Agricultural residues of cocoa, lemon, yam, cassava and oil palm for lead-loaded wastewater treatment

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Abstract- The presence of lead ions in water sources has motivated the search for easy-to-implement and low-cost alternatives such as biosorption using agricultural biomass. In this work, five biomasses available in North-Colombia region were selected to prepare biosorbents for the removal of lead ions. The optimum conditions of pH and particle size were defined by batch adsorption experiments. The kinetic curve was constructed from adsorption capacity over time. The adsorption process was pH-dependent and the initial solution pH=6.0 was the optimum value for all biomasses. The particle size showed different effects depending on the type of biomass. Kinetic modeling indicated that biosorbents from lemon, yam and cocoa residues were best predicted by pseudo-second order model. For biosorbents from African oil palm and cassava residues, kinetic data was best described by Elovich model. These results proved that agricultural wastes are promising biosorbents for lead removal from aqueous environments.

Keywords – Adsorption; Environment; Agricultural Residues; Lead

I. INTRODUCTION

The wide range of applications of Pb-containing products and the lack of proper waste management have contributed to the increase in water pollution by Pb (II) ions affecting the environment and public health [1]. Due to the characteristic of bioaccumulation, heavy metals may enter to food chain and cause serious diseases [2]. The presence of lead in fish species in Colombia is one of the alarming consequences of water sources pollution. A study reported that two commercially important fish presented lead bioaccumulation with levels that varied from 0 to 8.737 ± 1.299 mg/kg [3]. Lead is a non-biodegradable and toxic material that has widespread human uses and can cause acute or chronic poising when exposing to human [4]. Toxicological studies have proved that lead can cause mental retardation and semipermanent brain damage in young children [5]. All these effects of lead exposure have motivated the search for suitable alternative to treat wastewater highly polluted with heavy metals.

Among the wide variety of technologies tested for heavy metals uptake from aqueous solution, biosorption using agricultural residues seems to be a convenient, effective and low-cost alternative to face lead remediation of aqueous environments. As Sud et al.[6] stated, the major advantages of biosorption over conventional treatment are the regeneration of biosorbents, low cost, high efficiency and minimization of waste generation [7]. Different residues from agricultural activities have showed promising adsorption capacities when treating Pb (II) containing water [8, 9]. Dead biomass is of particular economic interest because it can be used in the same way as synthetic adsorbents and repeated regeneration is possible [10].

Salihi et al.[11] developed an activated carbon from sugarcane bagasse and evaluated its effectiveness in the removal of lead ions from aqueous solution reporting a maximum adsorption efficiency of 87.3% in batch studies. Gaur et al. [12] obtained an adsorbent from soya bean in order to assess the potential of this biomaterial to adsorb lead and arsenic ions reaching maximum removal percentages around 80%. Deng et al.[13] prepared biochar from rice straw to remove nickel and cadmium ions and reported maximum adsorption capacities in the order of cadmium (37.24 and 65.40 mg/g) > nickel (27.31 and 54.60 mg/g). Villen-Guzman et al.[14] synthetized a novel biosorbent from lemon peels and evaluated its adsorption capacity for nickel ions. Authors found that this material has capacity of 36.74 mg/g and can recover 90% of Ni(II) after five consecutives sorption-desorption cycles.

This study attempts to evaluate the applicability of five biomasses from agricultural activities as low-cost biosorbents in the removal of lead ions. The effect of particle size and solution pH was evaluated to identify optimum conditions at which highest removal yield are reached. Kinetic modeling was conducted to identify the mechanism of adsorption of Pb(II) ions onto biosorbents.

The rest of the paper is organized as follows. The methodology of bio-adsorbent synthesis and batch tests are explained in section II. Experimental results are presented in section III. Concluding remarks are given in section IV.

II. MATERIALS AND METHODS

2.1. Biomass preparation-

The dead biomasses used in this work were collected from *Theobroma cacao*, *Citrus lemon*, *Manihot esculenta*, *Dioscorea rotundata* and *Elaeis guineensis* crops available in local farms of North-Colombia. These biomaterials were pretreated by washing samples with distilled water and cutting into small pieces. Then, biomasses were dried at 100°C to remove moisture content and the particle size was reduced with a grounder and mesh-sieves to 0.355 mm, 0.5 mm and 1 mm. The resulting biosorbents were: cocoa pod husk (CPH), Citrus lemon peels (LP), cassava peels (CP), yam peels (YP) and oil palm bagasse (OPB).

