CARBON 2019
LEXINGTON, KY

A COMPARATIVE THERMODYNAMIC STUDY OF LEAD IONS ADSORPTION FROM AQUEOUS SOLUTION BY ZIF-8 and ZIF-8-DERIVED NANOMATERIALS CARBON

Juan Carlos Moreno-Piraján[1*], Liliana Giraldo[2]
[1]*Departamento de Quimica. Universidad de los Andes, Bogotá, Colombia*
[2]*Departamento de Qímica, Universidad Nacional de Colombia, Bogotá, Colombia*

**corresponding author e-mail: jumoreno@uniandes.edu.co*

Introduction

High levels of lead in the environment threaten human health, plants, soil quality and ecological systems[1,2]. Because heavy metals are not biodegradable, they must be removed from water[3,4]. Adsorption is a suitable process with the use of nanomaterials (NM) as adsorbents. In this work, the adsorption on ZIF-8 and NMZIF-8 for the elimination of Pb^{2+} ions from aqueous solution is studied. The lead ions adsorption properties on ZIF-8 and NMZIF-8 were then explored with respect to kinetics, isotherms, thermodynamics, mechanism, and recycling for the first time. The effect of the pH and the temperature of the solution on the removal efficiency is also studied. This work demonstrates that NMZIF-8 can be a good candidate as an adsorbent for the elimination of Pb^{2+} ions from water.

Materials and Methods

Samples synthesis.

ZIF-8 was synthesized according to Cravillon, et.al[5], and NM-ZIF-86 was prepared by heat treatment at 800 °C for 5 hours, and then cooled and washed. The nano-porous carbon obtained is denoted as NMZIF-8.

Characterization of Samples.

The S_{BET} surface area was determined to ZIF-8 and NMZIF-8. The average diameter of the pores was evaluated by the DFT method. The chemical-morphological characteristics were also determined by (SEM-EDS), XRD, FTIR and TGA.

Adsorption, kinetic and thermodynamic studies.

Measurements of Pb^{2+} adsorption were made from aqueous solutions on ZIF-8 and NMZIF-8 in equilibrium at different temperatures and as a function of time at 298 K, determining the residual concentration of the ion in the solution by atomic adsorption.

Results and Discussion

The adsorption-desorption isotherms of N_2 at 77 K for ZIF-8 and NMZIF-8 can be classified as type IV[7] isotherms. Table 1 shows the textural characteristics of the solids

Table 1. BET surface area (S), pore volumes (V) and pore sizes (D) for the synthetized samples

Samples	S_{BET}[a] (m^2/g)	V_{total}[b] (cm^3/g)	V_{micro}[b](cm^3/g)	V_{meso}[b](cm^3/g)	$V_{micro/meso}$
ZIF-8	1300	0.66	0.16	0.50	0.32
NMZIF-8	1450	0.32	0.11	0.21	0.52

[a]The specific surface area (SBET) was calculated by Brunauer-Emmet-Teller (BET method.
[b]V_{total}, V_{micro} and V_{meso} represented the total pore volume of micropore and the volume of mesopore calculated by Barret-Hoyner-Halenda (BJH) method, respectively.

Several kinetic models were applied to the experimental data. When performing the graphical

representations of t/q_t versus t, all the lines fit a significant linear correlation with t and the calculated q_e values that are in good agreement with the experimental q_e. This suggests that adsorption may be the limiting step of the speed involved in sharing the valence forces or the exchange of electrons between the metal ions and the adsorbents studied8.

The energy of Gibbs (ΔGo) was calculated for the sorption of Pb^{2+} for ZIF-8 and NMZIF-8 with values of -3.79 and -4.53 $kJmol^{-1}$ (298 K) respectively. The negative ΔG^o value obtained confirms that the process of Pb^{2+} adsorption on ZIF-8 and NMZIF-8 is spontaneous.

Conclusions

In summary, we have synthesized two porous adsorbents: ZIF-8 and NMZIF-8 and we investigated their extent in the elimination of Pb^{2+}. It was found that the capacities of saturated adsorption of Pb^{2+} on ZIF-8 and NMZIF-8, reach 1285.67 and 1489.45 mg/g, respectively, which are compared with other porous materials. When treating aqueous solutions of Pb^{2+}, in the presence of excess materials, more than 95% is eliminated. In addition, the two adsorbents exhibit rapid adsorption kinetics, and only take several minutes to reach the adsorption equilibrium. Kinetic studies of Pb^{2+} adsorption on ZIF-8 and NMZIF-8 can be described by the pseudo-second order model. In summary, these previous characteristics indicate that both ZIF-8 and NMZIF-8 are excellent candidates for the removal of heavy metal ions from wastewater. It was found that the driving force for Pb2 + adsorption for both ZIF-8 and NMZIF-8 is controlled by an entropic effect.

Acknowledgment

Authors thank agreement between University of the Andes (Colombia) and National University of Colombia and the agreement act established by Chemistry Departments of both universities. The authors also appreciate the grant for the funding of research programs for Associate Professors, Full Professors, and Emeritus Professors announced by the Faculty of Sciences of the University of the Andes, 20-12-2019-2020, 2019, according to the project "Enthalpy, free energy and adsorption energy of the activated carbon interaction and solutions of emerging organic compounds".

References

1. Fu, F., Wang, Q., (2011). Removal of heavy metal ions from wastewater: a review. *J. Environ. Manag*. 92, 401-418.
2. Soraya, P., Carmen, R., Inmaculada, F., Angel, J., Gutierrez, Dailos, G.,W., Veronica, M., Consuelo, R., Arturo, H., et al., (2018). Toxic metals (Al, Cd, Pb and Hg) in the most consumed edible seaweeds in Europe. *Chemosphere*.218, 879-884.
3. Moreira E, Vassilieff, S. (2001). Developmental lead exposure: behavioural alterations in the short and long term. *Neurotoxicol Teratol* 23, 489-495.
4. Shooto, N.D., Dikio, E.D. Wankasi, D.Sikhwivhilu, L (2015). Synthesis, Morphology and Lead Ion Adsorption Properties of Metal Organic Frameworks of Copper and Cobalt
5. Cravillon, J. Münzer, S, Lohmeier, S.-J., Feldhoff, A., Huber, K., Wiebcke, M. (2009). *Chem.Mater*. 21,1410–1412.
6. Bakhtiari, N., Azizian, S., Alshehri, S.m., Torad, N.L., Malgras, V., Yamauchi, Y. (2015). Study on adsorption of copper ion from aqueous solution by MOF-derived nanoporous carbon, Microporous and Mesoporous Materials, 217, 173-177.
7. Jiang H.L., Liu, B., Lan, Y.Q., Kuratani, K., Akita, T., Shioyama, H.(2011). From metal– organic framework to nanoporous carbon: Toward a very high surface area and hydrogen uptake. *J Am Chem Soc* .133,11854-11857.
8. Huanga,Y., Zenga,X., Guoa,L., Lanc,J., Zhanga,L., Cao,D. (2018). Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. Separation and Purification Technology 194, 462–469.