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Adsorption of Pb^{2+} ions using biogenic $CaCO_3$ in aqueous solutions

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— Abstract—

In the state of Tabasco, the oyster Crassostrea Virginica is cultivated, this production makes it an important economic activity and adversely a source of infection by the waste of the inedible part. However, these leaflets are composed of $CaCO_3$ with potential application as adsorbents for heavy metals dissolved in water and thus improve their quality. In this research, a $CaCO_3$ adsorbent obtained from oyster shells was used to remove lead (Pb^{2+}) from water. The shells were washed and dried in the sun, later they were crushed with a hammer to enter them in a high-energy mill and reduce their size. The powders were sieved in meshes #100, and #200, and what happens to #200 and the pH values of the lead solution were adjusted according to the metal species diagram to keep it in solution and identify the best experimental conditions. The best results were obtained under conditions of pH=5 and particle sizes of the order of 0.074 mm. With these conditions, the adsorption isotherms were obtained and maximum adsorption capacities of 44 mgg-1 of the Pb^{2+} ion were obtained.

Keywords:

Adsorption; Metal ions; Calcium carbonate; Biogenic.

Water pollution by organic and inorganic compounds is an environmental problem that requires immediate attention, due to population growth and industrialization (Mensah *et al*., 2022). Heavy metals according to the World Health Organization and the International Programs on Chemical Safety, are dispersed in the environment and are biologically important, since they present a high-risk toxicological profile with lethal and bioaccumulative characteristics that directly affect the environment and public health through the consumption of contaminated food and water (Igberase & Osifo, 2019; Kupeta *et al*., 2018).

Wastewater from the semiconductor industry, battery manufacturing, plating, and painting, is perhaps the most important sources of pollution due to the high concentrations of discarded heavy metals dumped into effluents. In particular, lead (Pb^{2+}), cadmium (Cd^{2+}), and copper (Cu^{2+}) are harmful metals to health. WHO recommends that adults with a level of ten micrograms per deciliter (10 µgdL^{-1}) and children with five micrograms per deciliter (5 µgdL^{-1}) of blood lead require immediate action (CDC, Center for Disease Control and Prevention, Atlanta, GA) as symptoms such as tiredness, poor ability to pay attention, agitation, lack of appetite, constipation, headaches, sudden change in behavior, vomiting and hearing loss can occur and even cause death by poisoning (Caravanos *et al*., 2016). In addition to the above, science has been given the task of creating processes that are able to reduce the impact of these pollutants on the environment through novel methods of high efficiency and low cost.

Various treatment systems have been developed to remove these metal contaminants from water; among them are flocculation, coagulation, chemical oxidation, chemical precipitation, ozonation, membrane filtration, reverse osmosis method, and adsorption (Gupta *et al*., 2021; Wahyuni *et al*., 2022). The latter is considered one of the most effective and economically viable techniques for the treatment of wastewater contaminated by toxic organic and inorganic compounds, including heavy metal ions if the appropriate adsorbent is used (Hernandez-Eudave *et al*., 2016; Reynel-Avila *et al*., 2015).

Natural materials and wastes from industrial or agricultural operations that are available in large quantities may have the potential as low-cost adsorbents to improve water quality. Today, proposals have been presented for adsorbents for the removal of metals such as clays, zeolites, rice husk, textile industry waste, and oyster shells, among others (Ahmad *et al*., 2012; Mendoza-Castillo *et al*., 2015). Oyster shells are composed mainly of calcium carbonate ($CaCO_3$), silicon oxide (SiO_2), proteins, and polysaccharides, are widely available in the environment, and were used in this research as a proposal of low-cost adsorbent for the removal of metal ions from water.

Muhammad Shafiq *et al*. (2021) used sawdust from *Eucalyptus camdulensis* for the production of a bio adsorbent for the removal of Ni^{2+} and

