutions was done by eleven sets of experiments in batch experimental techniques, and then it was found to be approximately (6.8). Results approved that the solution's

**Table 1.** Batch studies results for lead metal ions concentrations versus with time at adsorbent dose of 1 gram / 0.25 liter of liquid solution at temperature of  $25 \pm 1$  °C and solution pH of 6.8

Time (min)	Concentration of lead metal ions (mg/l)					
0	0.30	2.70	4.50	<b>9.00</b>	18.0	<b>60.0</b>
2	0.17	0.95	1.82	<b>6.13</b>	16.4	<b>55.0</b>
4	0.12	0.73	1.65	<b>3.68</b>	6.8	<b>30.0</b>
8	0.09	0.62	0.92	<b>1.75</b>	5.8	<b>26.0</b>
90	0.07	0.58	0.87	<b>1.58</b>	5.6	<b>23.0</b>
180	0.07	0.53	0.84	<b>1.58</b>	5.6	<b>22.0</b>
270	0.07	0.53	0.83	<b>1.58</b>	5.6	<b>21.0</b>
360	0.07	0.53	0.83	<b>1.58</b>	5.60	<b>21.00</b>
Equilibrium con. ( $C_e$ )	<b>0.07</b>	<b>0.53</b>	<b>0.83</b>	<b>1.58</b>	<b>5.60</b>	<b>21.00</b>
Removal efficiency %	78.3	80.4	81.7	<b>82.5</b>	68.9	<b>65.0</b>
Metal uptake $q_t$ (mg/gram)	5.9E-02	5.4E-01	9.2E-01	1.9E+00	3.1E+00	9.8E+00



**Figure 1.** Removal efficiencies of lead metal ions by using olive stone waste adsorbent at different  $Pb^{2+}$  initial concentrations versus time at solution pH of 6.8, adsorbent dose of 1-gram OSW/0.25 liters of solution, and process temperature of  $25 \pm 1$  °C

pH is one of the most important factors influencing the adsorption rate and the removal efficiency. This is due to the effects of the adsorbent's surface charge, the degree of ionization of the lead metal ions, and their speciation which are all influenced by the pH of the solution [Maleki et al., 2010; Nakano et al., 2001]. The most proper adsorbent dose was identified at 1 grams of adsorbent in 0.25 liters of solution. The proper adsorbent dose 1 g of adsorbent for 0.25 L of lead ions solutions (4 g/L) and the pH value of solution (pH of 6.8) are the most promising values for the highest removal efficiency at process temperature of  $25 \pm 1$  °C. The highest removal efficiency value hits 82.5% for lead ions initial concentration of 9 mg/L was happened at pH of 6.8 and adsorbent dose of (4 g/L) as shown in Figure 1. Results also approved that adsorption of heavy metals such as  $Pb^{2+}$  by using bio-sorbent manufactured from agricultural waste materials (olive stone waste) are efficient and effective even in case of diluted solution. In addition, these bio-sorbent is considered as low-cost adsorbent, and safe environmentally [Porpuri et al., 2009; Cui et al., 2016; Saadh et al., 2024]. According to Marwa Ben Amar et al. [2020] a removal efficiency of 94.5% was achieved for lead ions adsorbed by olive stone waste at pH of 6.

### Adsorption isotherm models

This part of research is aimed to analysis this results to understand the nature, mechanism, and adsorption rates of lead ion removed by OSW from prepared liquid solutions. Adsorption isotherms are the equilibrium data and property representations that show how adsorbent materials remove pollutants [Piccin et al., 2011]. Lead

metal ions contaminants removal by olive stone waste were typically tested and the results were analyzed using a four commonly used adsorption isotherms models: Langmuir model, Freundlich model, Temkin, and Dubinin-Radushkevich isotherms [Crini and Badot, 2008; Verma et al., 2006]. Batch's experimental results of the removal processes were analyzed to identify the mechanism of removal using the linear regression forms of the models [Nworie et al., 2019; Calero et al., 2009]. Following are the linear forms of Freundlich model, Langmuir model, Temkin, and Dubinin-Radushkevich isotherms:

1. Freundlich model: the linear form of Freundlich isotherm model is represented by the following:

$$\log(q_e) = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where:  $q_e$  – metals uptake (mg/g),  $K_f$  – Freundlich constant or sorption capacity is an indicator of adsorption capacity,  $C_e$  – equilibrium concentration of adsorbate (mg/l) and  $n$  – inearity constant  $1/n$  is the strength of adsorption in the adsorption process, when  $1/n$  is below 1 it indicates a normal adsorption and when  $1/n$  is above one it indicates a cooperative adsorption. Plotting  $\ln(q_e)$  versus  $\ln(C_e)$  Equation 1 results in a straight line of slope  $(1/n)$  and intercept  $\ln(K_f)$ .

