JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

# Kinetic Modeling of the Biosorption of Lead(II) from Aqueous Solutions by Solid Waste Resulting from the Olive Oil Production

M. Calero,[*,†] G. Blázquez,[*,†] and M. A. Martín-Lara[*,†]

Department of Chemical Engineering, University of Granada, 18071 Granada, Spain

**ABSTRACT:** Solid waste from olive oil production, the two-phase olive mill solid (OMS), was investigated for the removal of Pb(II) from aqueous solutions. This work focuses mainly on the kinetics of biosorption. The sorption kinetics was experimentally measured using stirred-batch systems under different initial concentrations and at varying solution temperatures. The pseudo-*n*th order kinetic model, pseudofirst-order kinetic model, pseudosecond-order kinetic model, and the Elovich equation were used to represent the kinetic data. The pseudosecond-order equation fitted the dynamic data very well under all the operating conditions. A contact time of approximately 60 min was required to reach the equilibrium. The results obtained for the effect of initial concentration on lead uptake by OMS showed that the equilibrium sorption capacity and the initial sorption rate increase as the initial metal concentration increases, while the kinetic constant of the process decreases. The effect of temperature on kinetic parameter values is less significant than the effect of lead concentration although a decrease on kinetic constant and initial sorption rate is produced as temperature rises, mainly at lower lead concentrations. Finally, the apparent activation energy of sorption was determined as $-18.62\ \mathrm{kJ \cdot mol^{-1}}$ for an initial lead concentration of $10\ \mathrm{mg \cdot L^{-1}}$. The negative value of activation energy showed that the Pb(II) adsorption process by OMS may involve a nonactivated chemical adsorption or a physical adsorption.

## INTRODUCTION

The importance of the olive mill industry in Mediterranean countries is well-known, as is the serious problem that the olive mill factories have in disposing of their byproduct. Over the last 10 years the manufacturing of olive oil has undergone important evolutionary changes in the equipment used for the separation of olive oil from the remaining components. The latest development has been the introduction of a two-phase centrifugation process in which a horizontally mounted centrifuge is used for a primary separation of the olive oil fraction from the vegetable solid material and vegetation water.[1] Spain was the first country to use the two-phase system, and thereafter this new technology has been installed around the world. The two-phase decanting has created a new solid residue, the two-phase olive mill solid (OMS). It is a thick sludge that contains pieces of stone and pulp of the olive fruit as well as vegetation water. This semisolid waste contains around (55 to 60) % moisture and some residual olive oil (2 to 4 %) and 2 % ash and has a dark color.

Composting has been shown to be a suitable method for recycling OMS. This study focuses on find new potential applications for OMS and proposes a possible use of OMS as a heavy metals biosorbent.

Biosorption is a passive process of metal uptake and sequestering.[2] This process has been proposed as one of the most promising technologies for the removal of toxic metals from wastewater which arouse special consideration because heavy metal pollution has become one of the most serious environmental problems today.[3−5]

The kinetic study of the biosorption process determines the rate at which the contaminants are removed from the aqueous media, and the kinetic constants can be used to optimize the residence time of a biosorption process. To examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. In this sense, numerous kinetic models have been proposed. The mechanism through which the biosorption process takes place is, in most cases, complex (chemical reactions between biosorbent functional groups and metal ions, ionic interchange reactions and/or formation of complexes).

The aim of this work was to carry out a kinetic evaluation of the lead biosorption using OMS as a solid biosorbent in a completely stirred tank reactor analyzing the effect of the initial concentration of lead and temperature. Pseudo-*n*th order, pseudofirst-order, pseudosecond-order, and Elovich models have been used to represent the kinetics of the process and obtain the main kinetic parameters.

## MATERIALS AND METHODS

**Preparation of Sorbent Solid.** OMS was supplied by a Spanish olive oil production plant (Cooperativa Nuestra Señora del Castillo) located in Vilches, Jaén. The biosorbent was dried overnight at 333 K. Then, the solid was ground with an electric grinder and was graded according size using an automatic sieve of high vibration. For the biosorption experiments, the size fraction with particle diameter less than 1 mm was used. Some chemical and physical characteristics of OMS reported in a previous work[6] are summarized in Table 1.

**Kinetic Batch Experiments.** Kinetic tests of $\mathrm{Pb^{2+}}$ sorption were performed by mixing 0.5 g of OMS in 50 mL of the synthetic lead ion solutions with a predetermined concentration of lead ion in a stirred, thermostatted batch reactor during different contact

**Received:** January 28, 2011
**Accepted:** May 11, 2011
**Published:** May 25, 2011

times [(0.5, 1, 2, 4, 8, 15, 30, 45, 60, 90, and 120) min]. Solutions of lead ion was prepared in distilled water using $Pb(NO_3)_2$, and the pH of the solution was adjusted with 0.1 M HCl or 0.1 M NaOH solutions at pH = 5. All reagents were supplied by Panreac Química S.A with a purity > 99 %.

Once the operation time had elapsed, the liquid phase was taken out of the reactor and centrifuged for 10 min; then the supernatant solution was filtered and analyzed for determined lead ion concentrations by an atomic absorption spectrophotometer (model: 3100, Perkin-Elmer).

In this work, the biosorption kinetics of lead by OMS was studied at different initial lead concentrations and temperatures. In the first experiments, the initial lead concentration were modified from (10 to 220) $mg \cdot L^{-1}$ keeping the temperature at 298 K. In the second ones, the biosorption experiments were conducted at several temperatures [(298, 313, and 333) K] and at three initial lead concentrations [(10, 20, and 100) $mg \cdot L^{-1}$].

## RESULTS AND DISCUSSION

**Operational Conditions.** The pH of the solution, amount of sorbent and sorbate, equilibration time, and temperature play a significant role on the sorption of heavy metal ions onto solid surfaces. Therefore, the biosorption of Pb(II) ions onto the two-phase olive mill solid was monitored step by step as a function of a parameter, keeping others constant. Table 2 reported the most suitable sorptive conditions selected for this kinetic study according to the results obtained in a previous work.[7]

**Table 1. Physical and Chemical Properties of OMS**[6]

| | |
|---|---|
| moisture, % | 54.18 |
| lignin, $g \cdot kg^{-1}$ free extracts | 432.00 |
| cellulose, $g \cdot kg^{-1}$ free extracts | 165.60 |
| hemicellulose, $g \cdot kg^{-1}$ free extracts | 356.80 |
| elemental analysis | C = 57.82 %, H = 7.05 %,<br>S = 0.05 %, N = 0.65 % |
| total titratable sites, $mmol \cdot g^{-1}$ | 1.25 |
| acid titratable sites, $mmol \cdot g^{-1}$ | 0.70 |
| point of charge zero ($pH_{pzc}$) | 4.88 |
| isoelectric point ($pH_{IEP}$) | 5.13 |
| total organic carbon released, $mg \cdot g^{-1}$ | 73.92 |