Pb^{2+} from wastewater; in their research, they used pyrolysis to obtain a carbonaceous material with adsorption results of 54 and 200mgg^{-1} respectively (Muhammad Shafiq, 2021). Donhatai Sruamsiri *et al.* (2022) employed an alkaline titanate ($Cs_2Ti_5O_{11}$) for the removal of Pb^{2+} from a solution of lead acetate trihydrate. The adsorption isotherm reported was H-type, indicating a strong interaction between titanate and Pb^{2+}. The maximum amount of Pb^{2+} adsorbed was 1.27 mmol Pb/g$Cs_2Ti_5O_{11}$, which corresponded to 86% of the cation exchange capacity (2,94 meq/g) of $Cs_2Ti_5O_{11}$. The adsorption isotherm obtained was fitted with the Langmuir equation with a high correlation coefficient ($R^2 = 0.9997$), suggesting a high affinity between the titanate surface and Pb^{2+} (Sruamsiri & Ogawa, 2022). Yang Zhou *et al.* (2017) prepared nanostructured hydroxyapatite from pig bone materials by mineralization. The obtained nanostructured bone was much better compared to the bone without nanostructure to remove Pb^{2+}. Their research was conducted under different conditions, including adsorbate and adsorbent contact time, initial Pb^{2+} concentration, and the pH of the solution. The pseudo-second-order kinetic model and the Langmuir isothermal model were best suited to describe the adsorption process. In addition, the maximum adsorption capacities of nanostructured bone and bone without nanostructure were 312.5 and 96.1 mgg^{-1}, respectively. Overall, the advantages of excellent simple adsorption and mineralization capacity coupled with low cost make nanostructured bone an attractive material for the removal of Pb^{2+} from an aqueous solution (Zhou *et al.*, 2017).

The adsorption process is suitable for removing those compounds of low concentration or high toxicity, which are not easily treated by biological processes. Based on its mode of operation, adsorption is classified into static adsorption and dynamic adsorption. Static or batch adsorption occurs in a closed system containing an amount of adsorbent in contact with a certain volume of adsorbate solution. Whereas dynamic adsorption occurs in an open system, where the adsorbate solution passes continuously through an adsorbent-filled column (Vo *et al.*, 2020). The aim of this research was to evaluate the adsorption capacity of nanostructured biogenic $CaCO_3$ as lead ion adsorbent (Pb^{2+}) in aqueous solutions in batch systems, and the isotherms were analyzed using Langmuir and Freundlich models.

METHODOLOGY

Adsorbent preparation

Samples of oyster shells were collected in the coastal areas of the municipalities of Comalcalco and Paraíso, Tabasco. Remains of organic matter and impurities were removed from the leaflets with washes in plenty of water and a sponge and dried in the sun for 48 h. Once dried the leaflets were subjected to spraying treatments in a high-energy mill and sieved into #10, 20, 40, 50, 100, and 200 meshes and what passes through #200; in total seven particle sizes. After sieving, the obtained powders were washed in beakers with deionized water on grills with constant stirring for 24 h. The powders were separated from the water by decantation and the pH values of the supernatants were measured, setting the constant pH reading as the cleaning parameter. Finally, the obtained powders were dried in an oven at 50°C for times of 2 h.

Adsorption experiments

Synthetic solutions were prepared from lead nitrate salts ($PbNO_3$) with deionized water with initial concentrations between 10 and 500 mgL^{-1}. All initial solutions were adjusted to pH=5 by adding NaOH and HNO_3 1N solutions. The batch experiments consisted of mixing 50 mL of each solution with 0.1 g of the adsorbent; they were placed on grills at room temperature and with constant stirring for 14 h. Subsequently, the metal solution $CaCO_3$ powders were decanted. The pH changes of the solutions after the experiments were measured and diluted with deionized water adjusted to pH=3 to measure the final concentration by Atomic Absorption. Experiments were replicated for confirmation of results.

Adsorption isotherm models

The adsorption capacities of the $CaCO_3$ powders were obtained under the following mass balance:

$$q_e(mgg^{-1}) = \frac{V(C_i - C_e)}{W} \quad (1)$$

Where C_i is the initial concentration of the metal solution in (mgL^{-1}), V is the volume in L, and W is the mass of the adsorbent in g.

On the other hand, to correlate the data of the Pb^{2+} isotherms, the mathematical models of Langmuir and Freundlich were considered. In the first instance, the Langmuir model assumes that adsorption occurs in a monolayer where the active sites are identical and energetically equivalent; this expression is given by:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)$$

Where q_e and C_e are the adsorption capacity in mgg^{-1} and the equilibrium concentration in mgL^{-1}, respectively; q_m is the theoretical maximum adsorption capacity in mgg^{-1} and K_L in Lmg^{-1} represents the Langmuir equilibrium constant. Both q_m and K_L are obtained from the correlation of the adsorption data.

Alternatively, the Freundlich model is an empirical model, the expression of which is used to describe a heterogeneous system, which is defined as:

$$q_e = K_f C_e^{\frac{1}{n_1}} \tag{3}$$

Where K_f ($mg^{1-1/n}L^{1/n}g^{-1}$) and n1 are characteristic parameters of the adsorbate-adsorbent system; these values are obtained from the correlation of the adsorption data.