2. Langmuir model: the linear form of the Langmuir isotherm model is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (4)$$

where:  $q_e$  (mg/grams) and  $C_e$  is the concentration of adsorbate at equilibrium in (mg/L),  $q_{max}$  – maximum adsorbent capacity in

(mg/g) and the adsorption isotherm constant is  $K_L$  in (L/mg); plotting of  $(\frac{C_e}{q_e})$  and  $(C_e)$  of Equation 2 will give a linear relationship from which  $q_{max}$  and  $K_L$  can be determined from the slope and intercept of the plotting.

Equation 5 gives the value of separation factor  $R_L$  which describes the Langmuir isotherm process [Al-Shaweesh et al., 2023]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

where:  $C_o$  – is the initial concentration of the adsorbate  $Pb^{2+}$  and  $R_L$  – is the separation factor of the adsorption process, which is unfavorable for value of  $> 1$ , linear for value of 1 and strong and irreversible for value = 0. The results are tabulated in Table 2.  $R_L$  values indicated that the process of removal is closed to pure adsorption.

3. Temkin adsorption isotherm: the linear form is given in the following formula:

$$\ln(A_T) + B_T \ln(C_e) \quad (6)$$

where:

$$B_T = \frac{RT}{b_T} \quad (7)$$

where:  $A_T$  – isotherm equilibrium binding constant (L/g); while  $b_T$  – Tempkin isotherm constant;  $R$  – universal gas constant and equals 8.314 J/mol/K;  $T$  – temperature of the process usually at a temperature of 298 K;  $B_T$  – constant related to the heat of sorption in (J/mol).

The constants were determined from the slope and intercept of the model fitting by plotting the metal uptake ( $q_e$ ) against  $\ln C_e$  as shown in Figure 2.

4. Dubinin-Radushkevich (D-R) model: The model liner form is given in the following

equation [Al-Meshragi et al., 2008]:

$$\ln(q_e) = \ln(Q_o) - K_{DR} \varepsilon^2 \quad (8)$$

Dubinin-Radushkevich model presents the required mean free energy for desorption of each molecule from its space site on the adsorbent surface and can be calculated by the following formula [Mohamed and Abu Al-Rub, 2003]:

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (9)$$

The parameter  $\varepsilon$  can be calculated from the following formula:

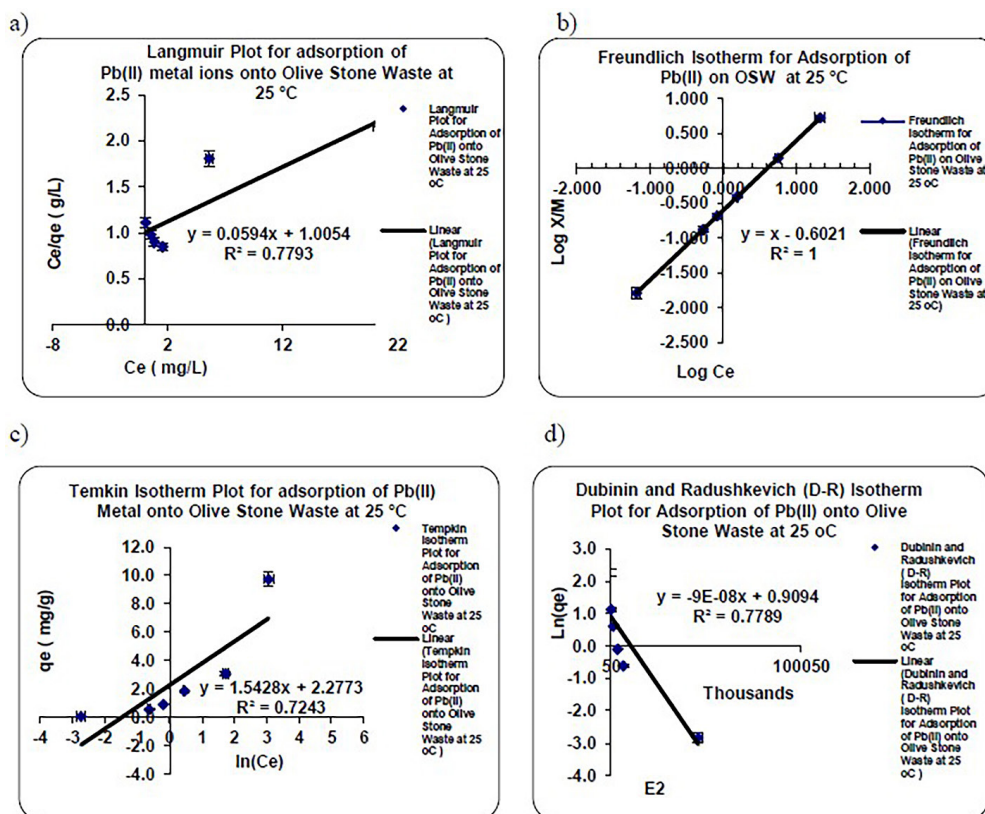
$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (10)$$