**Table 2. The Most Suitable Sorptive Conditions Selected for this Kinetic Study According to a Previous Work**[7]

| | |
|---|---|
| pH | 5 |
| dorbent concentration, $g \cdot L^{-1}$ | 10 |
| initial lead concentration, $mg \cdot L^{-1}$ | 10, 20, 40, 60, 100, 140, 180, 220 |
| equilibration time, min | 120 |
| temperature, K | 298, 313, 333 |

**Theoretical Aspects of the Kinetic Modeling in Batch System.** The numerical analysis of sorption kinetic models assuming external mass transfer and intraparticle diffusion (pore diffusion, surface diffusion) is frequently applied to describe the sorption kinetics in batch systems. However, the complicated mathematical computation limits their use from the viewpoint of engineering applications. Furthermore, the biosorption of heavy metals onto biosorbents involves many controlling mechanisms. Therefore, four of the main kinetic models proposed in literature were applied to the experimental data to determine the kinetic parameters and investigate the mechanism of biosorption of lead by OMS as a biosorbent. These kinetic models included pseudo-*n*th order, pseudofirst-order, pseudosecond-order, and Elovich equations. The correlation coefficients between experimental and theoretical data and the sum of the errors squared provided the "best fit" model. These kinetic models are summarized in Table 3.

**Kinetic Results Interpretation.** *Effect of Initial Lead Concentration.* First, the kinetics of Pb(II) sorption onto OMS was studied using solutions containing from (10 to 220) $mg \cdot L^{-1}$ of lead at pH 5 and at different time intervals (up to 120 min).

Figure 1 represents the amount of lead ion biosorbed ($q_t$, $mg \cdot g^{-1}$) as a function of time. Rapid accumulation of lead was observed, reaching 90 % of total biosorption capacity in the first (30 to 60) min for all of the initial lead concentrations tested. Therefore, equilibrium was reached in approximate 60 min, which showed saturation of the active points.

The results were fitted by nonlineal regression to the four kinetic models chosen: pseudo-*n*th order, pseudofirst-order, pseudosecond-order, and Elovich. Table 4 reports the parameter values obtained from the application of the kinetic models for the biosorption of lead ion by OMS.

To confirm the better kinetic model for the biosorption system, the data were analyzed using error analysis.

The results show that the kinetic data are found in good agreement with pseudo-*n*th order kinetic model. The order of sorption reaction ($n$) was found to be between 2.27 and 2.85 at an initial lead concentration range from (10 to 220) $mg \cdot L^{-1}$. The values of $n$ are close to 2, and this means that the experimental data could be fitted appropriately by the pseudo-second-order equation. It is confirmed by the high squared correlation coefficients of the pseudosecond-order model. In addition, the pseudosecond-order predicted $q_e$ are one of the most agreeing values with the experimental data. Thus, these

**Table 3. Kinetic Models Used in this Work for the Modeling of Experimental Data**

| model | parameters | ref |
|---|---|---|
| pseudonth order: $q_t = q_e - [(n-1)\, k_n^{\,t} + q_e^{(1-n)}]^{1/(1-n)}$ | $q_t$: amount of Pb(II) ions biosorbed at time $t$, $mg \cdot g^{-1}$ | 8 |
| | $q_e$: amount of Pb(II) ions biosorbed at equilibrium, $mg \cdot g^{-1}$ | |
| | $k_n$: rate constant of pseudo-*n*th order biosorption, $min^{-1} \cdot mg^{1-n} \cdot g^{n-1}$ | |
| | $n$: order of reaction | |
| pseudofirst order: $q_t = q_e(1 - e^{-k_1 t})$ | $k_1$: rate constant of pseudofirst-order biosorption, $min^{-1}$ | 9 |
| pseudosecond order: $q_t = t/(1/h + t/q_e)$ | $h$: initial biosorption rate, $mg \cdot g^{-1} \cdot min^{-1}$. It is equal to $k_2 \cdot q_e^2$ | 10−12 |
| | $k_{s2}$: rate constant of the pseudosecond-order biosorption, $g \cdot mg^{-1} \cdot min^{-1}$ | |
| Elovich: $q_t = 1/b \ln(ab) + 1/b \ln(t)$ | $a$: initial sorption rate, $mg \cdot g^{-1} \cdot min^{-1}$ | 13−15 |
| | $b$: parameter related to the extent of surface coverage, $g \cdot mg^{-1}$ | |

results suggest that the pseudosecond-order model, based on the assumption that the rate-limiting step might be chemical biosorption involving valency forces through sharing or exchange of electrons between lead cations and biosorbent, provides a good correlation of the dynamic data.[12,16,17]

An examination of the initial lead concentration effect (Table 4 and Figure 1) shows that the values of the initial sorption rate, $h$, increase from (0.296 to 5.476) $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$. Also, as the initial lead concentration rises, the equilibrium biosorption capacity, $q_e$, increases changing from (0.694 to 6.405) $\text{mg}\cdot\text{g}^{-1}$. However, the kinetic constant, $k_{s2}$, seems to decrease with increase in initial lead concentrations, this indicates that though, at first (in the early period), biosorption increases rapidly with increase in initial concentrations, after (at latter periods of the sorption process), the process is produced slowly until equilibrium is reached.

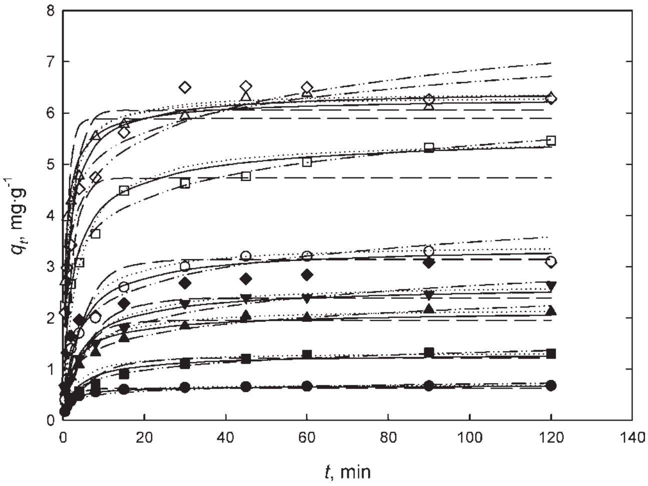

**Figure 1.** Biosorption capacity of OMS for Pb (II) versus operation time at different initial lead concentrations: ●, 10 $\text{mg}\cdot\text{L}^{-1}$; ■, 20 $\text{mg}\cdot\text{L}^{-1}$; ▲, 40 $\text{mg}\cdot\text{L}^{-1}$; ▼, 60 $\text{mg}\cdot\text{L}^{-1}$; ♦, 80 $\text{mg}\cdot\text{L}^{-1}$; ○, 100 $\text{mg}\cdot\text{L}^{-1}$; □, 140 $\text{mg}\cdot\text{L}^{-1}$; △, 180 $\text{mg}\cdot\text{L}^{-1}$; ◇, 220 $\text{mg}\cdot\text{L}^{-1}$; —, pseudonth order; ---, pseudofirst order; · · ·, pseudosecond order; -·-··-·-, Elovich.