For the adjustments of the experimental data with the mathematical models of proposed isotherms, a non-linear regression approximation was used based on the minimization of the error of the experimental data and those calculated with the objective function:

$$F_{obj} = \sum_{i=1}^{N_{dat}} \left(\frac{q_e^{exp} - q_e^{cal}}{q_e^{exp}} \right)_i^2 \tag{4}$$

Where q_e^{exp} and q_e^{cal} are the experimental and calculated adsorption capacities, respectively, and n_{dat} is the number of experimental data analyzed.

RESULTS

Figure 1 shows the interaction of pH factors of the initial solution and particle size in the Pb^{2+} adsorption process of water. Non-parallel lines on the graph indicate the effects of interaction between particle size and pH of the solution. This interaction effect indicates that the relationship between particle size and adsorption capacity depends on the pH of the initial metal solution. It is observed that for all cases the green line corresponding to group 3 of pH=5 is the one that has the greatest capacity of removing the metal from the solution by the adsorbent, this trend continues as the particle size decreases, group 7 according to our nomenclature, corresponds to those sieved in mesh #200, with sizes on the order of 0.074 mm.

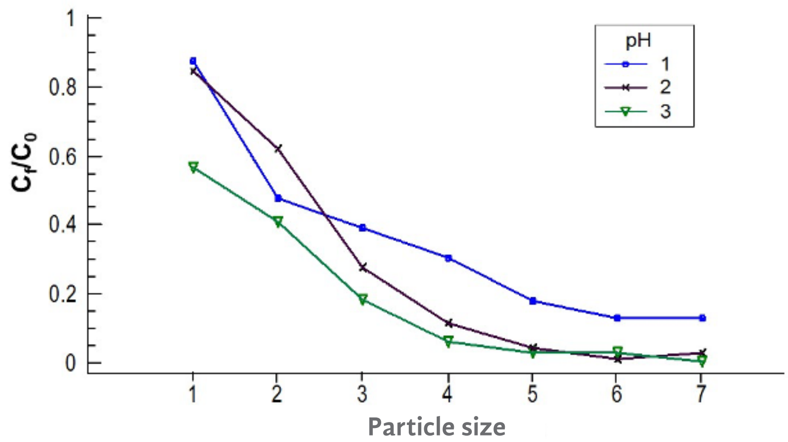

Figure 1. Interaction of Means of Particle Size and Solution pH Factors on Removal of Pb^{2+} from Water.
Source: Own elaboration

The full analysis demonstrates that there is no significant difference in the adsorption capacity results of particle size groups 5, 6, and 7, these sizes corresponding to 0.149, 0.074, and <0.074 mm respectively. The results of the statistical analyses for the pH values showed that the adsorption capacity is not favored in acidic environments and for the case of lead adsorption a pH=5 is recommended. Finally, by analyzing the interaction graph of both factors, it is recommended to use level 3 of pH=5 and level 7 of the mesh number (<0.074 mm).

The adsorption processes depend on the structure and characteristics of the adsorbent and the nature of the substance to be recovered from the medium (adsorbate). If the adsorbate is considered to be metal, the adsorption process depends on experimental conditions such as pH, metal and adsorbent concentration, competition with other ions, and particle size. The results of the experiments showed that the maximum experimental adsorption capacities for Pb^{2+} were 44 mgg^{-1}. These values obtained compared to other adsorbents such as zeolites, activated carbons, and hydroxyapatite offer advantages due to their high availability in the environment and because their preparation methods are simple and do not require complicated synthesis processes, which reduces production costs. The shape of the adsorption isotherms depends on factors such as pH and the initial concentration of the solutions and is not always linear. According to the classification of isotherm types, the curve type presented in Figure 2 is H-type, which results in high adsorption as a result of the strong adsorbate-adsorbent interaction.

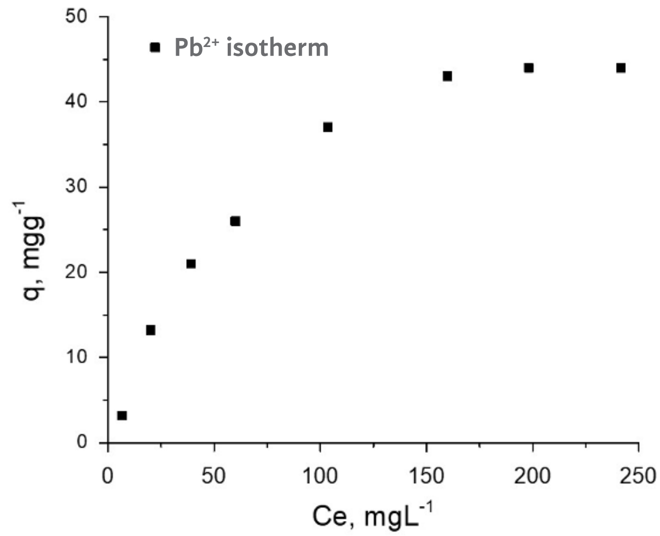

Figure 2. Ion Pb^{2+} adsorption isotherm. Initial conditions: 50 mL of metal solution with 0.1 g of adsorbent at 30 °C and pH=5. Concentrations between 10 and 500 mgL^{-1}. Source: Own elaboration