2.2. Adsorption study-

The adsorption experiments were conducted in batch mode using a synthetic solution of lead at 1000 ppm, which was prepared by adding 0.0799 g of lead nitrate $Pb(NO_3)_2$ onto 100 mL of water. The initial pH was adjusted to 2, 4 and 6 using solution of 0.1 M HCl and NaOH. Operating conditions such as temperature, stirring speed and biosorbent dosage were fixed in 25°C, 150 rpm and 0.5 g biomass/100 mL of synthetic solution. After six hour of contact time, the mixture of biosorbent and lead solution was subjected to centrifugation and the supernatant was collected. The remaining concentration of lead ions in supernatant simples was determined by UV-VIS spectroscopy. The adsorption efficiency was quantified using Equation 1, where C_o and C_e is the initial and remaining concentration of lead ions in the solution.

$$\text{Adsorption efficiency } (\%) = \frac{(C_o - C_e)\cdot}{C_o} 100\% \quad (1)$$

2.3. Kinetic modelling-

In order to model the kinetic behavior of lead adsorption onto biosorbents, samples were taken after 10 minutes of contact time and then, after 30 minutes. These samples were characterized by UV-Vis spectroscopy to determine heavy metal concentration. The adsorption capacity was calculated with the remaining concentration of the sample collected at time t as described in Equation 2. The adsorption capacity was plotted over time to build the kinetic curve.

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

where V is the volume of the solution in liters and m is the mass of adsorbent in grams.
Experimental data used for kinetic curve was adjusted to kinetic models of pseudo-first order, pseudo-second order and Elovich in order to identify the adsorption mechanism followed by the biomasses. Table 1 reports the mathematical formulation for these kinetic models.

Table-1 Mathematical expressions of kinetic models

Kinetic model	Equation	Parameters
Pseudo-1st-order	$q_t = q_e(1 - e^{-kt})$	**q_e, Adsorption capacity at equilibrium (mg/g)** **k_1, pseudo-1st-order constant (min^{-1})**
Pseudo-2nd-order	$q_t = \frac{t}{\left(\frac{1}{(k_2 q_e^2)}\right) + \left(\frac{t}{q_e}\right)}$	**k_2 pseudo-2nd-order constant (g/mg.min)** **q_e, Adsorption capacity at equilibrium (mg/g)**
Elovich equation	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	**α, Elovich constant (mg/g min)** **β, Elovich exponent (g/mg)**

III. EXPERIMENT AND RESULT

3.1. Adsorption study-

Effect of particle size: Figure 1 shows how the particle size of biosorbents contributed to reach high removal efficiencies for lead uptake. The CP and OPB biomasses reported more favorable performance when reducing particle size to 1 mm. The YP and CPH biomasses achieved the maximum adsorption efficiencies at 0.355 mm, which is the smallest particle size tested in this work. For LP biomass, optimum particle size was 0.5mm. These results revealed that the effect of particle size may vary among materials owing to the complexity associated with significant change in physical and chemical properties of substances [15]. Even though it is expected that the smaller particle size, the higher surface area and adsorption capacity, several works have reported different trends on adsorption performance when varying the particle size. For example, Nnaji et al. [16] used different species of sawdust to remove lead from water and stated that optimum particle size was 1.18 mm for *Pycnanthus angolensis* and 0.85 mm for *Khaya ivorensis* among a wide range that varied from 0.30 to 2.36 mm.