where:  $q_e$  – metal uptake at equilibrium conditions (mg/g);  $Q_o$  – theoretical isotherm saturation capacity (mg/g);  $K_{DR}$  – Dubinin-Radushkevich isotherm constant ( $\text{mol}^2\text{J}^{-2}$ );  $\varepsilon$  – adsorption potential constant;  $R$  – gas constant (8.314 J/mol/K),  $T$  – absolute temperature (K) and  $C_e$ , adsorbate equilibrium concentration (mg/L).

Experimental data were fitted according to Dubinin-Radushkevich model where  $\ln(q_e)$  versus  $\varepsilon^2$  as shown in Figure 2. Again, the previous batch experiments were done at critical values at  $25 \pm 1$  °C, by mixing 1-gram of adsorbent in 0.25 liter for each tested solution with different initial liquid concentrations of (0.3, 2.7, 4.5, 9, 18 and 60 mg/l). The experimental results were presented in Table 1, above. These resultant data were treated and prepared in a mathematically forms to calculate the investigated models' variables and parameters as shown in Table 2. The model's variables of (X–Y) coordinates prepared in Table 2 were plotted as shown in Figure 2. The adsorption isotherm constants, parameters and the corresponding correlation coefficients ( $R^2$ ) of the

**Table 2.** Fitting variables for plotting of adsorption isotherms adsorption system  $Pb^{2+}$ -OSW by: (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin–Radushkevich models

Variables of adsorption isotherm models plotting of lead ions – olive stone waste												
Co	Ce (mg/l)	$q_e$ (mg/g)	Ce/ $q_e$	X (mg)	x/ms (mg/g)	log (X/M)	log (Ce)	ln (Ce)	Ln ( $q_e$ )	$\varepsilon$	$\varepsilon^2$	$R_L$ separation factor
0.3	0.065	0.059	1.106	0.016	0.016	-1.789	-1.187	-2.733	-2.834	6770	4.6E+07	0.983
2.7	0.530	0.543	0.977	0.133	0.133	-0.878	-0.276	-0.635	-0.612	2570	6.6E+06	0.863
4.5	0.825	0.919	0.898	0.206	0.206	-0.686	-0.084	-0.192	-0.085	1920	3.7E+06	0.790
9.0	1.575	1.856	0.848	0.394	0.394	-0.405	0.197	0.454	0.619	1190	1.4E+06	0.653
18.0	5.600	3.100	1.806	1.400	1.400	0.146	0.748	1.723	1.131	398	1.6E+05	0.485
60.0	21.000	9.750	2.154	5.250	5.250	0.720	1.322	3.045	2.277	113	1.3E+04	0.220



**Figure 2.** Adsorption isotherm models variables plotting for adsorption system  $Pb^{2+}$ -OSW by: (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin and Radushkevich models

linearized forms of each investigated model were determined and tabulated in Table 3.

Results said that data are fitted well to Freundlich model with  $R^2$  equals of 1. It is obvious from data plotted in Figure 2 that fitting is following Freundlich’s isotherm model ( $R^2=1$ ). Table 3 shows that the correlation coefficients ( $R^2$ ) increased in the following order, Freundlich > Langmuir > D-R > Temkin models. As results, the Freundlich model is the one that best describes the adsorption of the lead metal ions for all the range of experimental conditions investigated.