The results of the model adjustments indicate that the Langmuir isotherm model offers the best correlation coefficient with an R^2 of 0.97 suggesting homogeneous adsorption at each adsorber active site. The results of the models are presented in Table 1, and for illustrative purposes, the fit of the models with respect to the experimentally obtained isotherm is presented in Figure 3.

In terms of the Langmuir isotherm, adsorption occurs when a free adsorbate (Pb^{2+}) molecule collides with an unoccupied adsorption site ($CaCO_3$ active sites), and each adsorbed molecule has the same percentage of desorption.

Table 1

Data of the adjustments of the Langmuir and Freundlich isotherm models of the experimental results of Pb^{2+} ion adsorption capacity

	Parameter	Calculated value
	Metal	Pb^{2+}
	pH	5
Langmuir	q_m (mgg^{-1})	72.5
$$q_e = \frac{K_L q_m C_e}{1+K_L C_e}$$	K_L (Lmg^{-1})	0.008
	R^2	0.97
	F_{obj}	0.12
Freundlich	K_f	1.37
$$q_e = K_f C_e^{\frac{1}{n_1}}$$	$1/n_1$	0.68
	R^2	0.91
	F_{obj}	0.54

Nomenclature: q_e and C_e are the adsorption capacity and equilibrium concentration, respectively; q_m is the theoretical maximum adsorption capacity, and K_L is the Langmuir equilibrium constant. K_f ($mg^{1-1/n}L^{1/n}g^{-1}$) and n_1 are characteristic parameters of the adsorbate-adsorbent system.

Source: Own elaboration

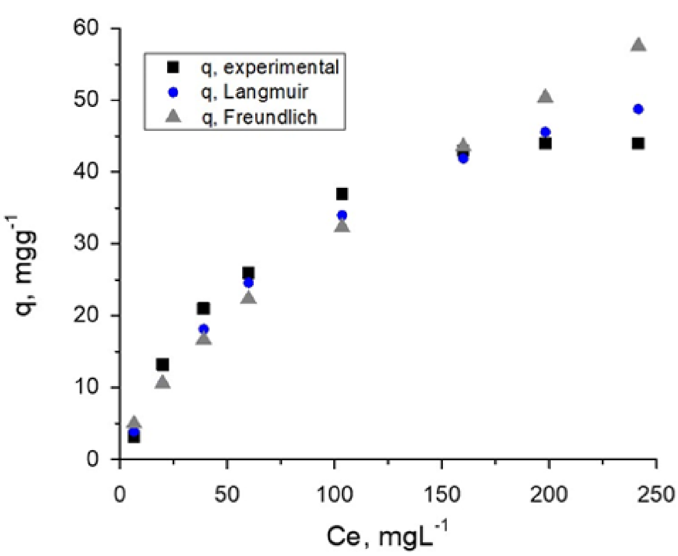

Figure 3. Comparison of experimental data settings with Langmuir and Freundlich isotherm models of Pb^{2+} isotherm. Source: Own elaboration

CONCLUSIONS

The results of the adsorption capacity of the biogenic $CaCO_3$ in the natural state for the Pb^{2+} ion was 44 mgg^{-1} and with isotherm representative of a high adsorbate-adsorbent affinity. The adsorption process was shown to be highly dependent on the pH and nature of the adsorbent. With these results, oyster shell powders in their natural state are proposed as an effective low-cost adsorbent alternative for the removal of Pb^{2+} from water. In addition to giving added value to a waste product for the benefit of oyster producers and the population. The evaluation of the adsorption process in packed columns and its analysis by means of mass transfer models is proposed for its escalation to real situations.

