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Removal of Lead from Aqueous Solutions By Brewer´s Spent Grain

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Abstract: The potential utilization of Brewer's Spent Grain (BSG) was investigated in the removal of Lead from aqueous system. Batch sorption process assessment of the effects of process variables showed that pH, initial metal ion concentration and dosage amount affect the sorption and uptake of Lead ions by BSG. Analysis of the sorption process showed that second-order kinetic model gave good description of the process for Pb, R^2 = 0.999. Kinetic studies showed that equilibrium was reached within 30 min. Equilibrium isotherm analysis of the sorption process data showed that the Langmuir isotherm fitted very well for lead sorption by BSG. The highest measured uptake was 28.57 mg g^{-1} at 0.33 g mg^{-1} min^{-1}. The results of the studies indicate that the metal ion was favorably adsorbed onto the adsorbent with a removal efficiency of 95.45%. This study suggests that biosorption by spent grain can be an effective way of metal ion treatment and can be consider another way to use the byproducts from the brewing industry.

Key words: Biosorption, lead, Brewer's spent grain, removal, Kinetics

INTRODUCTION

As globalization continues, and the earth's natural processes transform local problems into international issues, few societies are being left untouched by major environmental problems[1,2].Water-our most precious natural resource-is being threatened by a multitude of contaminants (toxic metals, recalcitrant organic compounds, pathogenic microorganisms), resulting in an unprecedented water contamination crisis with local and international implications[3]. Metals are unique among pollutants that can be extremely harmful to the soil, water, and human beings[4,5]. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. Traditional metal removal methods like chemical precipitation, chemical redox reactions, electrochemical treatment, membrane processes and ion exchange can be extremely expensive or inefficient, especially for large solution volumes at relatively very low concentrations[6.] Biosorption, the passive uptake of pollutants such as heavy metals by biological materials, can be both highly efficient and cost effective. Low cost sorbents with high metal binding need to be investigated. The process of biosorption uses nonviable or viable biological materials to bind contaminants via physico-chemical mechanisms, whereby factors like pH, size of biosorbent, ionic strength and temperature influence metal biosorption[7]. The effectiveness of biosorbents depends to a large extent on their biochemical composition, particularly on functional groups available. Using waste materials from agriculture and food industries as biosorbents has the dual advantage of waste reuse and low sorbent cost. A number of workers have used different adsorbent systems, developed from various industrial waste materials, for the removal of heavy metals[8-10]. There still exists a need to develop a low cost and efficient adsorbent for the removal of different heavy metals from wastewater. Various solid wastes are generated in the brewing process. They include spent grain and spent yeast. Although spent grain is used as a fodder, few studies have been conducted on its potential as a sorbent for toxic metals. We investigated brewer´s spent grain (BSG) as a sorbent for the removal of lead, the metal of interest in this work. It was chosen based on their industrial applications and potential pollution impact on the environment. Lead is a hazardous waste and is highly toxic to humans, plants and animals[11,12]. It causes plant and animal death as well as anemia, brain damage, mental and behavioral problems in humans. Lead substitutes for calcium in bony tissues and accumulates there. The presence of lead in drinking water is known to cause various types of serious health problems leading to death in extreme cases[13].

The objective of this study was to evaluate the removal capacity of brewer´s spent grain, studying the factors that affecting the sorption of lead, such as pH, temperature, contact time and concentration sorbent.

MATERIAL AND METHODS

Spent grain was obtained from a local brewing industry, in Monterrey, N.L., Mexico. The samples were dried at 90°C for 24 h. The dried biosorbent was ground and sieved through a sieve (FHC, SA de CV No. 35) to attain homogeneous particle size (0.46 mm). Stock Pb(II) solution (1,000 mg L^{-1}) was prepared by dissolving 1.0 g of $Pb(NO_3)_2$ in distilled water. To adjust the pH of the solution, 0.1 N HCl and NaOH were used. Different operational parameters such as the pH (2–6), temperature (25,35,45ºC) and contact time (0, 7.5, 15, 30, 60 and 120 minutes) at metal Pb(II) concentration of 30 ppm, were studied at biosorbent dose (1g/L) and biosorbent particle size (0.46 mm) in an Orbital shaker at 150 rpm. After removal of the flasks from the shaker, the solutions were filtered, and filtrates were stored in precleaned and acid (HNO_3)-washed airtight plastic bottles. Metal concentrations were analyzed by an operational Thermoscientific SOLAAR AA, Atomic Absorption Spectrophotometer. The metal uptake capacity *‘q’* (mg g^{-1}) was calculated as given:

$$q= V(C_i-C_e)/M$$

In this equation, V is the volume of the solution (L), C_i is the initial Pb(II) concentration (mg L^{-1}), C_e is the Pb(II) concentration at equilibrium (mg L^{-1}), and M is the mass of the biosorbent (g). The corresponding adsorption isotherms for Pb were quantitatively described by parameters through fitting the experimental data to the Langmuir isotherm.

