Recycling Poultry Feathers for Pb Removal from Wastewater: Kinetic and Equilibrium Studies

G. de la Rosa, H. E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodríguez, C. Velasco-Santos, and A. L. Martínez-Hernández

Abstract—Chicken feathers were used as biosorbent for Pb removal from aqueous solution. In this paper, the kinetics and equilibrium studies at several pH, temperature, and metal concentration values are reported. For tested conditions, the Pb sorption capacity of this poultry waste ranged from 0.8 to 8.3 mg/g. Optimal conditions for Pb removal by chicken feathers have been identified. Pseudo-first order and pseudo-second order equations were used to analyze the experimental data. In addition, the sorption isotherms were fitted to classical Langmuir and Freundlich models. Finally, thermodynamic parameters for the sorption process have been determined. In summary, the results showed that chicken feathers are an alternative and promising sorbent for the treatment of effluents polluted by Pb ions.

Keywords—Sorption, chicken feathers, Pb, water treatment.

I. INTRODUCTION

In recent years, water pollution with heavy metals has become an important environmental threat mainly because of the numerous industrial effluents containing these and other pollutants [1]. Heavy metals are highly toxic non-biodegradable, and tend to accumulate causing several diseases and health disorders in humans, and other living organisms [2]. In particular, Pb has been classified as a serious

Manuscript received March 31, 2008. Financial support is acknowledged from Universidad de Guanajuato, Instituto Tecnológico de Aguascalientes, CONCYTEG, DGEST and CONACYT.

- G. de la Rosa is with the Department of Chemical Engineering, Universidad de Guanajuato, Noria Alta, C.P. 36050, Guanajuato, Mexico (corresponding author, phone: 52-4737320006 ext 8139; fax: 52-4737320006 ext 8108; e-mail: delarosa@quijote.ugto.mx).
- H. E. Reynel-Avila is with the Department of Chemical Engineering, Universidad de Guanajuato, C.P. 36050, Guanajuato, Mexico (e-mail: hreynel@quijote.ugto.mx).
- A. Bonilla-Petriciolet is with the Department of Chemical Engineering, Instituto Tecnologico de Aguascalientes, C.P. 20256, Aguascalientes, Mexico (e-mail: abonilla@ita.mx).

Irene Cano-Rodríguez is with the Department of Chemical Engineering, Universidad de Guanajuato, Noria Alta, C.P. 36050, Guanajuato, Mexico (corresponding author, phone: 52-4737320006 ext 8139; fax: 52-4737320006 ext 8108; e-mail: irene@quijote.ugto.mx).

- C. Velasco-Santos is with Centro de Fisica Aplicada y Tecnologia Avanzada, UNAM, C.P. 76000, Queretaro, Mexico (e-mail: carlos@fata.unam.mx).
- A. L. Martinez-Hernandez is the Centro de Fisica Aplicada y Tecnologia Avanzada, UNAM, C.P. 76000, Queretaro, Mexico (e-mail: analaura@fata.unam.mx).

hazardous heavy metal with high priority in the context of environmental risk [3]. This metal is extremely toxic and can damage the kidney, liver, brain, nervous, and reproductive systems; among other adverse effects to humans [2]. At present, Pb pollution is considered a worldwide problem because this metal is commonly detected in several industrial wastewaters [1]. Examples of these wastewaters are those produced by processes such as mining, smelting, printing, metal plating, explosive manufacture, and dying. In this context, local legislations have established rigorous standards for Pb concentrations in industrial effluents. Therefore, special attention has been given to develop proper methods for Pb removal from water.

Until now, several technologies for heavy metal removal have been proposed [3]. The conventional approaches involve chemical precipitation and filtration, chemical oxidation, electrochemical treatment, reverse osmosis, evaporation, ionexchange, and sorption. However, most available methods may show economical and technical disadvantages such as high capital and operational costs, high sensitivity to operational conditions, significant energy consumption, or sludge generation [3]. Considering these circumstances, it is necessary to develop effective, low-cost, and environmentfriendly methods for water treatment. Particularly, sorption is considered a simple and suitable strategy for metal removal in polluted effluents because of its high efficiency, easy handling, and economical feasibility [3]-[5]. Furthermore, this method offers the possibility of metal recovery, sorbent regeneration, and minimization of residual sludge.

During the last decades, several studies have shown that different synthetic and natural sorbents can be used to remove Pb ions from aqueous effluents [4]-[24]. In particular, the use of natural sorbents promises to fulfill the desired requirements for a suitable treatment process: competitive, effective, and low-cost. One advantage of this approach is the use of biomass raw materials which are either abundant or wastes from industrial operations [3]. Under these conditions, the operational costs of treatment processes can be considerably reduced in comparison to techniques where synthetic sorbents are used [18]. Many examples of natural sorbents are available in the literature, and they include brewery biomass, cactus pulp, olive stone waste, chitosan, modified wool, cotton, nutshells, rice hulls, pine bark, sawdust, sugar cane bagasse, fruit stones, and pyrolyzed coffee, among others [17]-[24]. In

removal processes, most of these sorbents generally show Pb uptakes in the range of 1.0 - 100 mg/g.

In particular, chicken feathers are among the natural sorbents that can be used for water treatment [25]-[30]. They represent four to six percent of the total weight of mature chickens and, as a consequence, are a waste product generated in large quantities from commercial poultry industry [31]. As indicated by other authors [25], the application of chicken feathers for purification of industrial wastewaters and drinking water is a very economical method. In addition, the advantages of chicken feathers over similar sorbents lie in their high tensile strength, water insolubility, and stability over a wide range of pH, and structural toughness.