REFERENCES

Ahmad, M., Usman, A. R. A., Lee, S. S., Kim, S. C., Joo, J. H., Yang, J. E., & Ok, Y. S. (2012). Eggshell and coral wastes as low cost sorbents for the removal of Pb 2+, Cd 2+ and Cu 2+ from aqueous solutions. *Journal of Industrial and Engineering Chemistry, 18*(1), 198–204. https://doi.org/10.1016/j.jiec.2011.11.013

Caravanos, J., Carrelli, J., Dowling, R., Pavilonis, B., Ericson, B., & Fuller, R. (2016). Burden of disease resulting from lead exposure at toxic waste sites in Argentina, Mexico and Uruguay. *Environmental Health: A Global Access Science Source, 15*(1), 1–9. https://doi.org/10.1186/s12940-016-0151-y

Gupta, P., Nagpal, G., & Gupta, N. (2021). Fly ash-based geopolymers: an emerging sustainable solution for heavy metal remediation from aqueous medium. *Beni-Suef University Journal of Basic and Applied Sciences, 10*(1). https://doi.org/10.1186/s43088-021-00179-8

Hernandez-Eudave, M. T., Bonilla-Petriciolet, A., Moreno-Virgen, M. R., Rojas-Mayorga, C. K., & Tovar-Gómez, R. (2016). Design analysis of fixed-bed synergic adsorption of heavy metals and acid blue 25 on activated carbon. *Desalination and Water Treatment, 57*(21), 9824–9836. https://doi.org/10.1080/19443994.2015.1031710

Igberase, E., & Osifo, P. O. (2019). Mathematical modelling and simulation of packed bed column for the efficient adsorption of Cu (II) ions using modified bio-polymeric material. *Journal of Environmental Chemical Engineering, 7*(3), 103129. https://doi.org/10.1016/j.jece.2019.103129

Kupeta, A. J. K., Naidoo, E. B., & Ofomaja, A. E. (2018). Kinetics and equilibrium study of 2-nitrophenol adsorption onto polyurethane cross-linked pine cone biomass. *Journal of Cleaner Production, 179*, 191–209. https://doi.org/10.1016/j.jclepro.2018.01.034

Mendoza-Castillo, D. I., Rojas-Mayorga, C. K., García-Martínez, I. P., Pérez-Cruz, M. A., Hernández-Montoya, V., Bonilla-Petriciolet, A., & Montes-Morán, M. A. (2015). Removal of heavy metals and arsenic from aqueous solution using textile wastes from denim industry. *International Journal of Environmental Science and Technology, 12*(5), 1657–1668. https://doi.org/10.1007/s13762-014-0553-8

Mensah, K., Abdelmageed, A. M., & Shokry, H. (2022). Effect of eggshell/N,N-dimethylformamide (DMF) mixing ratios on the sonochemical production of $CaCO_3$ nanoparticles. *Journal of Engineering and Applied Science, 69*(1), 1–12. https://doi.org/10.1186/s44147-022-00070-y

Muhammad Shafiq Abdulrahman Alazba, M. A. (2021). Kinetic and Isotherm Studies of Ni^{2+} and Pb^{2+} Adsorption from Synthetic

Wastewater Using Eucalyptus camdulensis—Derived Biochar. *Sustainability, 13*(7), 3785. https://doi.org/10.3390/su13073785

Reynel-Avila, H. E., Bonilla-Petriciolet, A., & de la Rosa, G. (2015). Analysis and modeling of multicomponent sorption of heavy metals on chicken feathers using Taguchi's experimental designs and artificial neural networks. *Desalination and Water Treatment, 55*(7), 1885–1899. https://doi.org/10.1080/19443994.2014.937762

Sruamsiri, D., & Ogawa, M. (2022). Adsorption of Pb^{2+} on a layered alkali titanate from water. I*OP Conference Series: Earth and Environmental Science*, 950, 012040. https://doi.org/10.1088/1755-1315/950/1/012040

Vo, T. S., Hossain, M. M., Jeong, H. M., & Kim, K. (2020). Heavy metal removal applications using adsorptive membranes. *Nano Convergence, 7*(1). https://doi.org/10.1186/s40580-020-00245-4

Wahyuni, E. T., Pratama, N. A., Lestari, N. D., & Suherman, S. (2022). Enhancement of TiO2 activity under visible light by N,S codoping for Pb(II) removal from water. *Journal of Engineering and Applied Science, 69*(1), 1–12. https://doi.org/10.1186/s44147-022-00069-5

Zhou, Y., Chang, D., & Chang, J. (2017). Preparation of nano-structured pig bone hydroxyapatite for high-efficiency adsorption of Pb^{2+} from aqueous solution. *International Journal of Applied Ceramic Technology, 14*(6), 1125–1133. https://doi.org/https://doi.org/10.1111/ijac.12749