

Kinetics and equilibrium adsorption of lead (II) ions on olive residues: Effects of chemical activation

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ABSTRACT/RESUME

Abstract: This work reports on the influence of treatment conditions on the olive stones for adsorptive lead(II) ions. The olive stones were treated with acidic or alkaline solutions at various concentrations and contact time. The structure and surface properties of the resulting biosorbents were characterized by surface pH, Boehm's titration and N₂ adsorption-desorption isotherms. The olive stones sample, treated with HNO₃, possess the highest surface oxygen containing functional groups (3.76 mmol/g), surface area (198 m²/g) and pore volume (0.081cm³/g) and the more adsorption capacity to the lead ions. The adsorption efficiency was higher for treated of olive stones with HNO₃ than for treated with KOH. However, the weight loss of the adsorbent products was important with HNO₃ treatment. It was also found that the time to reach equilibrium takes less 15 minutes.

The effect of contact time, initial concentrations of adsorbate, ionic strength and adsorbent dose on the uptake of lead was studied in batch experiments. The kinetic data were fitted to the pseudo-first order and pseudo-second order, and follow closely the pseudo-second order model. Equilibrium adsorption of Pb(II) were analyzed by the Langmuir, Freundlich and Redlich-Peterson isotherm models. The results reveal that the Redlich-Peterson isotherm models fitted the data.

I. Introduction

Lead is ubiquitous in the environment but hazardous at the high concentration in the form of ion state (Pb(II)), leading to the poisonousness of human neuronal system [1]. The wastewater containing Pb(II) ions threatening the public health is largely generated by the battery manufacturing, basic steel, paper and pulp, metal plating, leather tanning, agrochemicals, petrochemicals and fertilizer industries. It is necessary to remove the Pb(II) ions highly-efficient from different effluents in order to maintain the security of natural water system [2,3].

Adsorption of heavy metals from aqueous solutions is a relatively new process that has proven to be

very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams [4, 5].

The adsorption capacity of lignocellulosics for metal ions is generally described as adsorption. The major advantages of the adsorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive adsorbent materials. The major advantages of adsorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of adsorbent, no

additional nutrient requirement, and the possibility of metal recovery [6].

The cost advantage of the adsorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries. The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste [7], sawdusts [8], hazelnut shells [9], pine bark [10], peanut hull [11], rice husk ash [12], coconut husk [13], peanut hull [14], coffee residue [15], modified cellulosic materials [16], chemically modified orange peel [17], corncobs and modified corncob [18], rice hulls [19], waste date stones [20], almond shells [21] and different agricultural byproducts have been used and investigated.

Heavy-metal adsorption onto carbonaceous materials is considered to mainly take place at oxygen-containing functional groups, such as carboxylic and lactonic groups [22-25]. Additionally, the amount of heavy metal ions adsorbed onto carbonaceous materials is not the stoichiometric one of the oxygen containing functional groups. The poor relation between the amount of functional groups and the adsorption capacity indicates that carbonaceous materials adsorption process is complex. The interaction between oxygen-containing functional groups and heavy metal ions is not yet understood well.

The present work aims to analyze the effect of the oxygen containing functional groups of olive stones in the adsorption of Pb(II). Strong oxidation acids and basics such as nitric acid and potassium hydroxide are used to increase the oxygen containing functional groups on olive stones. Batch experiments are performed to evaluate the effect of contact time, initial concentrations of adsorbate, ionic strength and adsorbent dose on the Pb(II) adsorption. The kinetic data were fitted to the models of pseudo-first order and pseudo-second order, and follow closely the pseudo-second order model. Equilibrium adsorption isotherms of Pb(II) were analyzed by the Langmuir, Freundlich and Redlich-Peterson isotherm models. The results reveal that the Redlich-Peterson isotherm models fitted the data.

II. Experimental methods

II.1 Biomass raw materials

The olive stones were collected from the factory of production of olives located at Akbou (Béjaïa). This material was first washed with distilled water to remove water-soluble impurities, surface adhered particles and then dried at 60 °C. The methods

outlined by Ramadevi et al. [26] were adopted to estimate the lignin, hemicelluloses and cellulose content. Briefly, the lignin content was measured by placing 2 g of sample in a 500 ml beaker and 15 mL of 72% sulfuric acid. The mixture was stirred at 100 rpm for three hours at 25 °C. 200 mL of water were then added to the mixture and everything is brought to a boil until precipitation of the lignin (two hours). Once cooled, after 24 h, lignin was transferred to a crucible and washed with hot water. The crucible with its content was dried at 105 °C and weighted every hour until a constant weight was reached. The holocellulose content was measured by placing 160 mL of water, 0.5 mL of acetic acid, 1.5 g of sodium chloride and 3 g of sample in a beaker placed in a water bath maintained at 75°C. After one and two hours at 75°C, 5 mL of acetic acid and 2.5 g of sodium chloride were added to the mixture. The beaker was then placed in an ice bath and cooled. The isolated holocellulose was sequentially washed with acetone, ethanol and water. The sample was finally dried at 105°C until constant weight was reached. The content of cellulose was measured by adding 10 mL of 18% (w/v) sodium hydroxide to 2 g of the isolated holocellulose. The mixture kept at 20°C was continuously stirred at 120 rpm. Every 5 min, 10 mL of the sodium hydroxide solution (18%) was added during half hour. 35 mL of water was added to the beaker and kept under 120 rpm agitation for another hour. The cellulose residue isolated was washed subsequently with 100 mL of 8.5% sodium hydroxide solution, 200 mL of water, 15 mL of 10% (w/v) acetic acid and water. The content of the crucible was dried at 105 °C until constant weight was reached. The hemicellulose content was calculated by subtracting the cellulose content from holocellulose [27]. ASTM Method D4442-07 was followed to determine the moisture content of the date stones samples. 0.5 g (done in triplicate) of sample was placed in a convection oven at 105 °C ± 5 °C for 5 h. The sample was removed, cooled in desiccators and then weighted. The moisture content was calculated basing on percentage mass lost. ASTM Method E1755-01 was used to estimate the ash content of the sample. The method involved weighting 0.5 g (done in triplicate) of sample into a pre-weighted crucible. The crucible was heated to 575 °C for 3 h. To avoid causing flames, the sample was heated to approximately 250 °C and gradually increased to 575 °C. The residue left after 3 h was cooled in desiccators and weighted. The content was heated in a convection oven at 105 °C until constant weight [26]. The Biopolymer content (wt %) of the initial material is shown in Table 1.