It is obvious from the results of adsorption isotherms as shown in Figure 1 and models fittings in Figure 2 that the removal of lead ions from liquid solutions is described as adsorption process. As can be seen in Figure 1, it is clear

that the process of removal for lead ions is occurred into two successive stages building two adsorbed layers of adsorbate  $Pb^{2+}$ ; the first layer is built inside the adsorbent (olive stone waste) until filled, and then the second one is occurred on the surface of adsorbent, respectively. In addition, the adsorption rate in the first stage is highly occurred within 5 to 10 minutes, while the second stage longed to 100 minutes before the constant rate situation occurred [Awad, 2024; Crini and Badot, 2008]. These two processes behavior are presented clearly in Figure 1, where the rate of removal is very high at first stage because of highly availability of adsorption sites on the adsorbent surface which fills first with lead ions and then the removal or adsorption is kept at constant rate [Khalfaoui et al., 2003; Calace et al., 2002] at the

**Table 3.** Adsorption isotherm models coefficients and correlation coefficients for adsorption system  $Pb^{2+}$ -OSW by: (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin–Radushkevich models

Isotherm Model	Slope	Parameters	Value	Intercept	Parameters	Value	$R^2$	E	
Langmuir	0.059	Equals ( $1/q_m$ )	$q_m$	16.835	1.0054	equals ( $KL \cdot q_m$ )	$k_L = 0.059$	<b>0.7793</b>	–
Freundlich	1.000	Equals ( $1/n$ )	n	1.000	-0.6021	equals $\ln(K_f)$	$K_f = 0.548$	<b>1.0000</b>	–
Temkin	1.543	Equals (BT)	BT	1.543	2.2773	$BT \cdot \ln(A_T)$	$A_T = 4.376$	<b>0.7243</b>	–
Dubinin–Radushkevich	-3.0E-08	Equals ( $-K_{DR}$ )	$K_{DR}$	3E-08	0.9094	$\ln(Q_0)$	$Q_0 = 2.483$	<b>0.7789</b>	4082

end state of equilibrium ( $C_e$ ) as shown in Table 1. The second layer of adsorption on adsorbent surface is always built after the grooves and sites for adsorption are filled and completed.

The correlation coefficients for adsorption models' equations investigated are found as follows: 1.0000, 0.7793, 0.7789, 0.7243 for Freundlich > Langmuir > Dubinin–Radushkevich > Temkin models, respectively. These results approve that the adsorption process is occurred definably between olive stone waste as adsorbent and lead metal ions as adsorbate and this was approved by [Calero et al., 2009]. The variations in correlation coefficients and the different parameters values resulted of the isotherms kinetics parameters defining may be due to the models' hypotheses and the type of adsorption mechanisms and the assumptions that adopted when constructed these models. In addition, it is known that all adsorption models used in this research are two adsorption parameters models using the equilibrium concentrations and metal uptakes data [El-Khaiary, 2008]. It is known that, Freundlich isotherm model is used for adsorption on heterogenous surfaces where the model describes the surface activity and the surface nature towards the adsorption of metal ions from aqueous solution [Ayawei et al., 2015] and this is complied with this research results. On the other hand, Langmuir model describes the coverage of the adsorbent surface by measuring the rate of adsorption and desorption at the dynamic equilibrium state conditions [Elmorsi, 2011; Gunay et al., 2007]. While, Dubinin–Radushkevich model is an empirical model using to describe the adsorption onto heterogenous surfaces for intermediate low adsorbate concentrations mostly in gaseous and vapors adsorption on adsorbate surface at low pressures [Travis and Etnier, 1981; Celebi et al., 2007; Theivarasu and Mysamy, 2011]. Therefore, this model is used to distinguish between the physical and chemical adsorptions [Vijayaraghavan et al., 2006]. And finally, the Temkin model which has a correlation coefficient of (0.7243) considers the indirect effectiveness of both adsorbent and adsorbate on each other during the surface coverage of adsorbent in adsorption processes for low range of metal ions concentrations [Ringot et al., 2007; Shahbeig et al., 2013]. In addition to accounting for the impact of indirect adsorbate–adsorbate interactions on the adsorption process, the Temkin isotherm model assumes that a rise in surface area causes the heat of adsorption of all molecules in the layer to fall linearly [Marwa et al., 2020; Calero et

al., 2009]. This may be the reason for that the data not fitted well to this model. Those features and facts about the models may consider for the differences in the fitted of the models for description the adsorption processes and consequentially responsible for those variations in correlation coefficients happened in this research. But all resultant coefficients and other parameters were approved that the processes are adsorption and mostly fitted the Freundlich isotherm model.