With respect to the rest of models studied in this work, the Elovich model was also found to be adequate to satisfactorily explain the present biosorption phenomenon with correlation coefficient values varying from 0.965 to 0.999, which consolidate the chemisorption hypothesis.[18] In contrast, the Lagergren model was not enough or satisfactory to explain the experimental kinetic data.

Finally, although experimental data showed a good fit to pseudosecond-order model and Elovich equation, the existence of other processes such as intraparticle diffusion, mass transfer, or ion interaction that not have been taken in account should be considered. Actually, according to many scientists, the physicochemical involved may be complex, and no single theory of sorption has been proposed to explain the overall adsorptive removal process.[19]

In Figure 2 the amount of Pb(II) ions biosorbed at equilibrium, $q_e$, was represented versus the initial concentration of lead in the solution, $C_i$. Each step on the curve represents different (or identical) types of adsorption sites with different affinities (or availabilities) for lead. The first capacity zone most likely corresponds to the saturation of the sites with a higher affinity for lead (or the saturation of the easily available sites). After this step, increasing the lead concentration in solution initiates the occupation of the sites with less affinity for lead (or the saturation of the less easily available sorption sites). Horsfall and Spiff[20] found similar results when studying the effects of temperature on the sorption of $Pb^{2+}$ and $Cd^{2+}$ from aqueous solution by *Caladium bicolour* (wild Cocoyam) biomass. Also Chubar et al.[21] have found the existence of two capacity zones in the biosorption of copper and zinc on cork biomass.

On the other hand, the results confirm that OMS has potential to remove lead ions with a good biosorption capacity (≈6.5 $\text{mg}\cdot\text{g}^{-1}$

**Table 4. Parameter Values of the Kinetic Models for the Biosorption of Pb(II) by OMS at Different Initial Lead Concentrations**

| | | initial Pb(II) concentration, $\text{mg}\cdot\text{L}^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 40 | 60 | 100 | 140 | 180 | 220 |
| pseudo-*n*th order | $k_n$, $\text{min}^{-1}\cdot\text{mg}^{1-n}\cdot\text{g}^{n-1}$ | 1.109 | 0.198 | 0.115 | 0.0640 | 0.057 | 0.020 | 0.111 | 0.077 |
| | $q_e$ | 0.698 | 1.343 | 2.210 | 2.686 | 3.447 | 5.774 | 6.350 | 6.473 |
| | $n$ | 2.36 | 2.51 | 2.73 | 2.44 | 2.33 | 2.85 | 2.51 | 2.27 |
| | $r^2$ | 0.997 | 0.994 | 0.994 | 0.993 | 0.992 | 0.985 | 0.991 | 0.986 |
| | $\Sigma(q_t - q_{t\text{cal}})^2$ | 0.002 | 0.077 | 0.091 | 0.117 | 0.159 | 0.777 | 0.270 | 0.759 |
| pseudofirst-order | $k_1$, $\text{min}^{-1}$ | 0.483 | 0.144 | 0.220 | 0.154 | 0.199 | 0.456 | 0.931 | 0.464 |
| | $q_e$ | 0.621 | 1.218 | 1.955 | 2.387 | 3.140 | 4.732 | 5.892 | 6.058 |
| | $r^2$ | 0.920 | 0.879 | 0.895 | 0.935 | 0.917 | 0.833 | 0.935 | 0.920 |
| | $\Sigma(q_t - q_{t\text{cal}})^2$ | 0.041 | 0.260 | 0.584 | 0.570 | 1.210 | 4.847 | 2.614 | 3.908 |
| pseudosecond-order | $k_{s2}$, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ | 0.614 | 0.253 | 0.121 | 0.077 | 0.084 | 0.056 | 0.163 | 0.133 |
| | $q_e$, $\text{mg}\cdot\text{g}^{-1}$ | 0.694 | 1.327 | 2.191 | 2.669 | 3.441 | 5.488 | 6.317 | 6.405 |
| | $h$, $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ | 0.296 | 0.445 | 0.582 | 0.550 | 0.996 | 1.675 | 6.502 | 5.476 |
| | $r^2$ | 0.999 | 0.997 | 0.998 | 0.997 | 0.999 | 0.997 | 0.999 | 0.999 |
| | $\Sigma(q_t - q_{t\text{cal}})^2$ | 0.025 | 0.218 | 0.287 | 0.257 | 0.501 | 4.172 | 1.099 | 1.677 |
| Elovich | $a$, $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ | 3.050 | 1.064 | 2.735 | 1.720 | 3.640 | 27.133 | 307.968 | 32.444 |
| | $b$, $\text{g}\cdot\text{mg}^{-1}$ | 11.568 | 4.704 | 3.102 | 2.274 | 1.877 | 1.558 | 1.640 | 1.213 |
| | $r^2$ | 0.999 | 0.977 | 0.990 | 0.989 | 0.988 | 0.990 | 0.969 | 0.965 |
| | $\Sigma(q_t - q_{t\text{cal}})^2$ | 0.005 | 0.049 | 0.053 | 0.099 | 0.177 | 0.284 | 1.235 | 1.736 |

for 220 mg·L$^{-1}$ of lead ion and 10 g·L$^{-1}$ of OMS), a value that is comparable to those observed for other similar agricultural wastes.[22,23]

*Effect of Temperature.* The effect of temperature (Table 5 and Figure 3) was studied in the temperature range (298 to 333) K at pH 5, for a solid concentration of 10 g·L$^{-1}$ and initial concentrations of Pb(II) of (10, 20, and 100) mg·L$^{-1}$.

An analysis of data showed that the biosorption of Pb(II) followed again the pseudo-*n*th order and pseudosecond-order kinetic models for all three initial concentrations and all temperatures tested. It is remarkable that the values of *n* are close to 2 at the range of temperatures studied. Therefore, the rate of sorption could be a pseudosecond-order mechanism.