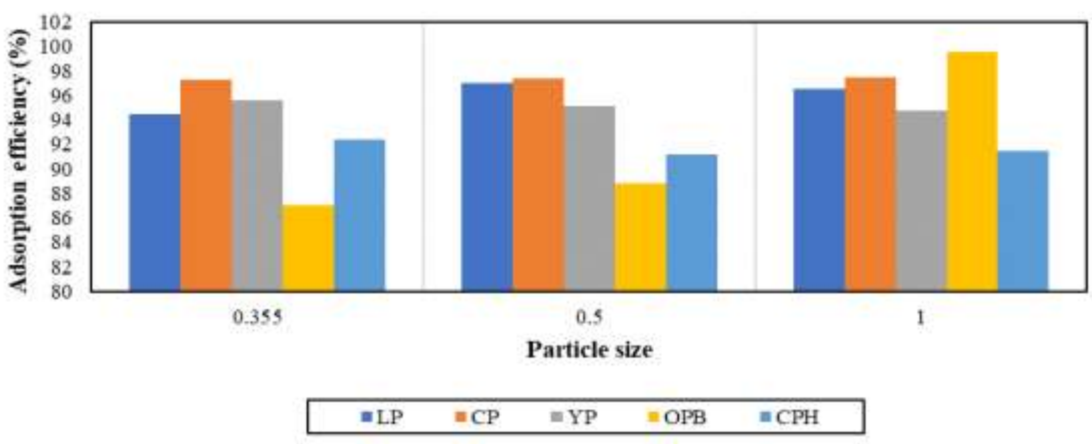

Figure 1. Influence of particle size on lead biosorption process

Effect of initial pH: Figure 2 depicts the adsorption efficiencies estimated for the three pH values (2, 4 and 6) selected in this study. For all biomasses, the optimum pH value was 6 revealing the favorability of lead adsorption when the system tends to more alkaline conditions and the high pH-dependency of this process. Gaur et al. [12] reported that the optimum adsorption (74.67%) of Pb(II) occurred at pH 4 using a biosorbent prepared from soya bean. Moyo et al. [17] used maize tassel based activated carbon to remove lead ions and evaluated the effect of solution pH indicating that the optimum adsorption was reached at pH 5.4, which is in concordance with the results obtained in this work. In acid solutions (e.g. pH=2), the presence of high concentration of hydronium ions affects the solubility of metal ions in the solution and occupies the available sites in biomass surface for heavy metal uptake [2].

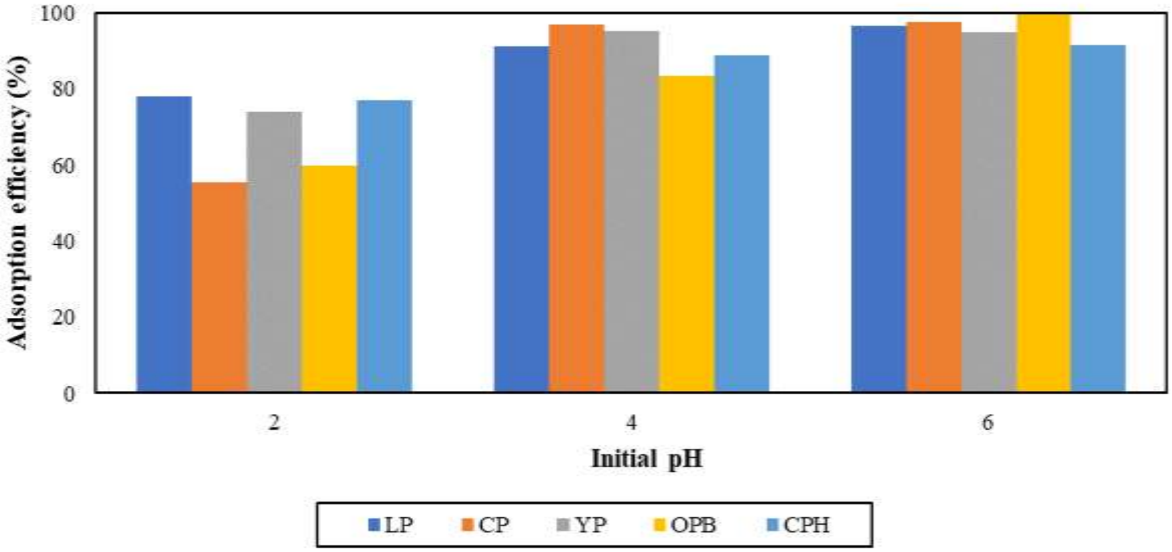

Figure 2. Influence of initial solution pH on lead biosorption process

3.2. Kinetic modeling

The experimental data of adsorption capacities over time was used to build the kinetic curve shown in Figure 3. Lemon peel biomass reached the lowest adsorption capacities while similar trends are observed for the CP, YP, CPH and OPB biomasses. For most of the biomasses, optimum adsorption performance is obtained in the first 30 minutes of contact time, which revealed the speed at which biomass get equilibrium conditions. These results were expected owing to the saturation of active sites when the biosorbent has interacted with the heavy metal ions for longer time.