Separation factor ( $R_L$ ) was calculated for the adsorption Pb(II) based on Langmuir isotherm model. Separation factors (RL) were obtained and tabulated in Table 2. The values of Separation factor ( $R_L$ ) are ranged from 0.22–0.983 for the adsorption of  $Pb^{2+}$  by olive stone adsorbent which means that the adsorption is favorable for lead removal by OSW [Awad, 2024; Nworie et al., 2019]. It is clear that as lead ions concentration increased the separation factor decreased and this behavior is consistency with a result of many researches [Marwa et al., 2020].

In case of calculation the (n) value which represents the strength of adsorption based on Freundlich isotherm model, the obtained value is (n=1) as shown in Table 3, this indicates that the adsorption processes are described as normal or cooperative adsorption process. This support the assumption of the model which adopted that the adsorption process according to Freundlich which is occurred for the metal ions on the heterogenous surface of adsorbent with multilayers [Nworie et al., 2019].

### Adsorption kinetics models

In this single metal research experiments with olive stone waste of (1 mg adsorbent/liter) adsorbent dose, for 360 minutes at pH 6.8 and temperature of  $25 \pm 1$ , olive stone waste adsorbed metal (82.5%) for lead initial concentration of 9 mg/liter. This value decreased to 65% (21% of reduction) in the case of initial metal concentration of 60 mg/liter as shown in Table 1. The batch experiments' results and the obtained data of the single adsorption system ( $Pb^{2+}$ ) - OSW were analyzed and fitted according to the four chosen kinetics models as follows: Pseudo First Order, Pseudo Second Order, Elovich, and Intraparticle Diffusion models. The linear regression forms of the kinetics adsorption models investigated in this part of the study are listed as follows:

1. Pseudo First-Order model: The model linear form is given in the following equation

[Al-Meshragi et al., 2008]:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}(t) \quad (11)$$

where:  $q_e$  and  $q_t$  – are amounts of chromium adsorbed at equilibrium and at time  $t$  (mg/g), respectively, and  $k_1$  – is the equilibrium rate constant of pseudo first-order adsorption (1/min).

A plot of linearization form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots of  $\log(q_e - q_t)$  versus  $t$  were used to determine the pseudo first-order constant  $k_1$  and equilibrium adsorption density  $q_e$  as shown in Figure 3a.

2. Pseudo second-order model: This adsorption kinetic model can be expressed in linear form as follows [Gao et al., 2021]:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (12)$$

The plot of the term  $(t/q_t)$  versus time as shown in Equation 10, should give a linear relation. The constants and parameters of the model  $q_e$  and  $k_2$  the pseudo-second order rate constant can be determined from the line slope and intercept of the fitted line as shown in Figure 3b, where  $k_2$  is the equilibrium rate constant of pseudo second-order adsorption (g/mg·min). The straight line in the plot of  $t/q_t$  versus  $t$  shows a good agreement of experimental data with the pseudo second-order kinetic model for different initial lead ions concentrations. At boundary conditions of  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_e$  the data fitted as shown in Figure 3b. The generated straight line of the fitted data of  $[t/q_t]$  versus  $[t]$  shows a good agreement of measured data with the kinetic model form for all initial lead

concentrations. The results also indicated that the sorption of  $Pb^{2+}$  removal behaves as pseudo second-order adsorption kinetics. It developed good correlation coefficient ( $R^2 = 1$ ) which approved the fittingness of as pseudo second-order adsorption model. Table 4 lists the calculated constants and parameters obtained from the kinetics models. The correlation coefficient for pseudo second-order kinetic model obtained is ranged from 0.9996 to 1.0000.

3. Elovich model: The linear form of the model is simplified by Chien and Clayton [93-New] assumed  $\alpha \beta \gg t$  and by applying the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q$  at  $t = t$  then they got the final linear form as in Equation 13:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (13)$$

where:  $\alpha$  – is the initial adsorption rate (mg/g·min) and  $\beta$  – is the adsorption constant (g/mg) during any experiment. If  $Pb^{2+}$  adsorption fits the Elovich model, a plot of  $q_t$  versus  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta)\ln(\alpha\beta)$ .

4. Intra-particle diffusion model: The linear form of intra-particle diffusion model is expressed as follows:

$$\log R = \log k_{id} + a \log(t) \quad (14)$$

where:  $R$  is the percent of  $Pb^{2+}$  adsorbed,  $k_{id}$  is a rate factor (percent  $Pb(I+2)$  adsorbed per minute and  $a$  depicts the adsorption mechanism. In general, the slope of the line is called as intra-particle diffusion rate constant,  $k_{id}$ . The rate parameters  $k_{id}$  together with the correlation coefficients are also listed in Table 6.