Also, the temperature effect on biosorption capacity is less significant than the effect of lead concentration although a decrease on the kinetic constant and initial sorption rate is produced as temperature rises, mainly at lower lead concentrations.

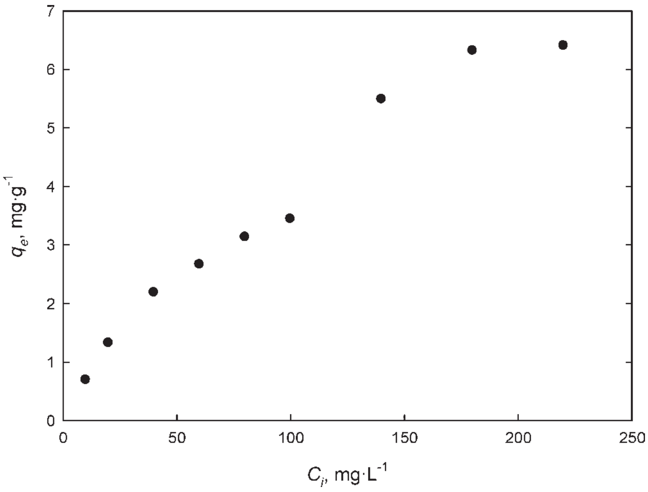

**Figure 2.** Representation of the amount of Pb(II) ions biosorbed at equilibrium, $q_e$, versus the initial concentration of lead in the solution, $C_i$.

On the other hand, if results obtained for an initial lead concentration of 10 mg·L$^{-1}$ and 100 mg·L$^{-1}$ are compared, it is noted that the pseudosecond-order constant and the equilibrium biosorption capacity remained practically constant with the temperature variation for an initial lead concentration of 100 mg·L$^{-1}$, which indicates that with increasing lead concentration the effect of the temperature, in the range studied, is even less important.

Finally, the activation energy for metal ions biosorption was calculated from the pseudosecond-order constants by the Arrhenius equation. Its linear form is,

$$\ln k = \ln A_0 - \frac{E_a}{RT}$$

where $A_0$ is the temperature-independent Arrhenius constant, $E_a$ is the apparent activation energy (kJ·mol$^{-1}$), $R$ is the gas constant, 8.314·10$^{-3}$ kJ·mol$^{-1}$·K$^{-1}$, and $T$ is the temperature (K).

Figure 4 shows the corresponding linear plot of ln $k_{s2}$ against 1/$T$ at initial lead concentrations of 10 mg·L$^{-1}$, 20 mg·L$^{-1}$, and 100 mg·L$^{-1}$.

The Arrhenius equation shows a good fit to the experimental data with high correlation coefficients ($r^2 > 0.95$). The activation energy for the biosorption system of Pb(II) ion onto OMS was calculated from the slope of the plot. The $E_a$ values were −18.62 kJ·mol$^{-1}$, −18.20 kJ·mol$^{-1}$, and −10.34 kJ·mol$^{-1}$ for an initial lead concentration of 10 mg·L$^{-1}$, 20 mg·L$^{-1}$, and 100 mg·L$^{-1}$, respectively. The magnitude of activation energy may give an idea about the type of sorption. Biosorption processes exhibiting these negative activation energies are typically barrierless processes. Therefore, the negative activation energy values suggest that the strength involved in the metal ion and the solid surface interaction could be physical. So, increasing the temperature leads to a reduced the forces of attraction between the binding sites of the sorbent surface and

**Table 5. Parameter Values of the Kinetic Models for the Biosorption of Pb(II) by OMS at Different Temperatures**

| initial lead concentration, mg·L$^{-1}$ | | 10 mg·L$^{-1}$ | | | 20 mg·L$^{-1}$ | | | 100 mg·L$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| temperature, K | | 298 | 313 | 333 | 298 | 313 | 333 | 298 | 313 | 333 |
| pseudo-*n*th order | $k_n$, min$^{-1}$·mg$^{1-n}$·g$^{n-1}$ | 1.109 | 0.521 | 0.404 | 0.198 | 0.218 | 0.121 | 0.034 | 0.127 | 0.074 |
| | $q_e$ | 0.698 | 0.614 | 0.524 | 1.343 | 1.307 | 1.135 | 4.147 | 4.016 | 3.741 |
| | $n$ | 2.36 | 2.40 | 2.27 | 2.51 | 2.79 | 2.31 | 2.87 | 2.47 | 2.70 |
| | $r^2$ | 0.997 | 0.996 | 0.995 | 0.994 | 0.996 | 0.994 | 0.997 | 0.994 | 0.992 |
| | $\Sigma(q_t - q_{tcal})^2$ | 0.002 | 0.003 | 0.004 | 0.077 | 0.026 | 0.061 | 0.043 | 0.049 | 0.175 |
| pseudofirst-order | $k_1$, min$^{-1}$ | 0.483 | 0.156 | 0.168 | 0.144 | 0.180 | 0.096 | 0.311 | 0.580 | 0.356 |
| | $q_e$ | 0.621 | 0.551 | 0.434 | 1.218 | 1.131 | 0.986 | 3.557 | 3.673 | 3.347 |
| | $r^2$ | 0.920 | 0.965 | 0.961 | 0.879 | 0.896 | 0.923 | 0.956 | 0.954 | 0.915 |
| | $\Sigma(q_t - q_{tcal})^2$ | 0.041 | 0.023 | 0.013 | 0.260 | 0.201 | 0.119 | 0.820 | 0.812 | 1.305 |
| pseudosecond-order | $k_{s2}$, g·mg$^{-1}$·min$^{-1}$ | 0.614 | 0.362 | 0.276 | 0.253 | 0.156 | 0.116 | 0.156 | 0.137 | 0.101 |
| | $q_e$, mg·g$^{-1}$ | 0.694 | 0.610 | 0.513 | 1.327 | 1.297 | 1.129 | 3.790 | 4.006 | 3.715 |
| | $h$, mg·g$^{-1}$·min$^{-1}$ | 0.296 | 0.135 | 0.073 | 0.445 | 0.263 | 0.147 | 1.812 | 2.198 | 1.394 |
| | $r^2$ | 0.999 | 0.999 | 0.994 | 0.997 | 0.997 | 0.992 | 0.999 | 0.999 | 0.999 |
| | $\Sigma(q_t - q_{tcal})^2$ | 0.025 | 0.007 | 0.010 | 0.218 | 0.102 | 0.084 | 0.279 | 0.531 | 0.629 |
| Elovich | $a$, mg·g$^{-1}$·min$^{-1}$ | 3.050 | 0.363 | 0.220 | 1.064 | 1.045 | 0.349 | 9.659 | 29.933 | 10.202 |
| | $b$, g·mg$^{-1}$ | 11.568 | 9.585 | 11.232 | 4.704 | 4.980 | 4.834 | 1.901 | 2.108 | 2.026 |
| | $r^2$ | 0.999 | 0.990 | 0.982 | 0.977 | 0.995 | 0.969 | 0.975 | 0.966 | 0.989 |
| | $\Sigma(q_t - q_{tcal})^2$ | 0.005 | 0.005 | 0.006 | 0.049 | 0.011 | 0.049 | 0.429 | 0.586 | 0.168 |