Table 1. The Biopolymer content (wt %) of the olive stones

	Moisture (%)	Ash ratio	Extractible	Lignin ratio	Cellulose	Hemicelluloses
Characteristics		(%)	ratio (%)	(%)	ratio (%)	ratio (%)
Olive stones	4.00	4.15	9.48	15.95	32.05	34.37

II.2 Treatment with acidic and alkaline solutions

Chemical modification of olive stones was done by immersing 10 g of raw material (with the size fraction 0.315–1 mm.) in 250 mL of acidic or alkaline solutions with various concentrations and contact time.

The general schematic diagram for the preparation is illustrated in Fig. 1.

After each treatment, the biomass was thoroughly washed with deionised water until a constant pH, and dried at 60 °C for 24 h.

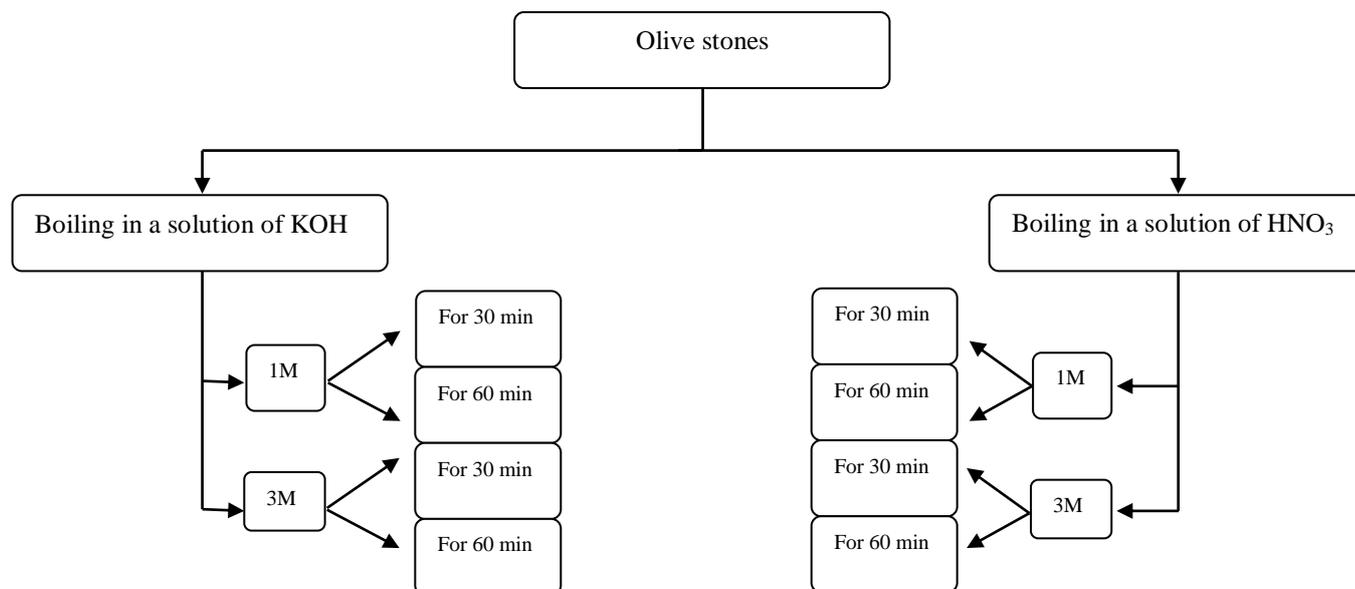


Figure 1. Schematic presentation for preparation of biosorbents

II.3. Characterization of the biosorbents

II.3.1 Surface area and porous structure

The pore structure characteristics of the resulting biosorbents were determined by nitrogen adsorption at -196 °C by Gas Sorption Analyzer (Quantachrome NOVA WIN2- Version 9.0). Prior to gas adsorption measurements, the biosorbents were degassed at 200 °C in a vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_0) range from approximately 0.005 to 0.985. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.985 and at this relative pressure all pores were completely filled with nitrogen gas. The

Dubinin–Radushkevich (D–R) equation represented below [28]:

$$\log V = \log V_{mic} - D \left(\log \left(\frac{P}{P_0} \right) \right)^2 \quad (1)$$

was applied to calculate the micropore volume (V_{mic}). The mesopore volume (V_{mes}) was obtained by deducting the micropore volume from the total pore volume.

II.3.2. pH_{PZC} Determination

The pH of the point of zero charge (pH_{PZC}) of the biosorbent sample was determined using the method reported by Villacanas et al. [29] Aliquots with 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH values were adjusted

between 2 and 12 with the addition of 0.01 M solution of HCl or NaOH. A 0.15 g portion of the biosorbent was added to each flask and shaken for 48 h. When the pH value remained constant, the final pH was measured using a pH meter. The pH_{PZC} value is the point where the curve pH_{final} versus $pH_{initial}$ crosses the line, that is, $pH_{initial} = pH_{final}$.