RESULTS

Effect of the initial pH of the solution on Pb(II) sorption : The pH is a dynamic and imperative environmental factor controlling heavy metals' site dissociation, speciation, adsorption, accessibility and solution chemistry[14,15].To investigate the effect of this parameter on metal sorption by spent grain, experiments were conducted at three different pH of the solution (2,4 and 6). At lower pH, the biosorbent sites are concentrated by hydronium ions that constrain the approach of metal ions to surface[16], and on rising pH the hydroxyl groups reside on the binding site and exert a pull on positive metal ions. At higher pH, metal hydroxide precipitation takes place, but sorption studies are unfeasible[17]. Thus, at lower and higher pH, the sorption capacity is less, which is analogous to the results of other studies[18]. As pH increases from 2–6, the percentage reduction of the Pb(II) concentration increases because of the available binding sites, and at pH 6 the percentage removal decreases because of hydroxide precipitation. The maximum percentage removal of Pb(II) was 92.58 % at pH 4 (Table 1).

Table 1: Effect of pH and temperature on the sorption of Pb(II) by spent grain

Parameters	Removal (%)
pH	
2	73.49
4	92.58
6	88.8
Temperature (°C)	
25	88.24
35	85.12
45	95.45

The experiment, concerning the influence of temperature on sorption efficiency, was carried out at pH 4.0 and Pb(II) concentration of 30 ppm, keeping these parameters constant. The results showing no significant difference with 88 to 95% of lead removal (Table 1); however, the increase in adsorption with increasing temperature indicated endothermic nature of the adsorption process.

The effect of contact time on the batch adsorption with an initial metal ion concentration of 30 ppm, using the pH (4.0) and temperature (45ºC) optimums is shown in Fig. 1. Removal of Pb at varying contact time of 0, 7.5, 15, 30, 60 and 120 minutes was studied. Kinetic results showed that equilibrium was reached within 30 min. The results showed that, using brewer's spent grain the chief removal of Pb(II) was 97.01 % at pH 4, 30 ppm of Pb(II) concentration and contact time 7.5 min. This contact time was less than other reported where 240 min were required to reach 75% removal of lead using sunflower stalk[19].

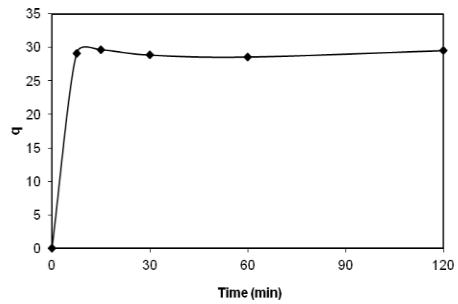

Figure 1: Effect of contact time in the removal of Pb(II) at 30ppm, pH 4 and a temperature of 45ºC , using a brewer`s spent grain.

Kinetic modeling: Kinetic experiments were conducted in order to determine the equilibration time and binding rate of Pb(II) by spent grain. The second-order model was used to modeling the experimental data of Pb(II) biosorption. This model is based on the assumption that biosorption follows a second-order mechanism, whereby the rate of sorption is proportional to the square of the number of unoccupied sites. The linear form can be written as follows:

$$t/q = t/(k_2\, q_e^{\ 2}) + t/q_e$$

Where k_2 is the rate constant of second-order biosorption (g/meq min). The parameters q_e and k_2 are calculated from the slope and the intercept of the plot t/q versus t. According to this model, the plot of uptake (q) vs the square root of time should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin, then intra-particle diffusion is the rate-controlling step. Sorption procedures occur through different steps of mechanisms including intra-particle diffusion, physiochemical sorption and extra-particle diffusion at the sorbent site[20]. The kinetic model illustrated adsorption rates well, depicted by a second order, which gives an indication concerning the rate-limiting step. The correlation coefficient of determination (R^2) of the second order kinetic model was very close to unity (0.999), and the calculated q_e value also agrees with the value. These results show that Pb(II) biosorption occurs parallel to the second-order kinetic model, suggesting chemisorptions may be the rate-limiting mechanism Fig. 2.