To date, the use of chicken feathers for sorption purposes has achieved satisfactory results for the removal of some heavy metals, colorants, and organic toxic compounds [15], [25]-[30]. However, to the best of our knowledge, only one work [25] has reported the application of chicken feathers for Pb removal from water. Unfortunately, these authors did not study the removal performance of this sorbent at different operational conditions.

Based on this fact, the objective of this research was to study the Pb sorption from aqueous solutions by chicken feathers. Specifically, sorption isotherms and kinetics where the effects of metal concentration, pH, and temperature are considered, are shown herein. These experiments are essential to supply the basic information required for the design and operation of sorption equipments in water treatment [32]. The experimental data were fitted to classical isotherm and kinetic models, and a proper comparison was performed. Finally, thermodynamic parameters for Pb sorption process have been calculated.

II. MATERIALS AND METHODS

A. Sorbent Preparation

Chicken feathers were collected from poultry industry facilities. They were washed several times with detergent and deionized water. Subsequently, feathers were treated with a solution of deionized water and ethanol (5:1 proportion) during 12 h. This step was performed for totally removing organic materials present in feathers. Finally, feathers were again washed with deionized water, dried, rachises removed, and soft barbs were cut to obtain fibers of about 0.5 cm in length. The material thus obtained was used in these experiments.

B. Sorption Studies: Kinetics and Isotherms

All sorption experiments were carried out in batch conditions using 15 mL of metal solution and 0.06 g of sorbent. Pb solutions in the concentration range of 10 - 200 mg/L were prepared from analytical reagent-grade Pb(NO₃)₂ and deionized water. A temperature-controlled shaker was used to mix the suspensions (metal solution-sorbent) at 210 rpm for all tested conditions.

In the first part, kinetic experiments were performed. For

this purpose, several Pb concentrations at different pHs (2 - 5) and temperatures (25 - 40 °C) were used. The initial pH was adjusted by adding diluted HNO₃. In addition, the sorbent was equilibrated at the desired pH by using diluted acid solutions. Sorbent and Pb solutions were mixed and allowed to react at different contact times. Later, the metal solution was separated from the sorbent by filtration and its concentration was determined using an atomic absorption Perkin Elmer AAnalist 100 spectrophotometer equipped with an air-acetylene burner. All the experiments were conducted in triplicate, and the average results are reported in this paper. Reproducibility of the measurements was in general within 5%.

The sorption capacity $q \pmod{g}$ of the chicken feathers was calculated using

$$q = \frac{C_0 - C_t}{W}V\tag{1}$$

where C_0 is the initial Pb concentration (mg/L) and C_t is the remaining metal concentration (mg/L) at time t (h), V is the volume of Pb solution (L), and W is the sorbent amount (g).

For sorption isotherms, the equilibrium concentrations and its corresponding metal uptakes were used. These isotherms were obtained by employing initial Pb^{+2} concentrations in the range 10- 200 mg/L at 25, 30, and 40 °C; and pH 2, 3, 4, and 5

C. Modeling of Sorption Experiments

The correlation of kinetic and equilibrium sorption data using either theoretical or empirical models, is essential for interpretation and prediction purposes. For this reason, the experimental information was analyzed using classical isotherm and kinetic equations. In fact, these models have been considered in other studies related to heavy metal removal using natural sorbents ([33], [34]). For interested readers, the theoretical basis, explanation, and derivation of applied models can be found in the review reported by Liu and Liu [35].

For kinetic data modeling purposes, the pseudo-first order and pseudo-second order equations were selected. These kinetic expressions are defined as:

$$q = q_{te} (1 - e^{-k_1 t}) (2)$$

$$q = \frac{q_{te}^2 k_2 t}{1 + q_{te} k_2 t} \tag{3}$$

where q is the metal uptake (mg/g) at time t (h), q_{te} is the theoretical metal uptake (mg/g) at equilibrium, k_1 is the rate constant of pseudo-first order sorption (h⁻¹), and k_2 is the rate constant of the pseudo-second order sorption (g/mg h), respectively. Pseudo-first order kinetic assumes that one sorbate species relates to one active site, whereas pseudo-second-order model considers that two surface sites could be occupied by one sorbate ion. In sorption literature, these kinetic models have been widely used to describe

experimental data from synthetic and natural sorbents [35]. For these expressions, two adjustable parameters q_{te} , and k_1 or k_2 are available.

On the other hand, the classical Langmuir and Freundlich models to correlate isotherm data were used. In first instance, Langmuir model assumes that sorption occurs in a monolayer where the actives sites are identical and energetically equivalent. This isotherm is given by

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{4}$$

where q_e and C_e are the metal uptake (mg/g) and concentration (mg/L) at equilibrium, q_m is the theoretical maximum sorption capacity (mg/g), and K (L/g) represents the Langmuir equilibrium constant, respectively. Both q_m and K are obtained from data correlation.

Freundlich model is an empirical expression used to describe a heterogeneous system, which is described by:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f (L/g) and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting. Both isotherm models have been widely used in sorption research [35], including the analysis of sorption data obtained from chicken feathers [25]-[30].

When performing data fitting, linear regression is generally used to determine the parameters of kinetic and isotherm models. Specifically, the linear least-squares method to the linearly transformed equations has been widely applied to correlate sorption data. However, some studies have shown that, depending on the way model is linearized, the error distribution changes either the worse or the better [36], [37]. Thus, a non-linear regression is more suitable for parameter estimation [33]. Furthermore, non-linear regression offers the advantage that the error distribution is not altered as in the case of linear technique [36], [37]. Thus, in the present study, this approach was applied.