II.3.3 Boehm titration

The Boehm titration method can be described as follows: 0.5 g of olive stones was placed to a series of flask which contain 50 ml of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide and hydrochloric acid. The flasks were sealed and shaken for 24 h. After 24 h, the solutions were filtered, and then 10 ml of each solution was pipetted and was titrated with 0.05 N sodium hydroxide and or hydrochloric acid, depending on the original solution used. The amount of acidic groups on the olive stones is calculated under the assumption that NaOH neutralizes carboxylic, lactic, and phenolic groups; Na_2CO_3 , carboxylic and lactic; $NaHCO_3$, only carboxylic group. The number of surface basic sites is calculated from the amount of HCl that reacted with the olive stones. The reaction between the reagents and the acidic oxygenated functional groups on the surface is based on the difference in acid/base strength. The strength of acidic groups is as follow: carboxyl > lactone > phenol [30].

II.3.4 Adsorbate and analytical measurements

All the compounds used to prepare reagent solutions are of analytic reagent grade. The mother solution of Pb(II) (1000 mg L^{-1}) is prepared by dissolving a weighed quantity of lead nitrate in distilled water. The concentration of metals solutions are ranged from 10 to 90 mg L^{-1} . Before mixing with the biosorbent, the pH of each solution is adjusted to the required value by adding 0.1 M NaOH or 0.1 M HNO_3 . SCHIMADZU AA6500 atomic absorption spectrophotometer (AAS) equipped with a Zeeman atomizer and a SSC-300 autosampler is used to determine the concentration of unadsorbed Pb(II) ions in the solution. All the instrumental conditions are optimized for maximum sensitivity as indicated by the manufacturer.

II.3.5 Batch sorption procedure

Batch experiments of adsorption were performed in batch reactor (3 L) placed in a temperature-controlled shaker (RCS LAUDA), at $25 \pm 2 \text{ }^\circ\text{C}$. A known weight of biosorbent is left in contact with 1000 mL of each solution ($10\text{-}90 \text{ mg/L}$) stirred at 200 rpm during 2 h. The initial pH value of the solution is adjusted with nitric acid (0.1 mol L^{-1}) or sodium hydroxide (0.1 mol L^{-1}). The pH value is chosen so that metallic species are present in their divalent form (5.8). Small-volume liquid samples

are withdrawn at different time intervals. Samples are filtered through glass-filter paper to remove adsorbent particles. The evolution of the adsorbed quantities of Pb(II) ions was evaluated using the following equation:

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (2)$$

where q_e is the amount of ions adsorbed per mass unit of biosorbent, C_0 is the initial metal ions concentration (mg L^{-1}), C_e is the equilibrium metal ions concentration (mg L^{-1}), V is the volume of the aqueous phase (L) and m is the weight of used biosorbents (g).

II.4 Adsorption isotherms

Langmuir, Freundlich, Sips and Redlich–Peterson models were tested at equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed ions. It can be represented by the equation [31]:

$$q_e = q_{mon} \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

where C_e is the solute concentration (mg L^{-1}) at equilibrium, q_e is the amount of solute at equilibrium (mg g^{-1}), q_{mon} and K_L are Langmuir constants related to adsorption capacity (mg g^{-1}) and the energy of adsorption respectively.

Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and given by [32]:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$) and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity respectively.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution.

Redlich and Peterson [33] proposed an empirical equation to represent equilibrium data:

$$q_e = \frac{k_R C_e}{1 + a_R C_e^\beta} \quad (5) \quad \text{where } \beta \leq 1$$

where k_R (L g^{-1}), a_R (L mg^{-1}) and β are Redlich–Peterson isotherm constants. This equation reduces to a linear isotherm in the case of low surface coverage and to a Langmuir isotherm when $\beta = 1$.

II.5 Adsorption kinetics

The controlling mechanism of the metal adsorption process was investigated by fitting first and second-order kinetic models to the experimental data. The linearized first-order kinetic model is given as [34]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min). The linearized form of the second-order kinetic model is [35]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 is the equilibrium rate constant of pseudo-second-order model ($\text{g mg}^{-1} \text{min}^{-1}$).

III. Results and discussion

III.1. Effect of oxidation agent and treatment time on the weight loss of adsorbent

The concentration of such acidic groups can be increased by chemical treatment involving oxidation. Depending on the chemical activation method, partial oxidation takes place and the

biomass surface becomes rich in a variety of functional groups whose nature and concentration depend on the oxidation method, chemicals used, and time of preparation. The effect of oxidation agent and treatment time on weight loss is shown in table 2. Weight loss of the adsorbent samples (W_L) is calculated according to:

$$W_L = \frac{(W_{pi} - W_{pf})}{W_{pi}} 100 \quad (8)$$

Where: W_{pi} and W_{pf} are the weights of products before and after oxidation.

The obtained results show that the weight loss depends on the nature of the oxidation agent, of its concentration and treatment time. Indeed:

- For the same concentration and the same treatment time, the weight loss is much more important in the presence of HNO_3 ;
- For the same oxidation agent and the same concentration, the increase of treatment time increases the weight loss;
- For the same treatment time and the same oxidation agent, the weight loss increases with an increase in concentration of oxidation agent.

The increase of weight loss is due to the effect of the chemical agent in which it promotes the extraction of soluble compounds.