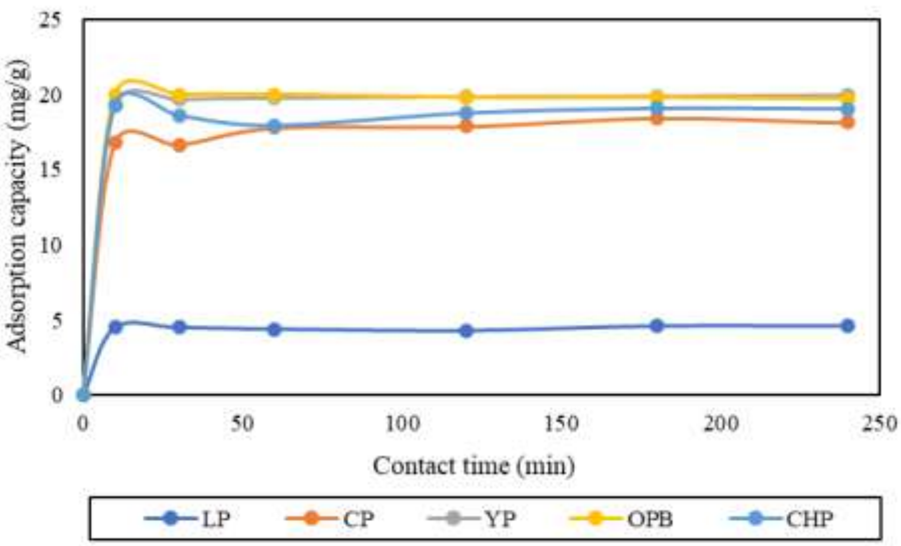

Figure 3. Kinetic curves of biosorbents for Pb(II) uptake

In order to analyze the mechanism governing adsorption of lead onto agricultural biomasses, the kinetic data shown in Figure 3 were fitted to pseudo-first order, pseudo-second order and Elovich following the mathematical expression of Table 1. Figures 4-6 depicts the predicted curves for the kinetic models as well as the sum of square errors (SSE) that inform how properly the model fit the experimental data. The biosorbents from lemon, yam and cocoa residues accounted for a kinetic phenomenon that best fitted pseudo-second order model. Based on the work conducted by Alghamdi et al.[18], the fitting to this model suggested that the rate-limiting step of lead adsorption is controlled by chemical adsorption by sharing or exchanging of electrons between biosorbent and heavy metal ions. The adsorption kinetic of biosorbents from African oil palm and cassava residues is best described by Elovich model, thus, adsorption of Pb(II) ions onto the studied biomasses may be controlled by a second order reaction, with an heterogeneous adsorbent surface and different activation energies [19].