For data fitting, the following objective function was used:

$$F_{obj} = \sum_{i=1}^{ndat} \left(\frac{q_{\text{exp}} - q_{calc}}{q_{\text{exp}}} \right)^2 \tag{6}$$

where q_{exp} and q_{calc} are the experimental and predicted metal uptakes (mg/g), and *ndat* is the overall number of experimental points.

Since the kinetic and isotherm models are nonlinear expressions, (6) is also nonlinear and potentially non-convex. In fact, previous research and the results reported in [38] suggest that the parameter estimation in sorption models may be a challenging optimization problem. In this case, conventional optimization methods are not reliable to find the global minima of objective function. It should be noticed that failing to identify the global optimum in parameter estimation may cause errors and uncertainties in equipment design, and erroneous conclusions about model performance.

Therefore, it is convenient to use a proper optimization strategy for sorption data correlation. For that reason, a stochastic global optimization method was used to determine the kinetic and isotherm parameters. Specifically, the Simulated Annealing method was applied for this purpose. This optimization strategy has been tested in several applications inside the chemical engineering field, including the fit of adsorption isotherms [38]. The reported results indicate that this method is suitable for parameter estimation using non-convex functions. Particularly, [39] provides a full description of this optimization strategy. In this investigation, the Fortran subroutine implemented by Goffe et al. [40] has been used. For illustrative purposes, Fig. 1 shows the overall algorithm of this method. In our calculations, the values reported by [38] were used for the cooling schedule of Simulated Annealing method.

- 1. Initialize parameters of Simulated Annealing method.
- 2. Guess initial values for optimization variables (in this case, parameters of kinetic and isotherm models).
- 3. Perform a cycle of random moves for each optimization variable. Accept or reject each new point according to the Metropolis criterion. Record the optimum point reached so far.
- 4. Adjust parameters of Simulated Annealing and set current point to the optimum.
- 5. Repeat steps 3 and 4 until satisfy the convergence criterion of Simulated Annealing optimization method.

Fig. 1 Pseudo-code of Simulated Annealing optimization method

To measure the goodness of a fit, the following criterions were considered: the coefficient of determination (R^2) , the objective function value (F_{obj}) , and the mean absolute percentage deviation (E) between calculated and experimental uptakes where

$$E = \frac{100}{ndat} \sum_{i=1}^{ndat} \frac{q_{\exp} - q_{calc}}{q_{\exp}}$$
 (7)

In addition, these statistics were accompanied by a study of the behavior of the residuals [41]. Taking into account that a relative objective function is used for data correlation, the relative residuals (e) should be considered [42]

$$e_i = \frac{q_{\rm exp} - q_{\rm calc}}{q_{\rm exp}} \bigg|_i \tag{8}$$

Thus, if a model is adequate, the residuals should contain no obvious pattern [41]. Finally, it is important to remark that this residual analysis is rarely used when testing the results of data fitting in sorption models.

D. Thermodynamics of Sorption Process

Thermodynamic parameters of sorption process are mainly based on the calculation of Gibbs free energy

$$\Delta G^0 = -RT \ln K_{eq} \tag{9}$$

where ΔG^0 is the change in free energy (kJ/mol), R is the gas constant (8.3145×10⁻³ kJ/mol K), K_{eq} is the equilibrium constant, and T is absolute temperature (K). So, the determination of equilibrium constant is a key step to obtain the thermodynamic variables of sorption process. Generally, K_{eq} is calculated from experimental data by using [32], [33]

$$K_{eq} = \frac{C_{se}}{C_{e}} \tag{10}$$

where C_{se} is the concentration of sorbed solute on sorbent at equilibrium (mg/L).

When this variable is known, the changes in enthalpy and entropy can be obtained by using

$$\ln K_{eq} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{11}$$

where ΔH^0 is the enthalpy change (kJ/mol), and ΔS^0 is the entropy change (kJ/molK). Both thermodynamic quantities are determined from the slope and intercept of the plot $\ln K_{eq}$ versus 1/T, or better known as van't Hoff plot.

III. RESULTS AND DISCUSSION

Figs. 2 - 4 show the kinetics of Pb sorption on chicken feathers where the effects of initial concentration, pH, and temperature are considered. In all experiments, Pb removal ranged from 0.9 to 81.6 %. The uptake rate of Pb⁺² ions by the sorbent initially increases with time, and all kinetics tended toward equilibrium at 24 h irrespective of the operation conditions. However, the results showed that most of the metal removal occurs during the first hours of contact. This trend is similar to that obtained by other studies [15], [27]–[30], and may indicate that most of the sorption process occurs on the external surface of the sorbent. It appears that the binding sites of chicken feathers that might be responsible for Pb removal are more accessible at the surface than the sorbent pores.

As expected, metal sorption is strongly influenced by the initial concentration (see Fig. 2). In fact, it was found that an increase in the initial Pb⁺² concentration resulted in an increase of metal uptake. This behavior can be associated to the increase in the mass transfer driving force caused by the increase in metal content [27]. On the other hand, Fig. 3 indicates that Pb uptake is improved at higher pH values. Regarding the sorbent, the changes in pH may cause the ionization of active sites thus affecting its removal performance. Certainly, pH plays an important role on Pb removal by chicken feathers.

The effect of temperature on the kinetics of Pb sorption by chicken feathers is shown in Fig. 4. As this Fig. shows, from 25 to 30 °C, an increase in Pb uptake occured. As indicated by [27], this phenomenon is partly caused by the stretching of chicken feathers and, as a consequence, more active sites for metal removal may be exposed. However, from 30 to 40 °C, Pb uptake clearly decreased. In these conditions, the metal mobility increases with respect to temperature. Consequently,

there may be an unfavorable effect on the ability of metal ions to interact with the active sites of the sorbent. In fact, this effect of temperature has been also reported for the removal of other metals using an immobilized sorbent obtained from this poultry waste [26].