Table 2. The weight loss for the olive stones

	Concentration	Treatment time	Weight loss (%)	Weight loss (%)
	(M)	(min)	(HNO_3)	(KOH)
Olive stones	1	30	16.6	17.9
		60	46.3	20.4
	3	30	55.6	28.7
		60	60.3	41.4

III.2. Effect of oxidation agent and treatment time on the sorption of lead (II) ions

The efficiency of the modified biomaterial has been tested by subjecting them to the adsorption of lead (II) ions under the following conditions: pH 5.8, adsorbent dose 1 g/L, agitation speed 200 rpm, ionic strength 0.005 M, initial concentration of Pb(II) 50 mg/L and 25 °C. The results are reported in Table 3.

The results show that the treatment of the biomaterial with the solutions of HNO_3 increases their effectiveness of elimination of the Pb(II) ions in aqueous solution.

In the following text, all sorption experiments are conducted with olive stones prepared with a treatment time of 30 minutes and a concentration in HNO_3 or KOH of 1M.

Table 3. The sorption amount for the olive stones

	Concentration	Treatment time	Sorbed amount q_e	Sorbed amount q_e
	(M)	(min)	(mg/g) (HNO_3)	(mg/g) (KOH)
Olive stones	1	30	45.44	41.75
		60	31.37	28.41
	3	30	45.51	37.04
		60	31.23	32.13

III.3. Effect of oxidation agent on the pH_{PZC} and on the concentration of surface groups

The pH_{PZC} and concentration of surface groups of lignocellulosic materials may give a good indication about the surface oxygen complexes and the electronic surface charges of biosorbents. This surface charge arises from the interaction between material surface and the aqueous solution. The complexes on sorbent surface are commonly classified as acidic, basic, or neutral. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone and ether groups are neutral or weakly acidic. Basic complexes are mainly pyrone and chromene groups. Based on the slurry pH, the nature of surface oxygen groups on the support and the dominant complexes can be

deduced. The values of pH_{PZC} and concentration of surface groups for various materials are shown in Table 4.

where: UOS: untreated olive stones, TOSH: treated olive stones with HNO₃ (t = 30 min and [HNO₃] = 1M), TOSK: treated olive stones with KOH (t = 30 min and [KOH] = 1M)

According to the obtained results, the pH_{pzc} and concentration of surface groups strongly depends on the modification agent. Indeed, the pH_{pzc} and concentration of surface groups of materials treated with HNO₃ is lower than that of untreated material. On the other hand, the pH_{pzc} and concentration of surface groups increases when one modifies the olive stones with KOH.

Table 4. The values of pH_{PZC} and concentration of surface groups for olive stones untreated and modified with a treatment time of 30 minutes and a concentration in HNO₃ or KOH of 1M

	UOS	TOSH	TOSK
pH _{PZC}	6.61	4.00	7.77
Acidity (mmol/g)	0.96	3.76	0.68
Basicity (mmol/g)	0.41	0.98	1.4

III.4. Effect of oxidation agent and treatment time on the Specific Surface Area and Pore Volume

The values corresponding to the physical characteristics results from the N₂ adsorption-desorption isotherms of all analyzed biosorbents, such as total surface area (S_{BET}), the total porous volume (V_{tot}), the microporous volume (V_{mic}) and the mesoporous volume (V_{mes}), are summarized in the Table 5.

It can be clearly seen that the BET surface area, the microporous volume and the mesoporous volume (V_{mes}) are slightly influenced by the chemical

modification of the olive stones. The surface area of treated olive stones with HNO₃ was much higher than that of untreated and treated olive stones with KOH. The improvement of these characteristics is due to the effect of the chemical agent in which it promotes the extraction of soluble compounds. The proportions of lignin increased and cellulosic materials, hemicellulosic materials, and extractives decreased during the modification process. This change is beneficial because previous research has demonstrated that heavy metals are adsorbed by lignin rather than by cellulose and hemicellulose.

Table 5. Textural Characteristics of olive stones untreated and modified with a treatment time of 30 minutes and a concentration in HNO₃ or KOH of 1M

	UOS	TOSH	TOSK
V _{tot} cm ³ /g	0.077	0.081	0.056
V _{mic} (DR) cm ³ /g	0.012	0.013	0.009
V _{mes} cm ³ /g	0.064	0.068	0.047
S _{BET} m ² /g	189	198	136

III.5. Effect of agitation time and initial lead concentration

The rate of metal removal is of great significance for developing sorbent-based water technology. In order to establish equilibration time for maximum uptake and to know the kinetics of sorption process, the sorption of Pb(II) by olive stones was carried

out using contact times ranging from 5 to 120 min and the results are shown in Figure 2.

It was observed that metals sorption occurred rapidly. The sorption capacity of metals by sorbents increased gradually with increasing contact times and reached a plateau afterwards. As seen in this figure, the sorption capacity increased as the initial

metals concentrations increased. Increasing initial metals concentrations would increase the mass transfer driving force and therefore the rate at which metals ions pass from the solution to the surface olive stones. For initial concentration of 90 mg L^{-1} , the ability of olive stones to sorb maximum amount of Pb(II) is within 30 min. This result

indicate that the olive stones is an effective adsorbent for the removal of Pb(II) from wastewater.

As shown in Fig. 2, the adsorbed quantity for lead (II) is in the order of TOSH > TOSK > UOS for the whole adsorption time.