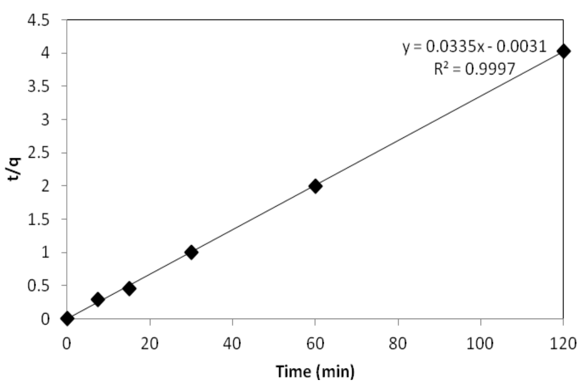

Figure 2: Kinetic of Pb(II) binding by spent grain at pH 4, and 30 ppm

Biosorption isotherms: Finally the relationship between equilibrium uptake (q_e) and final concentrations of lead was plotted as sorption isotherms in Figs. 3. Modeling equilibrium sorption is important for industrial applications of biosorption; it yields data that facilitates designing and optimizing the process. The classical Langmuir and Freundlich sorption isotherm models consider sorption by free binding sites rather than ion exchange. Nevertheless, these isotherm models are still widely used for modeling the biosorption equilibrium because of their simplicity[21,22]. Biosorption isotherms are useful in quantitatively evaluating and predicting the process performance of the binding capacity and affinity for different metal concentrations and sorbent dosages. The metal uptake as a function of the equilibrium concentration of Pb is presented in **Fig 3.**

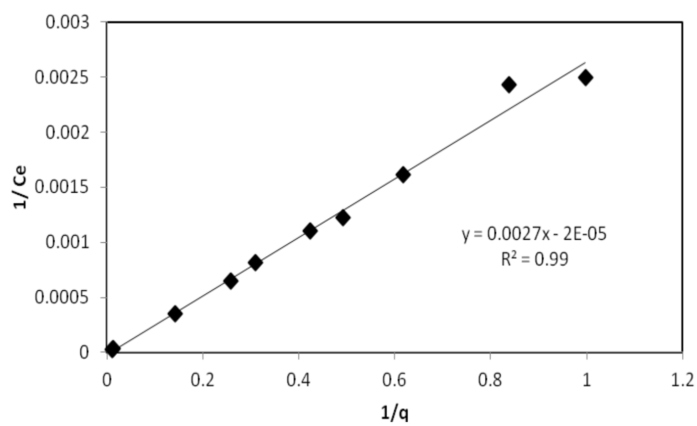

Figure 3: Biosorption isotherm for Pb(II) binding by spent grain at pH 4, initial concentration of sorbent 1 mg/L, 45◦C, and contact time: 7.5 min.

The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm is given by the following equation:

$$1/q_e = 1/Q_o + 1/bQ_oC_e$$

where q_e is the amount adsorbed (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg l^{-1}) and Q_o and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1=q_e$ was plotted against $1=C_e$; straight lines with slope $1=bQ_o$ were obtained which show that the adsorption of lead followed the Langmuir isotherm.

Diffusion of metal ions onto binding sites because of the wealth of elevated concentrations is attuned by the linearized form of the Langmuir isotherm[22]. The Langmuir isotherm model, showing Pb(II) sorption as accessible through the high value of the correlation coefficient (R^2 = 0.99), showed a q_{max} value of 28.57 mg g-1.

These results agree with other studies where R^2 values greater than 0.95 for different pretreated biomasses suggested this model to be most favorable to explain sorption[19,22].

CONCLUSIONS

A second-order model (with respect to the number of unoccupied binding sites) was suitable to describe the kinetics. Kinetic studies showed that equilibrium was reached within 30 min. Metal uptake decreased with decreasing pH, indicating competition of protons for binding to acidic sites. The Langmuir isotherm was able to fit equilibrium data. The highest measured Pb(II) uptake by spent grain was 28.57 mg g^{-1} at 0.33 g mg^{-1} min^{-1}. Overall, this study suggests that biosorption of Pb(II) ions by spent grain can be an effective way of metal ion treatment and can be consider another way to use the byproducts from the brewing industry.

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