Results of isotherm studies are reported in Fig. 5 and 6. In general, the maximum metal uptake ranged from 0.8 to 8.3 mg/g under tested conditions. As mentioned early, pH is a key parameter to control the Pb sorption by chicken feathers. According to [25], the metal removal in keratin compounds, such as chicken feathers, may occur by the combination of a trapping process of metal ions in the nano-porus network of the sorbent, in addition to the interaction between the ions and carboxylic binding sites. Thus, at the pHs tested, it appears that Pb⁺² ions compete with protons for the available binding sites of chicken feathers. In fact, at pH below 3, little sorption of metal ions was observed because the carboxylic sites are mainly protonated [21]; and therefore less sites for metal removal are available. Then, these conditions make sorption unfavorable. When pH increases, the negative charge density on the sorbent surface increases due to deprotonation of the metal binding sites [22], and thus Pb sorption improves. Since above pH 6 Pb ions precipitate as metal hydroxides, higher pHs were avoided in this study [21]. Results showed that optimum Pb removal occurs at pH 5. This optimal value agrees with the results reported by other authors that have used different natural sorbents for Pb removal [11], [23]. Considering the maximum uptake at pH 5, there is a decrease of 90.2, 81.5, and 46.2 % in sorption capacity at pH 2, 3, and 4, respectively.

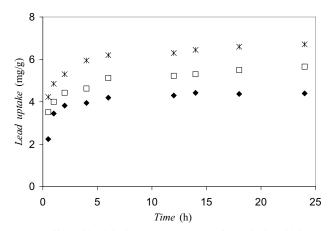


Fig. 2 Effect of initial Pb concentration on Pb uptake by chicken feathers. Experimental conditions: 15 mL of metal solution, 0.06 g of sorbent, 30 °C, and pH 5. Initial concentration (mg/L): (\spadesuit) 50, (\square) 80, and (\varkappa) 100

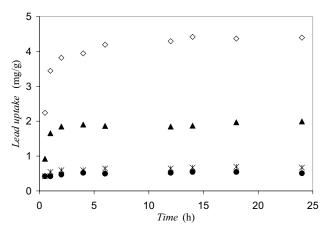


Fig. 3 Effect of pH on Pb uptake by chicken feathers. Experimental conditions: 15 mL of metal solution, 0.06 g of sorbent, 50 mg/L of initial Pb concentration, and 30 °C. pH: (\bullet) 2, (\star) 3, (\blacktriangle) 4, and (\Diamond) 5

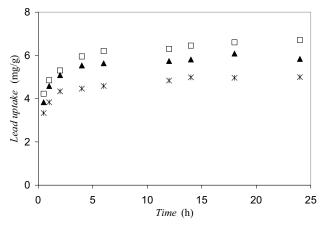


Fig. 4 Effect of temperature on Pb uptake by chicken feathers. Experimental conditions: 15 mL of metal solution, 0.06 g of sorbent, 100 mg/L of initial Pb concentration, and pH 5. Temperature (°C):

(※) 25, (□) 30, and (▲) 40

With respect to temperature, Fig. 6 shows the isotherms obtained at optimal pH and 25, 30, and 40 °C. By increasing the temperature from 25 to 30 °C, the metal uptake was enhanced from 6.2 to 8.3 mg/g, respectively. However, when temperature changed from 30 to 40 °C, the maximum sorption capacity decreased to 7.6 mg/g. This dual behavior has been also observed by other studies using natural and synthetic sorbents [14], [24], [26]. The decrease on heavy metal uptake, including Pb+2 ions, with respect to a temperature increment may be explained by considering kinetic aspects. At high temperatures, where physisorption is generally present, the average kinetic energy of the metal ions is increased, causing that the attractive force between metal ions and sorbent may be insufficient to retain the metal ions at the binding site. These conditions could lead to desorption or cause the metal ions to bounce off the surface of sorbent instead of colliding and combining with it [14]. Therefore, the raise of solution temperature is probably associated with instability of metal ion-sorbent complex.

Based on the results obtained herein, the optimal pH and temperature for Pb removal by chicken feathers are 5 and 30 °C where maximum sorption capacity is 8.3 mg/g. This maximum Pb uptake value agrees with that determined by [25]. Specifically, these authors reported Pb uptakes from 3.83 to 12.0 mg/g for keratin fibers at pH range 5 or above (temperature is not specified in this work).

Thermodynamic parameters of Pb sorption process are shown in Table I for an initial Pb concentration of 10 mg/L. The negative ΔG^0 values indicate the feasibility and spontaneous nature of this process at tested conditions. On the other hand, the positive value of enthalpy change from 25 to 30 °C suggests the endothermic nature of the process and possible strong bonding between the metal and sorbent [34]. Also, for this temperature increment, a positive entropy change value reflects the affinity of the sorbent to the Pb⁺² ions since there is an increase in randomness at the sorbent/solution interface during the process [21]. However, at temperatures between 30 - 40 °C, the negative enthalpy value indicates that sorption process is exothermic. This implies that there was a weak bonding between the sorbate and sorbent surface [32]. Also, negative entropy changes correspond to a decrease in the degree of freedom of the sorbed metal. In conclusion, calculated thermodynamic parameters are in agreement with the experimental data.