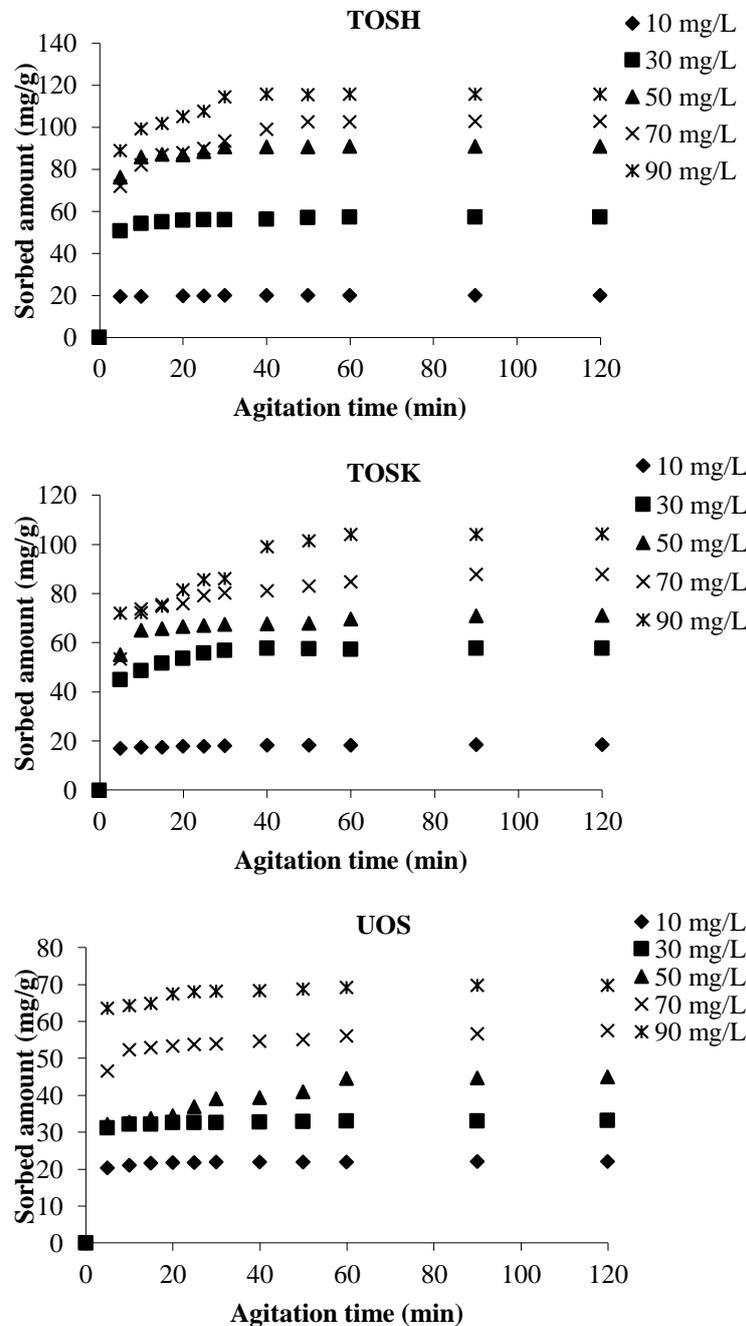


Figure 2. Effect of agitation time and initial concentration of Pb(II) on the sorption of lead by different adsorbents. Conditions: pH 5.8, agitation speed 200 rpm, ionic strength 0 M and 25 °C

III.6. Effect of adsorbent dose

The dose of adsorbents is varied from 0.5 to 1.5 g L⁻¹ for all the other experimental variables, viz. pH 5.8, initial concentration (50 mg L⁻¹) and agitation speed (200 min) constant. Fig. 3 presents the adsorbent dose profile versus Pb(II) sorbed amount. It may be observed that on increasing the adsorbent dose, the sorbed amount of Pb(II) decreases.

The decrease in the amount of lead sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentrations in the solution and on the sorbent surface. But the removal of lead increases with an increase in sorbent dosage. The increase in lead removal was due to the increase of the available sorption surface and availability of more sorption sites.