**Table 4.** Calculation example of kinetics adsorption parameters and variation coefficients @  $C_o$  of 0.3 mg/l for the models: (a) Pseudo first order, (b) Pseudo second order, (c) Elovich, (d) D-Intraparticle diffusion

Variables of kinetics adsorption models plotting of lead ions – olive stone waste											
Time (hr)	Con. (mg/l)	q (mg/g)	( $q_e - qt$ )	Log ( $q_e - q_t$ )	t/q	ln(t)	log R	log t	Ln ( $C_o/C_e$ )	x = c·v (mg)	x/m
0.00	0.30	0.000	0.059	-1.23	–	–	–	–	0.00	0.08	0.075
0.17	0.17	0.033	0.026	-1.57	5.23	-1.77	1.64	-0.77	0.57	0.04	0.043
0.50	0.12	0.045	0.014	-1.85	11.11	-0.69	1.78	-0.30	0.92	0.03	0.030
1.00	0.09	0.053	0.0068	-2.17	19.05	0.00	1.85	0.00	1.20	0.02	0.023
12.00	0.07	0.058	0.0018	-2.76	208.70	2.48	1.88	1.08	1.46	0.02	0.018
24.00	0.07	0.059	0.0005	-3.30	408.51	3.18	1.89	1.38	1.53	0.02	0.016
36.00	0.06	0.059	0.0003	-3.60	610.17	3.58	1.90	1.56	1.54	0.02	0.016
48.00	0.06	0.059	0.0003	-3.85	810.13	3.87	1.90	1.68	1.56	0.02	0.016

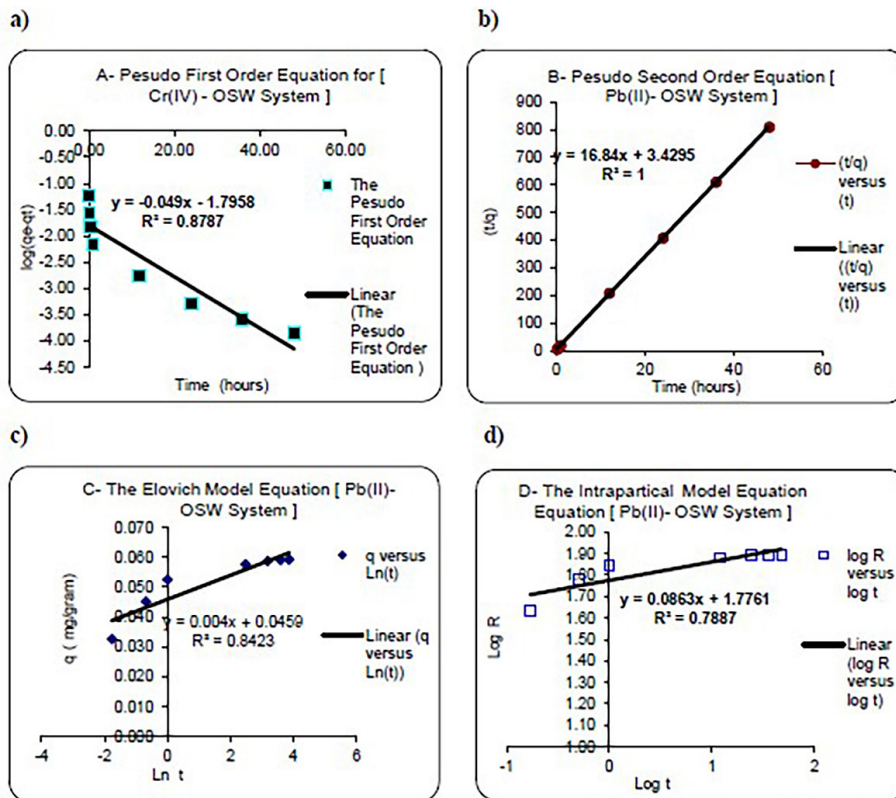


Plotting of the data obtained from batch experiments previously for fitting the linear forms of investigated models were done at the initial solution concentrations of (0.3, 2.7, 4.5, 9, 18, and 60) mg/l. This work aims to calculate and identify the models' constants and parameter. An example of calculation and fitting of the investigated models were done at initial adsorbate solutions concentrations of 0.3 mg/l as shown in Table 4 which shows the required variables values for curves plotting of the selected four kinetics models. Figure 3 represents the curves data plotting of the investigated models at the same operating conditions.