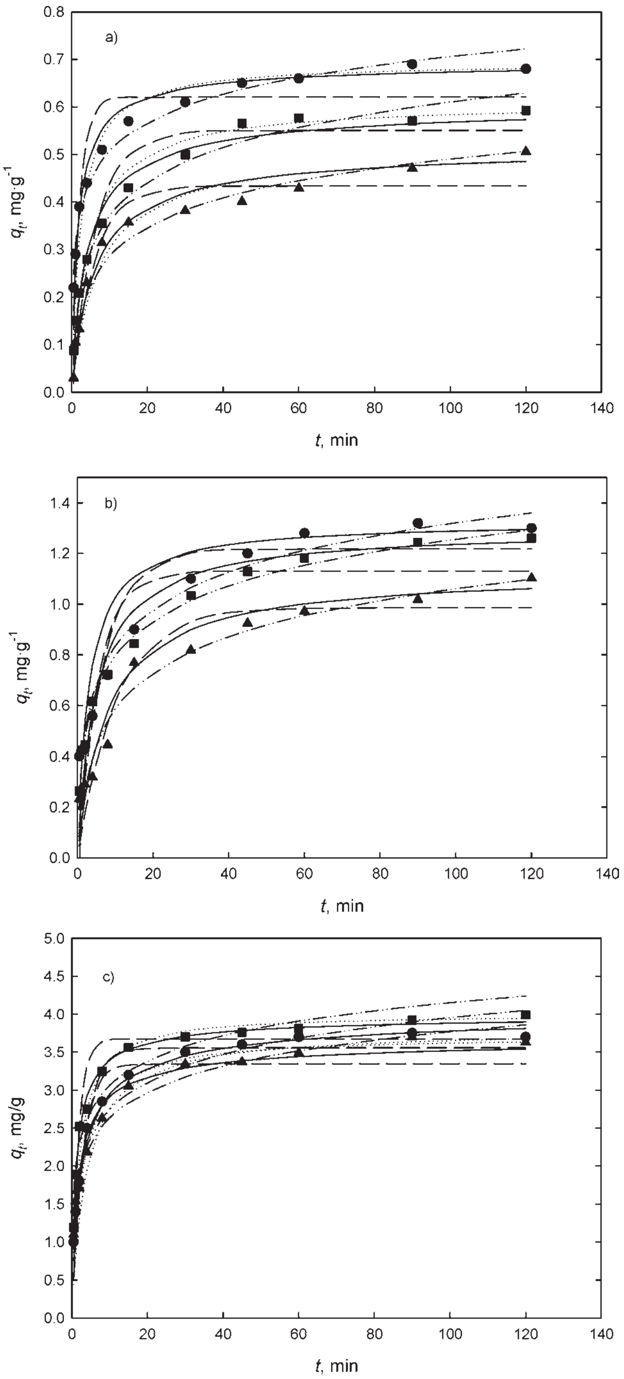

**Figure 3.** Biosorption capacity of OMS for Pb (II) versus operation time at different temperatures and for an initial lead concentration of (a) 10 mg·L$^{-1}$, (b) 20 mg·L$^{-1}$, and (c) 100 mg·L$^{-1}$: ●, 298 K; ■, 313 K; ▲, 333 K; —, pseudo-*n*th order; ---, pseudofirst-order; · · ·, pseudo-second-order; -·-··-··-, Elovich.

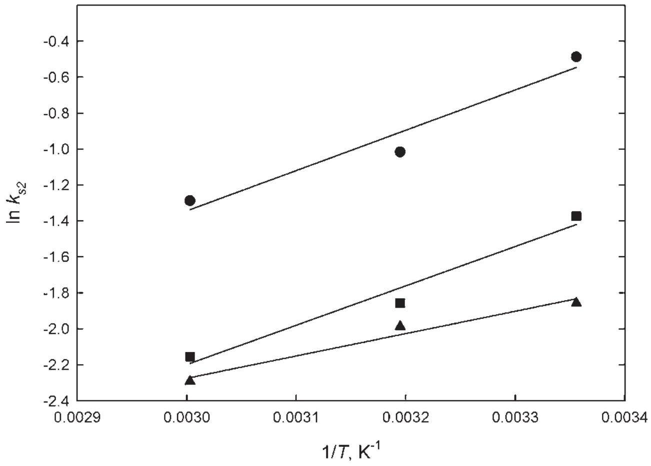

**Figure 4.** Linearized Arrhenius plot for the biosorption of Pb(II) ions on OMS at different initial lead concentrations: ●, 10 mg·L$^{-1}$; ■, 20 mg·L$^{-1}$; ▲, 100 mg·L$^{-1}$.

metal ions and there is a greater tendency of the metal to escape from the solid surface toward the liquid, resulting in a decrease in the retention of the metal. These results are similar to those found by other researchers; in this way, Aksu[24] also observed activation energy of −8.0 kJ·mol$^{-1}$ for the biosorption of cadmium(II) ion on to dried *C. vulgaris*. On the other hand, recent studies[25]on biosorption of reactive dyes on *C. vulgaris* showed that the activation energies of the biosorption processes of Remazol Red RR and Remazol Golden Yellow RNL were found to be (−10.63 and −23.15) kJ·mol$^{-1}$, respectively. However, the authors reported that negative values of activation energy have no obvious physical significance, and hence biosorption studies of these dyes should be performed at much lower solution temperatures to obtain biosorption activation energy.

**Comparison of OMS with Other Biosorbents.** Recent studies on the removal of lead using numerous types of biomasses are the subject of this section. A large quantity of materials has been investigated as biosorbents for the removal of lead.[26−31] The tested biosorbents can be basically classified into the following categories: bacteria, fungi, yeast, algae, industrial wastes, agricultural wastes and other polysaccharide materials, and so forth.[32]

First, the kinetic performance of sorbing materials has been compared. Table 6 shows the lead amount of Pb(II) ions biosorbed at equilibrium ($q_e$) and the rate constant of the pseudosecond-order biosorption ($k_{s2}$) values for the pseudosecond-order kinetic model, obtained for different biomasses used as the sorbent of lead. A comparison of $q_e$ and $k_{s2}$ for OMS with the other sorbents under different experimental conditions implied that OMS is a possible good biosorbent of lead from aqueous solutions particularly because the kinetic constant is higher than other biosorbents and the process is faster.