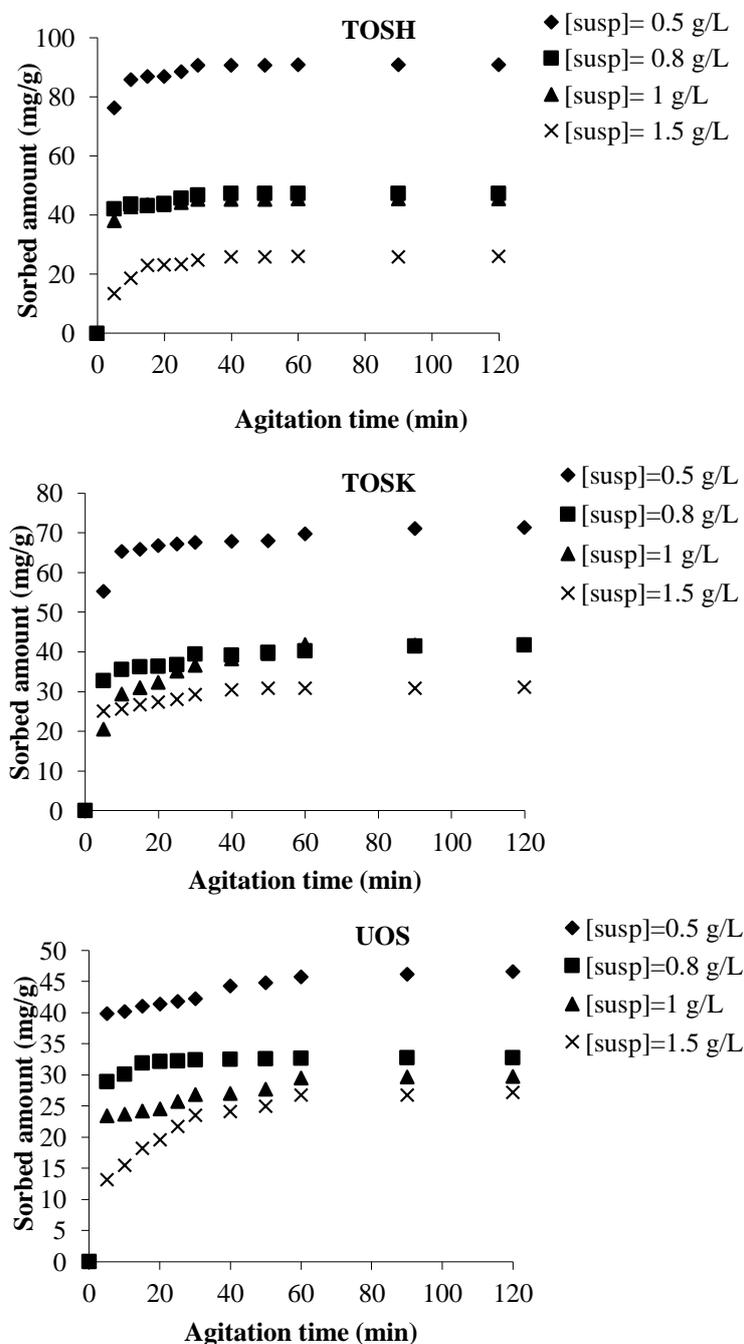


Figure 3. Effect of adsorbent dosage on the sorption of lead by different adsorbents. Conditions: pH 5.8, initial concentration of Pb(II) 50 mg L⁻¹, agitation speed 200 rpm, ionic strength 0 M and 25 °C

III.7. Effect of ionic strength

Wastewaters from electroplating industries, textiles, tanneries, oil refineries, mining, and smelters industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the biosorption process. Fig. 4 presents the effect of ionic strength on the uptake of lead (II) ions. It was observed that the sorption potential decreased with increased concentration of

NaCl in the medium. The adverse effect of ionic strength on lead(II) ions suggests the possibility of ion exchange mechanisms being in operation in the biosorption process (competitive effect between lead ions and cations from the salt (Na^+) for the sites available for the sorption process). Another reason is the influence of the great ionic strength on the activity coefficient of lead which reduces its transfer to the sorbent surface.

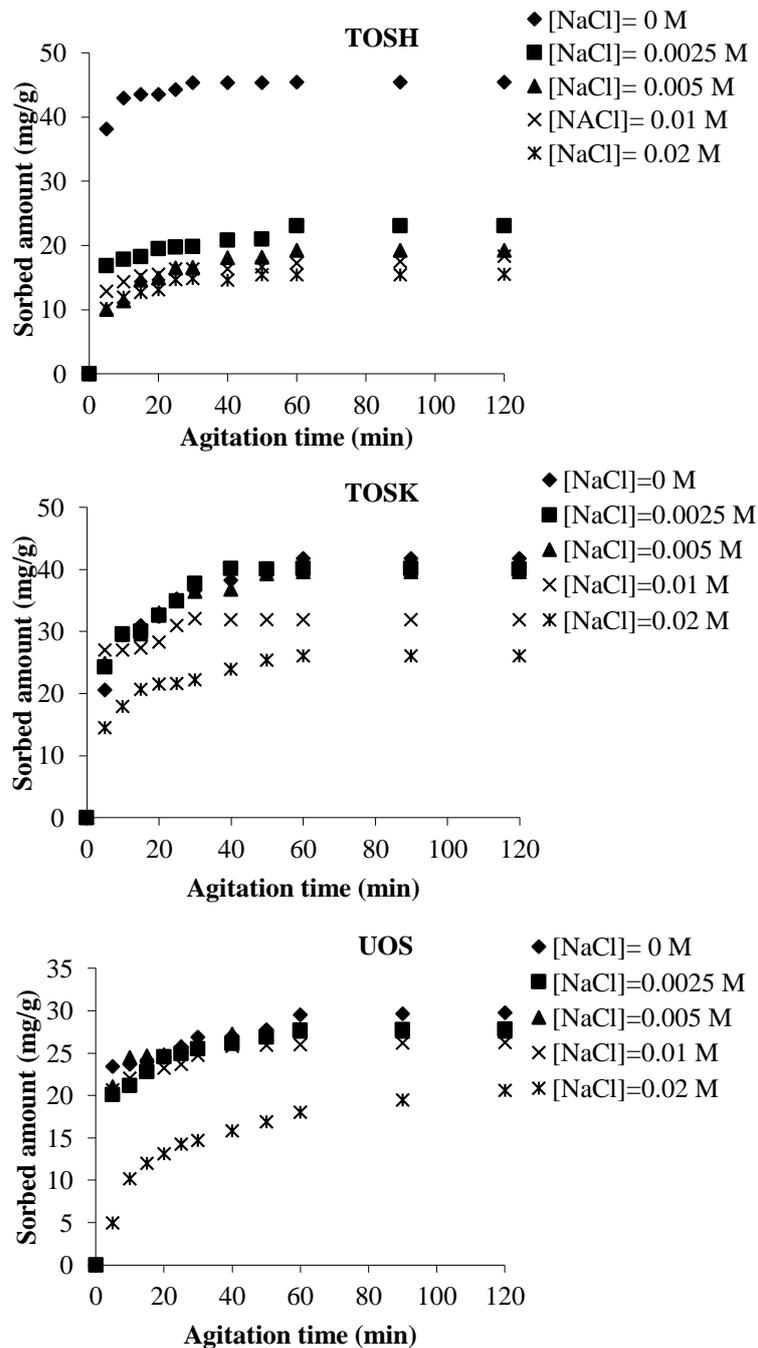


Figure 4. Effect of ionic strength on the sorption of lead by different adsorbents. Conditions: pH 5.8, initial concentration of Pb(II) 10 mg L^{-1} , agitation speed 200 rpm and $25 \text{ }^\circ\text{C}$