Generally, physical sorption involves an enthalpy change from 2 to 21 kJ/mol, while enthalpy change of chemisorption falls in the range of 80–200 kJ/mol [35]. In addition, as indicated by [28], if a physical sorption process was involved, a decrease of this process with an increase in temperature should be expected. On the other hand, when chemisorption is involved, it is usually favored with rises in temperature. According to this, the results showed that, below optimal temperature, Pb removal may be principally controlled by a chemisorption process. However, for temperatures higher than 30 °C, it can possible that Pb⁺² sorption onto chicken feathers is caused by a combination of both physical and chemical processes.

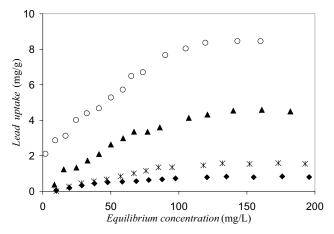


Fig. 5 Isotherms for Pb sorption by chicken feathers. Experimental conditions: 15 mL of metal solution, 0.06 g of sorbent, and 30 °C. pH: (•) 2, (ж) 3, (•) 4, and (•) 5

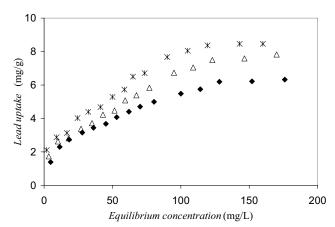


Fig. 6 Isotherms for Pb sorption by chicken feathers. Experimental conditions: 15 mL of metal solution, 0.06 g of sorbent, and pH 5. Solution temperature (°C): (♦) 25, (ж) 30, and (Δ) 40

TABLE I
THERMODYNAMIC PARAMETERS FOR PB SORPTION FROM
AQUEOUS SOLUTIONS USING CHICKEN FEATHERS ¹

T (°C)	ΔG^{0} (kJ/mol)	ΔH^{0} (kJ/mol)	ΔS ⁰ (kJ/mol K)	
25	-0.375			
		201.501	0.677	
30	-3.761			
		-61.356	-0.189	
40	-1.861			

¹ Initial Pb concentration: 10 mg/L.

Results of sorption data fitting for both kinetic and isotherm models are presented in Figs. 7-10, and Tables II-IV. For kinetic data, the results showed that the pseudo-second order model gave better data correlations than those for the pseudo-first order model (see Fig. 7, and Tables II and III). In fact, pseudo-first order equation showed a greater mean absolute deviation (E) than that obtained with other kinetics (6.3 and 3.2%, respectively). Residual analysis also indicated that (3) is more suitable to represent the Pb uptake by chicken feathers. For illustrative purposes, Fig. 9 compares the residual plots of both kinetic models. As observed, the residuals of (3) appear to be more randomly distributed than those obtained for other kinetic equation. In general, this kinetic expression showed correlation coeficients R^2 from 0.81 to 0.98. Table III reports the model parameters, F_{obj} , and R^2 of this sorption equation for all correlations performed. At tested conditions, k_2 ranged from 0.42 to 11.88 g/mg h.

Alternatively, the kinetic data were also subjected to analysis by the intraparticle diffusion model [34]. Previous results showed that particle diffusion was involved in the sorption process, but it was not the rate-controlling step (data not shown).

TABLE II
KINETIC PARAMETERS OF PSEUDO-FIRST ORDER MODEL FOR PB SORPTION
FROM AQUEOUS SOLUTION USING CHICKEN FEATHERS

$C_{\theta}(\text{mg/L})$	T (°C)	рН	q _{te} (mg/g)	k_{I} (h ⁻¹)	R^2	F_{obj}
50	30	2	0.50	3.00	0.49	4.0×10 ⁻²
		3	0.64	2.03	0.86	2.0×10 ⁻²
		4	1.92	1.43	0.89	3.0×10 ⁻²
		5	4.24	1.52	0.92	1.0×10 ⁻²
	25	5	3.16	2.05	0.65	7.0×10^{-2}
	40	5	3.50	2.00	0.66	4.0×10^{-2}
80	30	2	0.58	1.46	0.74	8.0×10^{-2}
		3	1.04	1.39	0.79	7.0×10^{-2}
		4	3.24	2.07	0.90	2.0×10 ⁻²
		5	5.04	2.04	0.67	6.0×10^{-2}
	25	5	4.32	3.11	0.93	1.0×10^{-2}
	40	5	4.81	2.17	0.73	4.0×10^{-2}
100	30	2	0.69	1.33	0.90	2.0×10 ⁻²
		3	1.25	0.58	0.95	2.0×10 ⁻²
		4	3.44	2.06	0.90	1.0×10^{-2}
		5	6.14	1.99	0.74	5.0×10^{-2}
	25	5	4.69	2.21	0.78	3.0×10^{-2}
	40	5	5.64	2.05	0.84	3.0×10 ⁻²

With respect to isotherm data, Langmuir and Freundlich isotherms failed to model the metal uptakes at low pH and equilibrium concentrations. Specifically, both models are incapable of fitting the data at pH 3. Excluding this isotherm, it appears that remaining experimental data are best described by the Freundlich model. The plots of the experimental equilibrium Pb uptakes against the values predicted by isotherm equations are given in Fig. 8. In addition, Freundlich model provides a better behavior of the residuals, and suitable values of \mathbb{R}^2 are obtained in most of the correlations performed (see Fig. 10 and Table V).

Model parameters of both isotherms and results of data correlation are reported in Table IV and V. The parameter n in the Freundlich equation is an indicative of the sorption intensity. If n lies between one and ten, this indicates a favorable sorption process. Since the calculated values are in the range 1-3, this indicates favorable Pb sorption by chicken feathers.