An example of determination the constants and parameters of kinetics adsorption models the process of lead metal ions removal by olive stone waste was done at initial concentration of adsorbate's solution ( $Pb^{2+}$ ) of 0.3 mg/l. Results are

shown in Table 5. This calculation method was applied for all other investigations cases at initial concentrations of (2.7, 4.5, 9, 18 and 60) mg/l where the results are tabulated in Table 6.

This part is concentrated on discussion of the reaction kinetics models investigation. It is obvious that data are fitted well to Pseudo second order model as shown in Table 6 and Figure 3, where the correlation coefficients ( $R^2$ ) are approximately equal to 1 for all tested cases done at different adsorbate solutions' initial concentrations of (0.3, 2.7, 4.5, 9, 18, and 60) mg/l. Again, the correlation coefficients values ( $R^2$ ) of the four reaction kinetic models investigated are as follows; 1, 0.8787, 0.8423, 0.7887 for Pseudo second order > Pseudo first order > Elovich > Intraparticle diffusion models, respectively. These figures say that removal kinetics are applicable by



**Figure 3.** Kinetics models plotting of  $Pb^{2+}$ -OSW adsorption system of the models; (a) Pseudo first order, (b) Pseudo second order, (c) Elovich, (d) Intraparticle diffusion @  $C_0 = 0.3$  mg/l

**Table 5.** Calculation example of kinetics adsorption parameters and variation coefficients @  $C_0$  of 0.3 mg/l for the models; A – Pseudo first order, B – Pseudo second order, C – Elovich, and D – Intraparticle diffusion

Model	Pseudo first order		Pseudo second order		Elovich		Intraparticle diffusion		
Slope =	-0.049	$k_1/2.303$	16.84	$1/q_e$	$q_e = 0.0594$	0.004	$1/\beta$	0.0863	a
Intercept =	-1.796	$\log(q_e)$	3.4295	$1/h = k_2 q_e^2$		0.0459	$1/\beta * \ln(\alpha\beta)$	1.7761	$\log(k_i)$
					250	$\alpha$		59.7173	

**Table 6.** Kinetics adsorption parameters and variation coefficients for Pb<sup>2+</sup>-OSW adsorption system for the models; (a) Pseudo first order, (b) Pseudo second order, (c) Elovich, (d) Intraparticle diffusion

Reaction model		Initial concentration (mg/l )					
Model name	Parameters & Correlation coefficients	Co= 60	Co= 18	Co= 9	Co= 4.5	Co= 2.7	Co= 0.3
Pseudo first order model	$k_1$ (l/min)	1.87E-01	1.39E-01	1.40E-01	1.63E-01	1.46E-01	1.13E-01
	R <sup>2</sup>	0.91	0.76	0.82	0.90	0.90	0.88
Pseudo second order model	$k_2$ (g/mg·hr)	5.797E+00	1.137E+00	3.122E-01	9.525E-02	6.754E-02	1.209E-02
	h (mg/g·hr)	1.68E+01	8.58E+00	1.12E+01	8.89E+00	4.42E+00	2.92E-01
	R <sup>2</sup>	0.9996	0.9996	1.0000	1.0000	1.0000	1.0000
Elovich model	$\alpha$ (mg/g·hr)	9.27E-01	3.30E+00	6.27E+00	2.42E+01	6.41E+01	2.50E+02
	$\beta$ (g/mg)	3.67E+02	4.22E+02	8.73E+02	6.94E+06	8.02E+11	3.85E+02
	R <sup>2</sup>	0.66	0.44	0.69	0.78	0.82	0.84
Intraparticle diffusion model	$k_{id}$	3.16E+01	3.60E+01	5.67E+01	6.91E+01	7.27E+01	5.97E+01
	$\alpha$	2.37E-01	2.21E-01	1.25E-01	5.19E-02	3.14E-02	8.63E-02
	R <sup>2</sup>	0.52	0.48	0.63	0.77	0.80	0.79

four models but the Pseudo second order model is the one that describes the sorption of lead ions by olive stone waste [Calero et al., 2009].