III.8. Sorption kinetics

In most cases, the first-order equation did not apply well throughout the whole range of contact times and is generally applicable over the initial 5–30 min of the sorption process. The plotting of $\log(q_e - q_t)$ versus time (curves not shown) deviated considerably from the theoretical. The plots and intercepts of curves were used to determine the first-order constant K_1 and equilibrium capacity q_e . The calculated values of $q_{e(cal)}$ (Table 6) from the first-order kinetics model are lower than the experimental ones. This suggests that the sorption of lead does not follow first-order kinetics. The insufficiency of the first-order model to fit the kinetic data could possibly be due to a boundary layer controlling the beginning of the sorption process. This is also consistent with most cases in the literature.

Using Eq. (7), t/q_t was plotted versus t at different adsorbate concentrations and the second order sorption rate constant (K_2) and q_e values were determined from the slopes and intercepts of the plots. The correlation coefficients for the linear plots are superior than 0.996 in all cases. The values of these parameters are presented in Table 6. The theoretical $q_{e(cal)}$ values agree perfectly with the experimental $q_{e(exp)}$ values. This suggests that the sorption system is not a first-order reaction and that a pseudo-second-order model (Eq. (7)) can be considered. The latter is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. It provides the best correlation of the data.

III.9. Sorption isotherm (Non-linear Method)

The analysis and design of sorption separation process require the relevant equilibrium sorption, which is the most important piece of information in understanding the sorption process. In the present study, the sorption capacity and equilibrium

isotherm for lead ions onto olive stones are estimated using Langmuir, Freundlich and Redlich-Peterson isotherms equations.

The q_{mon} , K_L , n , K_F and R^2 values calculated from isotherms are presented in Table 7. The determination of the correlation coefficients ($R^2 = 0.955$) suggests that the Langmuir isotherm provides a good fit to the isotherm data for the sorption of used metal.

The equilibrium data were further analyzed using the Freundlich model. The calculated Freundlich isotherm constants, the corresponding coefficients of determination are shown in Table 7. The coefficients of determination were high showing a best fit of equilibrium data.

The magnitude of the exponent n gives an indication on the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor sorption characteristics [31]. The results show that the values of n are superior to 2 indicating that the sorption is good.

The abilities of Redlich-Peterson isotherms to model the equilibrium data were also examined. The Redlich-Peterson isotherm constants as well as the determination coefficient R^2 , for the lead sorption systems were summarized in table 7. In all cases, the Redlich-Peterson isotherm exhibited the highest determination coefficient. Consequently, these three models were found to be the most-suitable for this sorption system.

In order to check the validity of these models, it is interesting to recalculate the adsorbed amount using the calculated constant parameters determined using the linear forms. The simulated curves at 25 °C determined using Freundlich, Langmuir and Redlich-Peterson isotherms are given in Figure 5. As can be seen from isotherms (Figure 5) the fit is better with Redlich-Peterson model than with Langmuir and Freundlich models.

Table 7. Langmuir, Freundlich and Redlich-Peterson constants for sorption of lead on different biomaterials

	Langmuir constants			Freundlich constants			Redlich-Peterson			
	q_{mon}	K_L	R^2	K_F	n	R^2	k_R	a_R	β	R^2
UOS	70.32	0.352	0.965	24.68	3.34	0.995	70.07	2.02	0.799	0.992
TOSH	116.20	0.761	0.958	61.83	5.48	0.956	94.09	0.85	0.985	0.990
TOSK	94.50	0.549	0.955	34.15	3.43	0.956	124.69	2.56	0.808	0.953