On the other hand, the comparison of lead sorption performance is best based on a complete lead sorption isotherm curve. The sorbents can be compared by their respective maximum biosorption capacities, $q_{max}$ values which are calculated, for example, from fitting the Langmuir isotherm model to the actual experimental data (if it fits). This approach is feasible if there exists the characteristic $q_{max}$ sorption performance plateau (the maximum biosorbent saturation).

OMS isotherms for lead were previously published in an earlier work.[44] In Table 7 OMS has been compared with other sorbents reported in literature based on their maximum uptake capacity of Pb(II) ions. It is important to emphasize that a direct comparison of $q_{max}$ of OMS with other maximum capacities of other biosorbent materials is difficult, since experimental conditions applied are different. Nevertheless, the results can demonstrate that the maximum uptake capacity of OMS for Pb(II) ions was comparable to other corresponding biosorbents reported in

Table 6. A Comparison of the Parameters of the Pseudosecond-Order Kinetic Model for the Biosorption of Lead Ions by Different Biosorbents[a]

| | operation conditions | | | pseudosecond-order model | | |
|---|---|---|---|---|---|---|
| biosorbent | pH | $T$, K | $C_i$, $\text{mg}\cdot\text{L}^{-1}$ | $q_e$, $\text{mg}\cdot\text{g}^{-1}$ | $K_{s2}$, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ | ref |
| deoiled allspice husk | 5 | 298 | 5 | 5.32 | 0.056 | 33 |
| | | | 25 | 20.79 | 0.036 | |
| FA-treated *N. zanardini* | 5.5 | 298 | 104 | 106.39 | $0.72\cdot10^{-3}$ | 34 |
| groundnut hull | 5.0 | n.a. | 100 | 15.74 | 0.009 | 35 |
| gum kondagogu (*Cochlospermum gossypium*) | 5.0 | 298 | 10 | 10.13 | 0.019 | 36 |
| | | | 100 | 31.84 | $0.50\cdot10^{-3}$ | |
| lichen (*Parmelina tiliaceae*) | 5.0 | 293 | 25 | 1.020 | 0.190 | 37 |
| | | 323 | | 0.910 | 0.110 | |
| maize (*Zea mays*) stalk sponge | 6.0 | n.a. | 21 | 15.86 | 0.581 | 38 |
| modified peanut husk | 4.0 | 298 | 10 | 4.51 | 0.042 | 39 |
| *Nostoc* sp. | 5.0 | 298 | 100 | 44.05 | $0.86\cdot10^{-3}$ | 40 |
| | | | 200 | 117.60 | $0.64\cdot10^{-3}$ | |
| olive stone | 5.0 | 298 | 10 | 0.60 | 1.210 | 22 |
| | | 333 | | 0.69 | 2.141 | |
| *Oedogonium* sp. | 5.0 | 298 | 100 | 63.29 | $0.80\cdot10^{-3}$ | 40 |
| | | | 200 | 89.28 | $0.38\cdot10^{-3}$ | |
| pine bark (*Pinus brutia Ten.*) | 4.0 | n.a. | 100 | 10.98 | 0.009 | 41 |
| pine cone powder | 5.0 | 291 | 120 | 9.34 | 0.689 | 42 |
| sawdust | 4.0 | 298 | 10 | 4.64 | 0.029 | 39 |
| *Spirogyra* sp. | 5.0 | 298 | 100 | 59.17 | 545 | 43 |
| | | | 200 | 111.11 | 317 | |
| two-phase OMS | 5.0 | 298 | 10 | 0.69 | 0.614 | this work |
| | | | 100 | 3.44 | 0.084 | |
| | | | 180 | 6.32 | 0.163 | |

[a] n.a.: not available.

Table 7. Comparison of Maximum Biosorption Capacities of $Pb^{2+}$ Ions by Different Biosorbents[a]

| | operation conditions | | | | |
|---|---|---|---|---|---|
| biosorbent | pH | $T$, K | $C_i$, $\text{mg}\cdot\text{L}^{-1}$ | $q_{max}$, $\text{mg}\cdot\text{g}^{-1}$ | ref |
| activated sludge | 2.0 | 298 | 10−150 | 142.83 | 45 |
| arca shell | 5.5 | room | n.a. | 18.33 | 46 |
| bagasse fly ash | 5.0 | 303 | 10−100 | 2.50 | 47 |
| brewery waste | 4.0 | 303 | 33.1−1656 | 85.49 | 48 |
| *Bacillus cereus* | 5.5 | 298 | 5−100 | 36.71 | 49 |
| chaff | 5.5 | 298 | 8−96 | 11.90 | 50 |
| modified peanut husk | 4.0 | 298 | 10−50 | 29.14 | 39 |
| pretreated crab shell | 5.5 | room | n.a. | 19.83 | 46 |
| *Cupriavidus taiwanensis* | n.a. | 310 | 100−1500 | 50.01 | 51 |
| *Garcinia mangostana* L. fruit shell | 5.0 | n.a. | 10−150 | 3.56 | 52 |
| red mud | 5.0 | 303 | 100−1000 | 71.27 | 53 |
| *Rhoidococcus opacus* | 5.0 | 301 | 15−200 | 94.19 | 54 |
| sawdust | 4.0 | 298 | 10−50 | 21.05 | 39 |
| seed husk of *Calophyllum inophyllum* | 4.0 | 301 | 25−400 | 34.51 | 55 |
| *Spirogyra* sp. | 5.0 | 298 | n.a. | 140.84 | 43 |
| two-phase OMS | 5.0 | 298 | 10−1000 | 23.70 | 44 |
| | | 313 | | 25.10 | |
| | | 333 | | 23.10 | |
| waste beer yeast | 5.0−6.0 | 293 | 10−145 | 5.72 | 56 |

[a] n.a.: not available.

the literature. However, the lead sorption capacity of OMS is relatively smaller than some other biomaterials like fungi and algae but unlike some of these biosorbents needs pretreatment before it can be used as an effective biosorbent, and OMS has been used without any previous treatment. This decreases the initial cost and hence OMS could find their significantly important place in the list of cost-effective and economical materials used for lead sequestering.