Refer to Figure 1 for removal isotherms it is obvious that as the initial concentration of adsorbate (Pb<sup>2+</sup>) increase the adsorption capacity (metal uptake  $q_e$ ) and removal efficiency (R%) increased till certain concentration which is 9 mg/l (see Figure 1). This means that the behavior of removal is similar and affected by initial concentration of the adsorbate. For certain value of adsorbate initial concentration of 9 mg/l the removal efficiency was found to be the maximum removal efficiency equals (R = 82.5%) as shown in Table 1 and Figure 1. After that initial concentration of (9 mg/L) the removal efficiency is decreased as the adsorbate's initial concentration increased. This means that the rate of removal (adsorption) decreased as the initial concentration of adsorbate increased and the process subsequently

proceeds slowly till equilibrium is achieved as seen in Figure 1. This behavior is attributed to maximum capacity of adsorbent for the used adsorbent dose used (1 gram per 0.25 liters of adsorbate solution). This is in consistence with many researches' results assumed that the rate of occupation of sorption sites is proportional to the number of unoccupied sites [Awad, 2024; Shahbeig et al., 2013]. This also could be clarified by the changes of the sorption constant ( $k_2$ ) and the initial sorption rate (h) of the pseudo-second order model as follows; it is clear that sorption constants  $k_2$  (g/mg·hr) the pseudo-second order rate constant increases as the initial concentration increases as follows, 0.01209, 0.06754, .09525, 0.31220, 1.13700, 5.79700 and also  $h = ks^2 \cdot q_e^2$  the initial sorption rate, in mg/g·hr increases as the initial concentration increases, changing from 0.292, 16.800. In addition, Figure 1 reflects this behavior where the adsorption process done into two stages,

**Table 7.** Olive stone bio-sorbent metal uptake capacity comparison with different biomasses that are fitted (pseudo-second order kinetic model)

Initial concentration (mg/l)	Biosorbent	Metal uptake $q_e$ (mg/gram)	Temperature (°C)	Reference
50	<i>Ulmus carpinifolia</i>	4.83	25	Sangi et al. (2008)
500	<i>Spirulina platensis</i>	98.62-98.62	25-50	Seker et al. (2008)
-	Sawdust	4.59	25	Li et al. (2007)
-	Modified peanut husk	4.66	25	Li et al. (2007)
20	<i>Syzygium comini</i> L.	0.24-5.32	20-30	King et al. (2007)
20	Lichen ( <i>Cladonia furcata</i> )	0.06-0.12-1.02	40-30-20	Sari et al. (2007)
25	<i>Parmelina tiliaceae</i>	0.95-0.99	40-30	Uluozlu et al. (2008)
220	Olive stone	5.66	25	M. Cale et al. (2009)
9	Olive stone waste	1.9	25	This study

the first one increases rapidly and fast and the second one subsequently is slow until equilibrium is achieved. As a result, it is concluded that the behavior of the removal process of the contaminates  $Pb^{2+}$  by the olive stone adsorbent (OSW) is an adsorption behaves. According to the pseudo-second-order kinetic model assumption that the rate-limiting step is related to chemical sorption, then the results also approve that the adsorption has the nature of chemical removal beside the physical removal properties [Sarwar et al., 2024; Marwa et al., 2020].

Table 7 shows different adsorbents that were used to remove lead ions from aqueous solution such as: *Ulmus carpinifolia*, *Spirulina platensis*, sawdust, modified peanut husk, *Syzygium comini* L., lichen (*Cladonia furcata*), *Parmelina tiliaceae*, and olive stone waste [Kobyta et al., 2005; Martín et al., 2016; Sreejalekshmi et al., 2009]. It is obvious that most of these adsorbents recorded about 15% on average of removal percentage of the lead solutions' initial concentrations were used. It is clear that olive stone waste adsorbent has lower removal efficiency at higher lead ions initial concentration.

## CONCLUSIONS

This research is inconsistent with other researches results which approved that olive stone waste could be used as a cheap and good adsorbent for lead ions contaminates removal. A maximum removal efficiency of 82.5% was achieved for aqueous lead ions initial concentrations of 9 mg/l at a solution pH of 6.8 and adsorbent dose of 1-gram OSW per 0.25 liters of solution at temperature of  $25 \pm 1$  °C. Results for biosorption kinetics of lead ions  $Pb^{2+}$  by using olive stone waste adsorbent fitted well to Freundlich and Pseudo second order kinetics models at all operation conditions. The sorption kinetics of  $Pb^{2+}$  ions using olive stone waste is fitted well according to Pseudo second order model under the above conditions at all initial concentrations were tested of (0.3, 2.7, 4.5, 9, 18, and 60) mg/l. It was found that sorption constants  $k_2$  (g/mg·hr) the pseudo-second order rate constant and  $h = ks^2 \cdot q_e^2$  the initial sorption rate, in mg/g·hr are increases as the initial concentration increases. The parameter values obtained from the isotherms and kinetic models for olive stone - lead ions system approved that the process of removal is adsorption process.

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