TABLE III
KINETIC PARAMETERS OF PSEUDO-SECOND ORDER MODEL FOR PB SORPTION
FROM AQUEOUS SOLUTION USING CHICKEN FEATHERS

C_{θ} (mg/L)	T (°C)	рΗ	q _{te} (mg/g)	k2 (g/mg h)	R^2	F_{obj}
50	30	2	0.52	11.88	0.89	2.0×10 ⁻²
		3	0.68	5.05	0.95	7.9×10^{-3}
		4	2.04	0.99	0.81	7.0×10^{-2}
		5	4.52	0.49	0.96	2.0×10 ⁻²
	25	5	3.37	0.97	0.91	2.0×10 ⁻²
	40	5	3.69	0.94	0.96	1.0×10^{-2}
80	30	2	0.63	3.51	0.95	2.0×10 ⁻²
		3	1.12	1.83	0.96	2.0×10 ⁻²
		4	3.40	1.05	0.95	7.6×10^{-3}
		5	5.35	0.62	0.90	2.0×10^{-2}
	25	5	4.43	1.72	0.90	5.3×10 ⁻³
	40	5	5.08	0.72	0.95	8.8×10^{-3}
100	30	2	0.72	3.99	0.94	1.5×10 ⁻²
		3	1.45	0.42	0.97	5.0×10^{-2}
		4	3.69	0.88	0.97	5.8×10^{-3}
		5	6.51	0.50	0.95	1.0×10 ⁻²
	25	5	4.92	0.79	0.96	5.4×10^{-3}
	40	5	5.93	0.60	0.98	2.5×10 ⁻³

TABLE IV
ISOTHERM PARAMETERS OF LANGMUIR MODEL FOR PB SORPTION FROM AQUEOUS SOLUTION USING CHICKEN FEATHERS

T (°C)	рН	$q_m (\text{mg/g})$	K(L/g)	R^2	F_{obj}
30	2	2.64	3.20×10 ⁻³	0.77	1.05
	4	9.80	6.27×10 ⁻³	0.95	0.28
	5	8.63	4.22×10 ⁻²	0.85	0.71
25	5	6.36	4.40×10 ⁻²	0.91	0.16
40	5	7.57	4.06×10 ⁻²	0.85	0.48

TABLE V

ISOTHERM PARAMETERS OF FREUNDLICH MODEL FOR PB SORPTION FROM AQUEOUS SOLUTIONS USING CHICKEN FEATHERS

T (°C)	рН	$K_f(L/g)$	n	R^2	F_{obj}
30	2	9.32×10 ⁻³	1.10	0.57	1.36
	4	9.59×10 ⁻²	1.26	0.84	0.56
	5	1.26	2.65	0.95	0.16
25	5	0.77	2.38	0.99	0.02
40	5	0.92	2.39	0.97	0.07

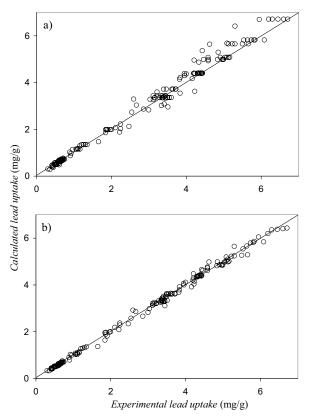


Fig. 7 Comparison of experimental and calculated Pb uptakes by chicken feathers. Kinetic model: a) Pseudo-first order, and b)

Pseudo-second order

Finally, a comparison was performed for the maximum Pb sorption capacity obtained in this work with respect to data reported in the literature. For example, it appears that the Pb uptake of chicken feathers was better than those obtained for *Aspergillus niger* biomass (7.2 mg/g) [22], river sediments (0.6 mg/g) [43], and waste maize bran (5.0 mg/g) [44]. However, the sorbent tested in this work displayed lower

sorption capacities than those of phospatic clay ($\approx 30.0 \text{ mg/g}$) [11], fly ash (22.0 mg/g) [14], olive cake (18.4 mg/g) [21], and modified peat-resin particles ($\approx 47.0 \text{ mg/g}$) [23]. It is convenient to remark that the sorption capacities reported herein have been obtained under a broad diversity of operational conditions (e.g., sorbent particle size, pH, and temperature). Moreover, in some cases, the sorbent was treated by a physical or chemical process to enhance its metal uptake. Based on this observation, a proper comparison of sorption capacities is not possible.

In this context, it can be concluded that chicken feathers, without any pretreatment, show an acceptable Pb sorption capacity. It is possible that such capacity may be improved using chemical treatments as those reported by [15], [28]-[30]. In these conditions, it is likely that Pb removal performance of this sorbent will be very competitive.

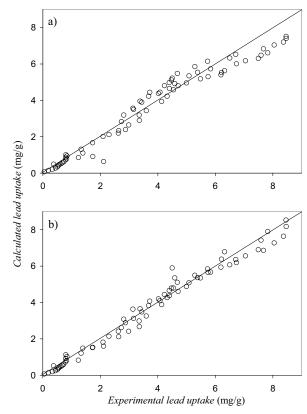


Fig. 8 Comparison of experimental and calculated Pb sorptions by chicken feathers. Isotherm model: a) Langmuir, and b) Freundlich

IV. CONCLUSION

This study shows that chicken feathers can be used as a suitable natural sorbent for Pb removal from aqueous solutions. The maximum Pb sorption capacity was obtained at 30 °C and pH 5. In addition, these studies indicated that metal sorption was favored with an increment in pH. On the other hand, an endothermic process was observed below the optimal temperature, whereas an exothermic behavior was displayed at higher temperatures. Proper parameter estimations and suitable statistics have been useful to identify that, in general,

pseudo-second order kinetic and Freundlich isotherm models are suitable to represent the experimental data obtained in this investigation. Based on thermodynamic calculations, it appears that the Pb sorption by chicken feathers may be controlled by a chemisorption process, or by a combination of both physical and chemical processes depending on temperature. However, the exact mechanism of sorption process is unknown. Therefore, further studies should be focused on this topic.