The variations in uptake capacity are associated with biosorbent properties, such as structure and functional groups. It is believed that the various functional groups on OMS such as carboxylic and hydroxyl groups play the role of active sites that are responsible for biosorption.[6]

## CONCLUSIONS

The two-phase olive mill waste from the two-decanter olive-oil-production system offers potential for the removal of lead ions by biosorption. The biosorption kinetic of Pb(II) using this waste as biosorbent is well-represented by the pseudosecond-order kinetic model, and the rate-limiting step of this sorption system may be chemical sorption inside of mass transfer. The equilibrium sorption capacity and the initial sorption rate rise as the initial metal concentration increases, while the kinetic constant of the process decreases, indicating that though, at first (in the early period), biosorption increases rapidly with the increase in initial concentrations, after (at latter periods of the sorption process), the process is produced slowly until equilibrium is reached. The effect of temperature on kinetic parameter values is less significant than the effect of lead concentration although a decrease on kinetic constant and initial sorption rate is produced as temperature rises, mainly at lower lead concentrations. Finally, the negative value of activation energy showed that Pb(II) adsorption process by OMS may involve nonactivated chemical adsorption.

## AUTHOR INFORMATION

### Corresponding Author

*M.C.H.: phone, 34 958 243311; fax, 34 958 248992; e-mail, mcaleroh@ugr.es. G.B.G.: phone, 34 958 240770; fax, 34 958 248992; e-mail, gblazque@ugr.es. M.A.M.-L.: phone, 34 958 240770; fax, 34 958 248992; e-mail, marianml@ugr.es.

### Author Contributions

†All authors have contributed equally to this work.

### Funding Sources

The authors are grateful to the Ministerio de Ciencia e Innovación for financial support received (Project CTM2009-10294).

## REFERENCES

(1) Borja, R.; Raposo, F.; Rincón, B. Treatment technologies of liquid and solid wastes from two-phase olive oil mills. *Grasas Aceites (Sevilla, Spain)* **2006**, *57*, 32–46.

(2) Volesky, B. Detoxification of metal-bearing effluents: Biosorption for the next century. *Hydrometallurgy* **2001**, *59*, 203–216.

(3) Brady, J. M.; Tobin, T. M.; Roux, J. C. Continuous Fixed Bed Biosorption of Cu$^{2+}$ ions: Application of a simple two parameter mathematical model. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 71–77.

(4) Pagnanelli, F.; Papini, M. P.; Toro, L.; Trifoni, M.; Vegliò, F. Biosorption of metal ions on *Anthrobacter sp.*: biomass characterization and biosorption modeling. *Environ. Sci. Technol.* **2000**, *34*, 2773–2778.

(5) Zhou, D.; Zhang, L.; Guo, S. Mechanisms of lead biosorption on cellulose/chitin beads. *Water Res.* **2005**, *39*, 3755–3762.

(6) Martín-Lara, M. A.; Hernáinz, F.; Calero, M.; Blázquez, G.; Tenorio, G. Surface chemistry evaluation of some solid wastes from olive-oil industry used for lead removal from aqueous solutions. *Biochem. Eng. J.* **2009**, *44*, 151–159.

(7) Hernáinz, F.; Calero, M.; Blázquez, G.; Martín-Lara, M. A. Influencia de algunas variables en la biosorción de plomo con residuos agrícolas. *Afinidad* **2008**, *65*, 286–292.

(8) Özer, A. Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated wheat bran. *J. Hazard. Mater.* **2007**, *141*, 753–761.

(9) Lagergren, S. Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven. Vetenskapsakad. Handl.* **1898**, *24*, 1–39.

(10) Ho, Y.; Ng, J.; McKay, G. Kinetics of pollutant sorption by biosorbents: Review. *Sep. Purif. Rev.* **2000**, *29*, 189–232.

(11) Ho, Y.; McKay, G. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* **1998**, *70*, 115–124.

(12) Ho, Y.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* **2000**, *34*, 735–742.

(13) Low, M. J. D. Kinetics of Chemisorption of Gases on Solids. *Chem. Rev.* **1960**, *60*, 267–312.

(14) Günay, A.; Arslankaya, E.; Tosun, I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *J. Hazard. Mater.* **2007**, *146*, 362–371.

(15) Chien, S. H.; Clayton, W. R. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 265–268.

(16) Bayramoglu, G.; Arica, M. Y. Construction a hybrid biosorbent using *Scenedesmus quadricauda* and Ca-alginate for biosorption of Cu(II), Zn(II) and Ni(II): Kinetics and equilibrium studies. *Bioresour. Technol.* **2009**, *100*, 186–193.

(17) Dursun, A. Z. A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated Aspergillus niger. *Biochem. Eng. J.* **2006**, *28*, 187–195.

(18) Ho, Y. S. Review of second-order models for adsorption systems. *J. Hazard. Mater.* **2006**, *136*, 681–689.

(19) Ncibi, M. C.; Mahjoub, B.; Seffen, M. Investigation of the sorption mechanisms of metal-complexed dye onto *Posidonia oceanica* (L.) fibres through kinetic modeling analysis. *Bioresour. Technol.* **2008**, *99*, 5582–5589.

(20) Horsfall, J. M.; Spiff, A. I. Effects of temperature on the sorption of Pb$^{2+}$ and Cd$^{2+}$ from aqueous solution by *Caladium bicolour* (Wild Cocoyam) biomass. *Electron. J. Biotechnol.* **2005**, *8*, 43–50.

(21) Chubar, N.; Carvalho, J. R.; Correia, M. J. N. Heavy metals biosorption on cork biomass: effect of the pre-treatment. *Colloids Surf., A* **2004**, *238*, 51–58.

(22) Hernáinz, F.; Calero, M.; Blázquez, G.; Martín-Lara, M. A.; Tenorio, G. Comparative study of the biosorption of cadmium(II), chromium (III), and lead(II) by olive stone. *Environ. Prog.* **2008**, *27*, 469–478.

(23) Martín-Lara, M. A.; Rico, I. L. R.; Vicente, I. d. l. C. A.; Blázquez, G.; Calero, M. Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions. *Desalination* **2010**, *256*, 58–63.

(24) Aksu, Z. Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature. *Sep. Purif. Technol.* **2001**, *21*, 285–294.

(25) Aksu, Z.; Tezer, S. Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. *Process Biochem.* **2005**, *40*, 1347–1361.

(26) Ghaedi, M.; Ghezelbash, G. R.; Marahel, F.; Ehsanipour, S.; Najibi, A.; Soylak, M. Equilibrium, thermodynamic and kinetic studies on lead (II) biosorption from aqueous solution by *Saccharomyces cerevisiae* biomass. *Clean* **2010**, *38*, 877–885.

(27) Ariel, V. O.; Trilestari, K.; Sunarso, J.; Indraswati, N.; Ismadji, S. Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: Characterization, biosorption parameters and mechanism studies. *Clean* **2008**, *36*, 937–962.