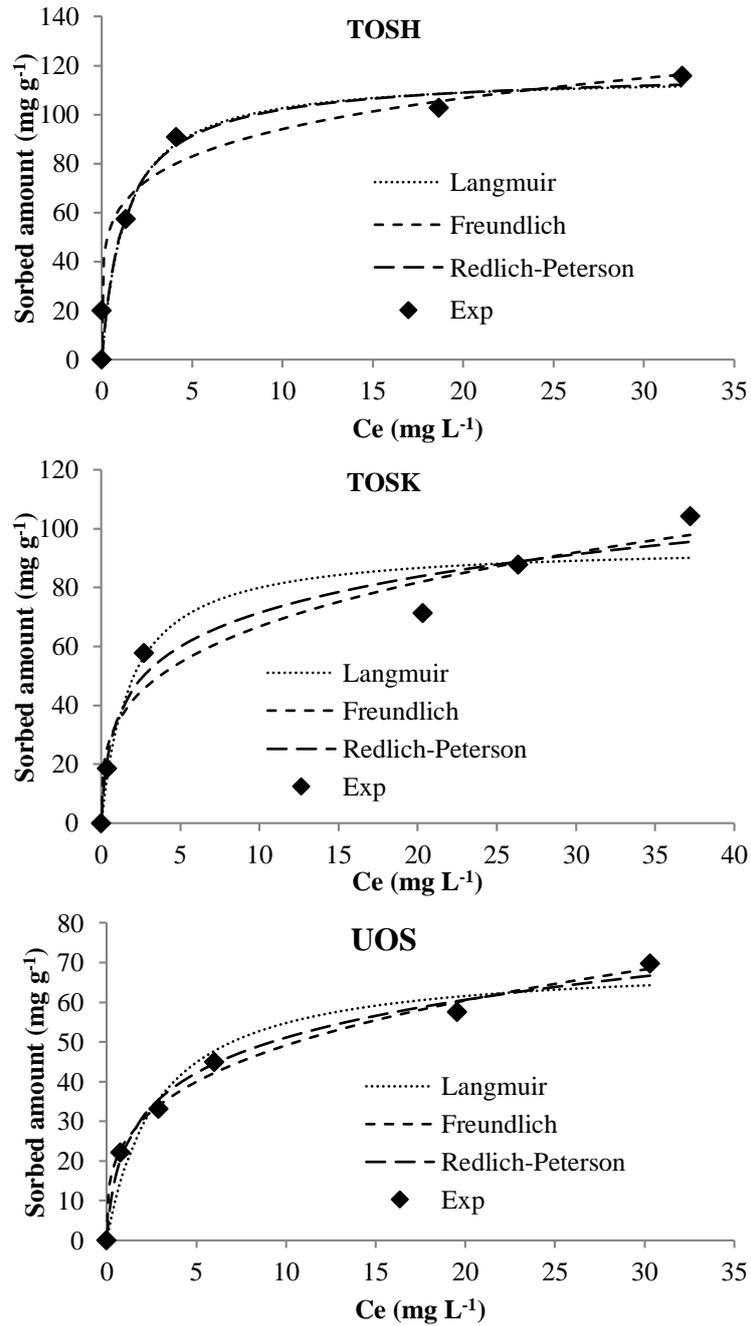


Figure 5. Adsorption isotherms for lead onto olive stones.
Conditions: pH 5.8, agitation speed 200 rpm, ionic strength 0 M and 25 °C

Table 6. Pseudo-first and second order kinetic model rate constants of olive stones at different concentrations

	Pseudo-first order kinetic			Pseudo-second order kinetic		
	UOS	TOSH	TOSK	UOS	TOSH	TOSK
R^2	1	1	1	1	1	1
q_e (cal) (mg/g)	18.62	58.48	71.94	89.29	108.70	108.70
q_e (exp) (mg/g)	18.52	57.73	71.34	87.90	104.30	104.30
K_2 (g mg ⁻¹ min ⁻¹)	0.093	0.015	0.009	0.004	0.006	0.006
R^2	1	1	1	0.999	1	1
q_e (cal) (mg/g)	20.04	57.47	91.74	105.26	117.65	117.65
q_e (exp) (mg/g)	20.00	57.332	90.88	102.71	115.77	115.77
K_2 (g mg ⁻¹ min ⁻¹)	0.212	0.028	0.019	0.004	0.006	0.006
R^2	1	1	0.996	1	1	1
q_e (cal) (mg/g)	22.07	66.22	46.30	57.80	69.93	69.93
q_e (exp) (mg/g)	22.03	33.11	44.90	57.55	69.68	69.68
K_2 (g mg ⁻¹ min ⁻¹)	0.015	0.157	0.005	0.012	0.019	0.019
R^2	0.859	0.927	0.814	0.825	0.912	0.912
q_e (cal) (mg/g)	3.37	20.39	18.71	36.12	107.34	107.34
q_e (exp) (mg/g)	18.52	57.73	71.34	87.90	104.30	104.30
K_1 (min ⁻¹)	0.073	0.081	0.045	0.045	0.087	0.087
R^2	0.684	0.747	0.882	0.879	0.921	0.921
q_e (cal) (mg/g)	4.12	12.32	33.08	100.58	96.25	96.25
q_e (exp) (mg/g)	20.00	57.332	90.88	102.71	115.77	115.77
K_1 (min ⁻¹)	0.137	0.073	0.124	0.109	0.139	0.139
R^2	0.736	0.606	0.903	0.693	0.751	0.751
q_e (cal) (mg/g)	2.03	2.84	28.62	12.21	13.56	13.56
q_e (exp) (mg/g)	22.03	33.11	44.90	57.55	69.68	69.68
K_1 (min ⁻¹)	0.058	0.042	0.054	0.032	0.060	0.060
C_0 (mg/l)	10	30	50	70	90	90

IV. Conclusion

Olive stones can be effectively used as a raw material for the removal of lead from aqueous solutions. Upon treatment with KOH or HNO₃, the surface area and functional groups, such as carboxyl, lactone and phenol groups were enhanced. The effect of the concentration and the treatment time on the adsorption performance was limited. The highest total acidic functional groups of 3.76 mmol/g was obtained for olive stones prepared with a treatment time of 30 minutes and a concentration in HNO₃ of 1M.

The adsorption of lead ions by the olive stones treated with HNO₃ was higher than that of the raw material. This can be explained according to Lewis acid–base theory, lead ions are Lewis base, which are easy to be adsorbed at acid sites.

The sorption of lead onto olive stones prepared with an optimal conditions depends on contact time, initial concentration of Pb(II), adsorbent dose and ionic strength. The maximum sorption uptake is achieved at pH 5.8 and the results show that the capacity of sorption increases with the rise in initial concentration of lead in solution. The time, ionic strength and adsorbent dose corresponding to the maximum sorption are less than 15 min, 0 M and 0.5 g L⁻¹ respectively.

The equilibrium data fit perfectly the Redlich-Peterson model of sorption, showing heterogeneous distribution of active sites on the olive stones surface. The kinetic of lead(II) sorption onto olive stones follows the pseudo-second order model. The cost and sorption characteristics of olive stones make it favourable to be used as an effective sorbent for the removal of lead(II) ions from wastewater.

V. References

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