Finally, it has been found that this poultry waste may be used as a low-cost sorbent for the Pb removal of polluted effluents. In future work, the sorption capacity of chemically modified chicken feathers as well as sorbent regeneration will be studied.

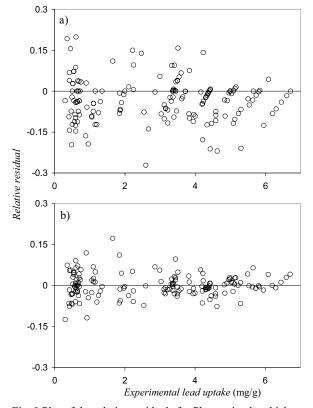


Fig. 9 Plot of the relative residuals for Pb sorption by chicken feathers. Kinetic model: a) Pseudo-first order, and b) Pseudo-second order

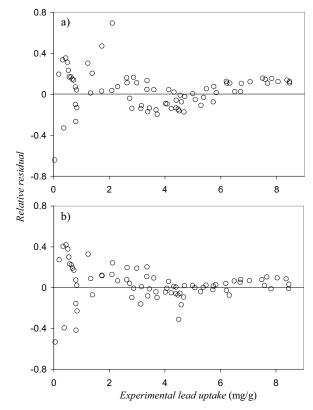


Fig. 10 Plot of the relative residuals for Pb sorption by chicken feathers. Isotherm model: a) Langmuir, and b) Freundlich

REFERENCES

- [1] S. Davydova, "Heavy metals as toxicants in big cities," *Microchemical Journal*, vol. 79, pp. 133-136, 2005.
- [2] H.A. Godwin, "The biological chemistry of lead," Current Opinion in Chemical Biology, vol. 5, pp. 223-227, 2001.
- [3] B. Volesky, "Detoxification of metal-bearing effluents: biosorption for the next century," *Hydrometallurgy*, vol. 59, pp. 203-216, 2001.
- [4] S. Al-Asheh, Z. Duvnjak, "Adsorption of metal ions by moss," Advances in Environmental Research, vol. 1, pp. 194-211, 1997.
- [5] S. Bailey, T. Olin, R. R. Bricka, D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Research*, vol. 33, pp. 2469-2479, 1999.
- [6] M. Machida, Y. Kikuchi, M. Aikawa, H. Tatsumoto, "Kinetics of adsorption and desorption of Pb(II) in aqueous solution on activated carbon by two-site adsorption model," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 240, pp. 179-186, 2004.
- [7] L. Lv, M. Peng, F. Su, X. S. Zhao, "Competitive adsorption of Pb²⁺, Cu²⁺, and Cd²⁺ ions on microporous titanosilicate ETS-10," *Journal of Colloid and Interface Science*, vol. 287, pp. 178-184, 2005.
- [8] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, "Removal of lead (II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach," *Industrial Engineering Chemistry Research*, vol 44, pp. 1987-1994, 2005.
- [9] T. Bahadir, G. Bakang, L. Altas, H. Buyukgungor, "The investigation of lead removal by sorption: an application at storage battery industry wastewater," *Enzime and Microbial Technology*, vol. 41, pp. 98-102, 2007
- [10] O. Gercel, H. Gercel, "Adsorption of lead (II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*," *Chemical Engineering Journal*, vol. 132, pp. 289-297, 2007.
- [11] K. Günay, E. Arslankaya, I. Tosun, "Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics," *Journal of Hazardous Materials*, vol. 146, pp. 362-371, 2007.

World Academy of Science, Engineering and Technology International Journal of Chemical and Molecular Engineering Vol:2, No:11, 2008