(28) Amini, M.; Younesi, H. Biosorption of Cd(II), Ni(II) and Pb(II) from aqueous solution by dried biomass of *Aspergillus niger*: Application of response surface methodology to the optimization of process parameters. *Clean* **2009**, *37*, 776–786.

(29) Ahmad, A.; Ghufran, R.; Faizal, W. M. Cd(II), Pb(II) and Zn(II) removal from contaminated wáter by biosorption using activated sludge biomass. *Clean* **2010**, *38*, 153–158.

(30) Baytak, S.; Koçyigit, A.; Türker, A. R. Determination of lead, iron and nickel in water and vegetable samples after preconcentration with *Aspergillus niger* loaded on silica gel. *Clean* **2007**, *35*, 607–611.

(31) Gupta, V. K.; Carrott, P. J. M.; Ribeiro Carrott, M. M. L.; Suhas. Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 783–842.

(32) Vijayaraghavan, K.; Yun, Y. S. Bacterial biosorbents and biosorption. *Biotechnol. Adv.* **2008**, *26*, 266–291.

(33) Cruz-Olivares, J.; Pérez-Alonso, C.; Barrera-Díaz, C.; López, G.; Balderas-Hernández, P. Inside the removal of lead(II) from aqueous solutions by De-Oiled Allspice Husk in batch and continuous processes. *J. Hazard. Mater.* **2010**, *181*, 1095–1101.

(34) Montazer-Rahmati, M. M.; Rabbani, P.; Abdolalli, A.; Keshtkar, A. R. Kinetics and equilibrium studies on biosorption of cadmium, lead and nickel ions from aqueous solutions by intact and chemically modified brown algae. *J. Hazard. Mater.* **2011**, *185*, 401–407.

(35) Qaiser, S.; Saleemi, A. R.; Umar, M. Biosorption of lead(II) and chromium(VI) on groundnut hull: Equilibrium, kinetics and thermodynamic study. *Electron. J. Biotechnol.* **2009**, *12*, 1–17.

(36) Vinod, V. T. P.; Sashidhar, R. B.; Sreedhar, B.; Rama Rao, B.; Nageswara Rao, T.; Abraham, J. T. Interaction of $Pb^{2+}$ and $Cd^{2+}$ with gum kondagogu (*Cochlospermum gossypium*): A natural carbohydrate polymer with biosorbent properties. *Carbohydr. Polym.* **2009**, *78*, 894–901.

(37) Uluozlu, O. D.; Sari, A.; Tuzen, M.; Soylak, M. Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. *Bioresour. Technol.* **2008**, *99*, 2972–2980.

(38) García-Rosales, G.; Colín-Cruz, A. Biosorption of lead by maize (*Zea mays*) stalk sponge. *J. Environ. Manage.* **2010**, *91*, 2079–2086.

(39) Li, Q.; Zhai, J.; Zhang, W.; Wang, M.; Zhou, J. Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solutions by sawdust and modified peanut husk. *J. Hazard. Mater.* **2007**, *141*, 163–167.

(40) Gupta, V. K.; Rastogi, A. Biosorption of lead(II) from aqueous solutions by non-living algal biomass *Oedogonium* sp. and *Nostoc* sp.—A comparative study. *Colloids Surf., B* **2008**, *64*, 170–178.

(41) Gundogdu, A.; Ozdes, D.; Duran, C.; Bulut, V. N.; Soylak, M.; Senturk, H. B. Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia* Ten.). *Chem. Eng. J.* **2009**, *153*, 62–69.

(42) Ofomaja, A. E.; Naidoo, E. B.; Modise, S. J. Kinetic and pseudo-second-order modeling of lead biosorption onto pine cone powder. *Ind. Eng. Chem. Res.* **2010**, *49*, 2562–2572.

(43) Gupta, V. K.; Rastogi, A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *J. Hazard. Mater.* **2008**, *152*, 407–414.

(44) Blázquez, G.; Calero, M.; Hernáinz, F.; Tenorio, G.; Martín-Lara, M. A. Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive-oil production. *Chem. Eng. J.* **2010**, *160*, 615–622.

(45) Hammaini, A.; González, F.; Ballester, A.; Blázquez, M. L.; Muñoz, J. A. Biosorption of heavy metals by activated sludge and their desorption characteristics. *J. Environ. Manage.* **2007**, *84*, 419–426.

(46) Dahiya, S.; Tripathi, R. M.; Hegde, A. G. Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. *Bioresour. Technol.* **2008**, *99*, 179–187.

(47) Gupta, V. K.; Ali, I. Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste. *J. Colloid Interface Sci.* **2004**, *271*, 321–328.

(48) Chen, C.; Wang, J. L. Investigating the interaction mechanism between zinc and *Saccharomyces cerevisiae* using combined SEM-EDX and XAFS. *Appl. Microbiol. Biotechnol.* **2008**, *79*, 293–299.

(49) Pan, J. H.; Liu, R. X.; Tang, H. X. Surface reaction of *Bacillus cereus* biomass and its biosorption for lead and copper ions. *J. Environ. Sci. China* **2007**, *19*, 403–408.

(50) Han, R.; Zhang, J.; Zou, W.; Shi, J.; Lui, H. Equilibrium biosorption isotherm for lead ion on chaff. *J. Hazard. Mater.* **2005**, *125*, 266–271.

(51) Chen, W. M.; Wu, C. H.; James, E. K.; Chang, J. S. Metal biosorption capability of *Cupriavidus taiwanensis* and its effects on heavy metal removal by nodulated *Mimosa pudica*. *J. Hazard. Mater.* **2008**, *151*, 364–371.

(52) Zein, R.; Suhaili, R.; Earnestly, F.; Indrawati; Munaf, E. Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana* L. fruit shell. *J. Hazard. Mater.* **2010**, *181*, 52–56.

(53) Gupta, V. K.; Gupta, M.; Sharma, S. Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste. *Water Res.* **2001**, *35*, 1125–1134.

(54) Bueno, B. Y. M.; Torrem, M. L.; Molina, F.; de Mesquita, I. M. S. Biosorption of lead(II), chromium(III) and copper(II) by *R. opacus*: Equilibrium and kinetic studies. *Miner. Eng.* **2008**, *21*, 65–75.

(55) Lawal, O. S.; Sanni, A. R.; Ajayi, I. A.; Rabiu, O. O. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. *J. Hazard. Mater.* **2010**, *177*, 829–835.

(56) Han, R.; Li, H.; Li, Y.; Zhang, J.; Xiao, H.; Shi, J. Biosorption of copper and lead ions by waste beer yeast. *J. Hazard. Mater.* **2006**, *137*, 1569–1576.