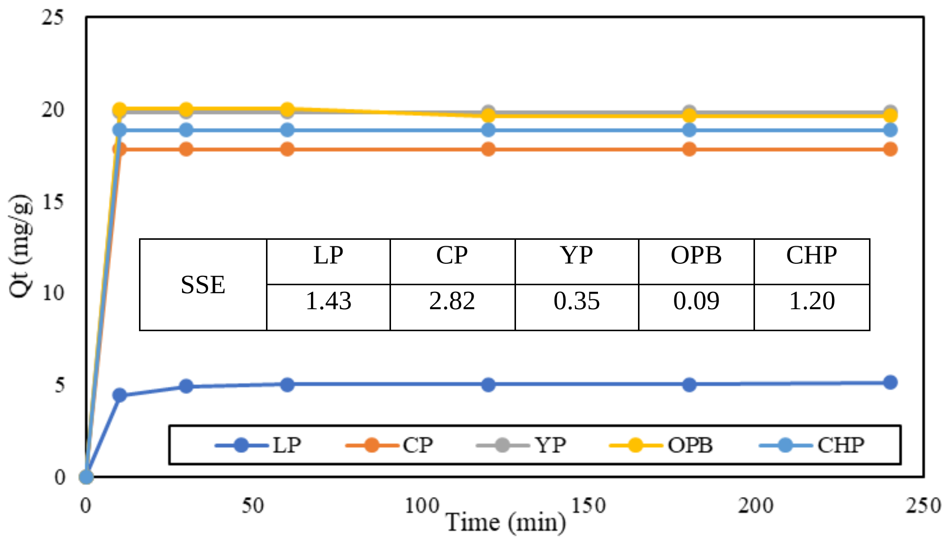

Figure 4. Pseudo-first order modeling of experimental data

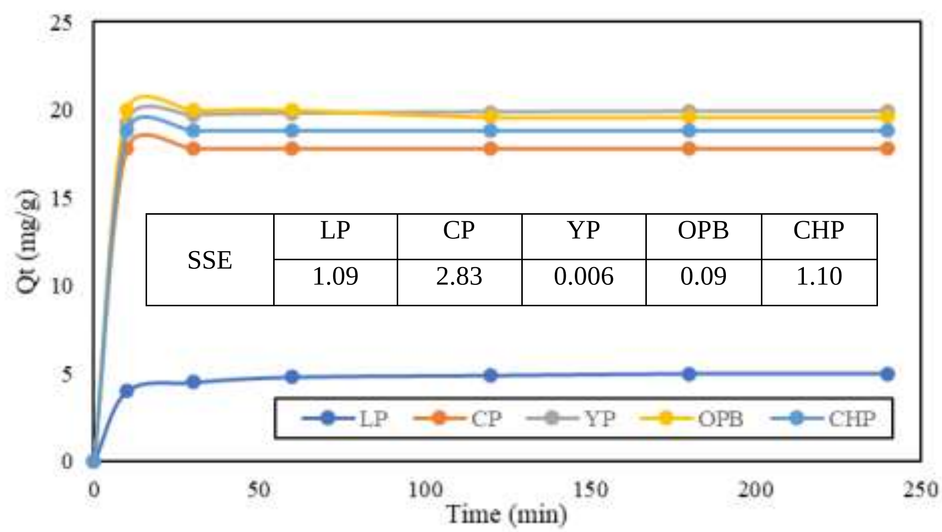

Figure 5. Pseudo-second order modeling of experimental data

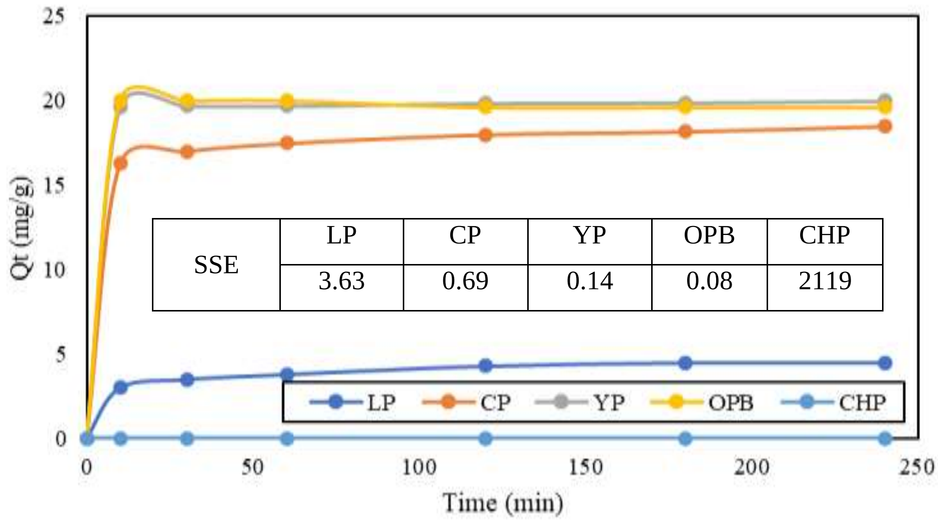

Figure 6. Elovich modeling of experimental data

IV.CONCLUSION

This work provided key findings on the optimum conditions to perform batch adsorption experiments to remove lead ions from aqueous solution by using agricultural residues. The pH solution showed to be an important parameter for all biosorbents and optimum adsorption efficiencies were reached at higher pH value (pH=6.0). In the case por particle size, results differed from what was expected of adsorption enhancement with small size particles and difference optimum values were obtained depending on the type of biomass. The biosorbents from lemon, yam and cocoa residues accounted for a kinetic phenomenon that best fitted pseudo-second order model. The adsorption kinetic of biosorbents from African oil palm and cassava residues is best described by Elovich model.

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