- [12] S.P. Singh, L.Q. Ma, M.J. Hendry, "Characterization of aqueous lead removal by phosphatic clay: Equilibrium and kinetic studies," *Journal of Hazardous Materials*, vol. B136, pp. 654-662, 2006.
- [13] P. Marques, H. Pinheiro, J. Teixeira, M. Rosa, "Removal efficiency of Cu²⁺, Cd²⁺ and Pb²⁺ by waste brewery biomass: pH and cation association effects," *Desalination*, vol. 124, pp. 137-144.
- [14] I.J. Alinnor, "Adsorption of heavy metal ions from aqueous solution by fly ash," Fuel, vol. 86, pp. 853-857, 2007.
- [15] S. Al-Asheh, F. Banat, D. Al-Rousan, "Beneficial reuse of chicken feathers in removal of heavy metals from wastewater," *Journal of Cleaner Production*, vol. 11, pp. 321-326, 2003.
- [16] M. Al-Ghouti, M. Khraisheh, M. Tutuji, "Flow injection potentiometric stripping analysis for study of adsorption of heavy metal ions onto modified diatomite," *Chemical Engineering Journal*, vol. 104, pp. 83-91, 2004.
- [17] S. Babel, T. Kurniawan, "Low-cost adsorbents for heavy metals uptake from contaminated water: a review," *Journal of Hazardous Materials*, vol. B97, pp. 219-243, 2003.
- [18] G. de la Rosa, J.L. Gardea Torresdey, J.R. Peralta-Videa, I. Herrera, "Use of silica-immobilized humin for heavy metal removal from aqueous solution under flow conditions," *Bioresource Technology*, vol. 90, pp. 11-17, 2003.
- [19] M. Dávila-Jiménez, M. Elizalde-González, W. Geyer, J. Mattusch, R. Wennrich, "Adsorption of metal cations from aqueous solution onto a natural and a model biocomposite," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 209, pp. 243-252, 2003.
- [20] N. Fiol, I. Villaescusa, M. Martínez, N. Miralles, J. Poch, J. Serarols, "Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste," *Separation and Purification Technology*, vol. 50, pp. 132-140, 2006.
- [21] S. Doyorum, A. Celik, "Pb(II) and Cd(II) removal from aqueous solutions by olive cake," *Journal of Hazardous Materials*, vol. B138, pp. 22-28, 2006.
- [22] A. Kapoor, T. Viraraghavan, D. Cullimore, "Removal of heavy metals using the fungus Aspergillus niger," Bioresource Technology, vol. 70, pp. 95-104, 1999.
- [23] Q.Y. Sun, P. Lu, L.Z. Yang, "The adsorption of lead and copper from aqueous solution on modified peat-resin particles," *Environmental Geochemistry and Health*, vol. 26, pp. 311-317, 2004.
- [24] R. Senthilkumar, K. Vijayaraghavan, M. Thilakavathi, P.V.R. Iyer, M. Velan, "Application of seaweeds for the removal of lead from aqueous solution," *Biochemical Engineering Journal*, vol. 33, pp.211-216, 2007.
- [25] P. Kar, M. Misra, "Use of keratin fiber for separation of heavy metals from water," *Journal of Chemical Technology and Biotechnology*, vol. 79, pp. 1313-1319, 2004.
- [26] S.A. Sayed, S.M. Saleh, E.E. Hasan, "Removal of some polluting metals from industrial water using chicken feathers," *Desalination*, vol. 181, pp. 243-255, 2005.
- [27] F. Banat, S. Al-Asheh, "Biosorption of phenol by chicken feathers," Environmental Engineering and Policy, vol. 2, pp. 85-90, 2000.
- [28] V. Gupta, A. Mittal, L. Kurup, J. Mittal, "Adsorption of a hazardous dye, erythrosine, over hen feathers," *Journal of Colloid and Interface Science*, vol. 304, pp. 52-57, 2006.
- [29] A. Mittal, "Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers," *Journal of Hazardous Materials*, vol. B133, pp. 196-202, 2006a.
- [30] A. Mittal, "Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater," *Journal of Hazardous Materials*," vol. B128, pp. 233-239, 2006b.
- [31] G. Coward-Kelly, V. Chang, F. Agbogbo, M. Holtzapple, "Lime treatment of keratinous materials for the generation of highly digestible animal feed: 1. Chicken feathers," *Bioresource Technology*, vol. 97, pp. 1337-1343, 2006.
- [32] A. Ozcan, E. Oncu, A. Ozcan, "Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 277, pp. 90-97, 2006.
- [33] S. Basha, Z. Murthy, B. Jha, "Sorption of Hg(II) from Aqueous Solutions onto *Carica papaya*: Application of Isotherms," *Industrial Engineering Chemistry Research*, vol. 47, pp. 980-986, 2008.
- [34] G. Uslu, M. Tanyol, "Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions

- onto *Pseudomonas putida*: Effect of temperature," *Journal of Hazardous Materials*, vol. B135, pp. 87-93, 2006.
- [35] Y. Liu, Y.-J. Liu, "Biosorption isotherms, kinetics and thermodynamics," Separation and Purification Technology, 2008, To be published.
- [36] K.V. Kumar, S. Sivanesan, "Comparison of linear and non-linear method in estimating the sorption isotherm parameters for safranin onto activated carbon," *Journal of Hazardous Materials*, vol. B123, pp. 288-292, 2005.
- [37] K.V. Kumar, S. Sivanesan, "Pseudo second order kinetic models for safranin onto rice husk: comparison of linear and non-linear regression analysis," *Process Biochemistry*, vol. 41, pp. 1198-1202, 2006.
- [38] A. Bonilla-Petriciolet, M.G. Lira-Padilla, C.A. Soto-Becerra, "Aplicación del método de optimización de recocido simulado en la regresión de isotermas de adsorción," Revista Internacional de Contaminación Ambiental, vol. 21, pp. 201-206, 2006.
- [39] A. Corana, M. Marchesi, C. Martini, S. Ridella, "Minimizing multimodal functions of continuous variables with the simulated annealing algorithm," *Transactions on Mathematical Software*, vol. 13, pp. 262-280, 1987.
- [40] W.L. Goffe, G.D. Ferrier, J. Rogers, "Global optimization of statistical functions with simulated annealing," *Journal of Econometrics*, vol. 60, pp. 65-99, 1994.
- [41] J. Wisniak, A. Polishuk, "Analysis of residuals a useful tool for phase equilibrium data analysis," *Fluid Phase Equilibria*, vol. 164, pp. 61-82, 1999.
- [42] P.B. Saez, B.E. Rittman, "Model-parameter estimation using least squares," Water Research, vol. 26, pp. 789-796, 1992.
- [43] C.K. Jain, D. Ram, "Adsorption of lead and zinc on bed sediments of the river kali," *Water Research*, vol. 31, pp. 154-162, 1997.
- [44] K.K. Singh, M. Talat, S.H. Hasan, "Removal of lead from aqueous solutions by agricultural waste maize bran," *Bioresource Technology*, vol. 97, pp. 2124-2130, 2006.