Ultrasonic Synthesis for the Efficient Zr^{4+} Modification of Hydrotalcite Adsorbents for Fluoride Removal

Gloribel Vázquez-Cornejo[1*], Sasirot Khamkure[2], Sofía E. Garrido-Hoyos[1], Victoria Bustos-Terrones[3], Prócoro Gamero-Melo[4]

1 Mexican Institute of Water Technology, Jiutepec, Morelos 62550, Mexico, 2 Conahcyt:- Antonio Narro Autonomous Agrarian University (UAAAN) Saltillo, Coahuila, México. 3 Polytechnic University of the State of Morelos, Jiutepec, Morelos 62550, Mexico, 4 Center for Research and Advanced Studies of the National Polytechnic Institute Saltillo Unit, Ramos Arizpe, Coahuila 25900, México. *gloribel.vazquez@posgrado.imta.edu.mx

INTRODUCTION & AIM

Hydrotalcites belonging to the family of Laminar Double Hydroxides (LDH), are synthetic compounds of metal hydroxides structured in positively charged layers with divalent and trivalent metal ions. These layers are stabilized by strong electrostatic interactions with anionic species between the layers, favoring the adsorption of anionic contaminants in water (Gautam *et al*, 2022; Huo *et al*, 2022). That is why they have received greater attention due to their applicability in cases of environmental decontamination (Goh *et al*., 2008). As adsorbent, they have been widely used in the elimination of fluoride in recent years and interest is growing in the use of high valence metals as part of the LDH structure (Wei *et al*., 2022).

The objective of this work is to incorporate Zr^{4+} in the LDH structure due to its high affinity towards fluorides, in different molar proportions to investigate the impact on its structural and morphological properties that influence the removal of fluorides from water, since it is a groundwater environmental problem that mainly affects arid and semi-arid regions, representing great pressure on supply sources worldwide (Podgorski & Berg, 2022).

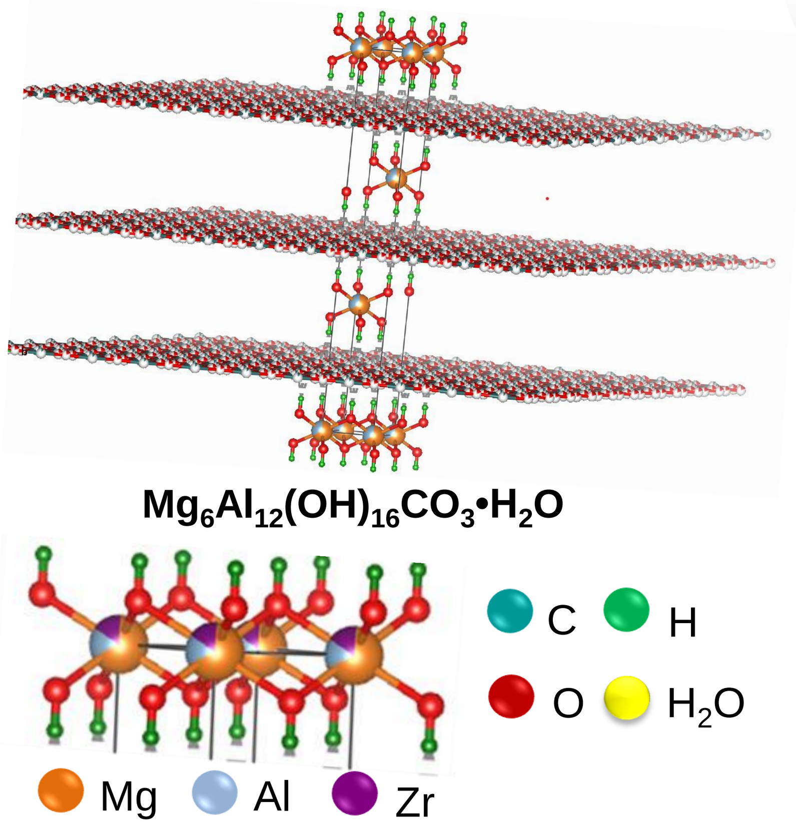
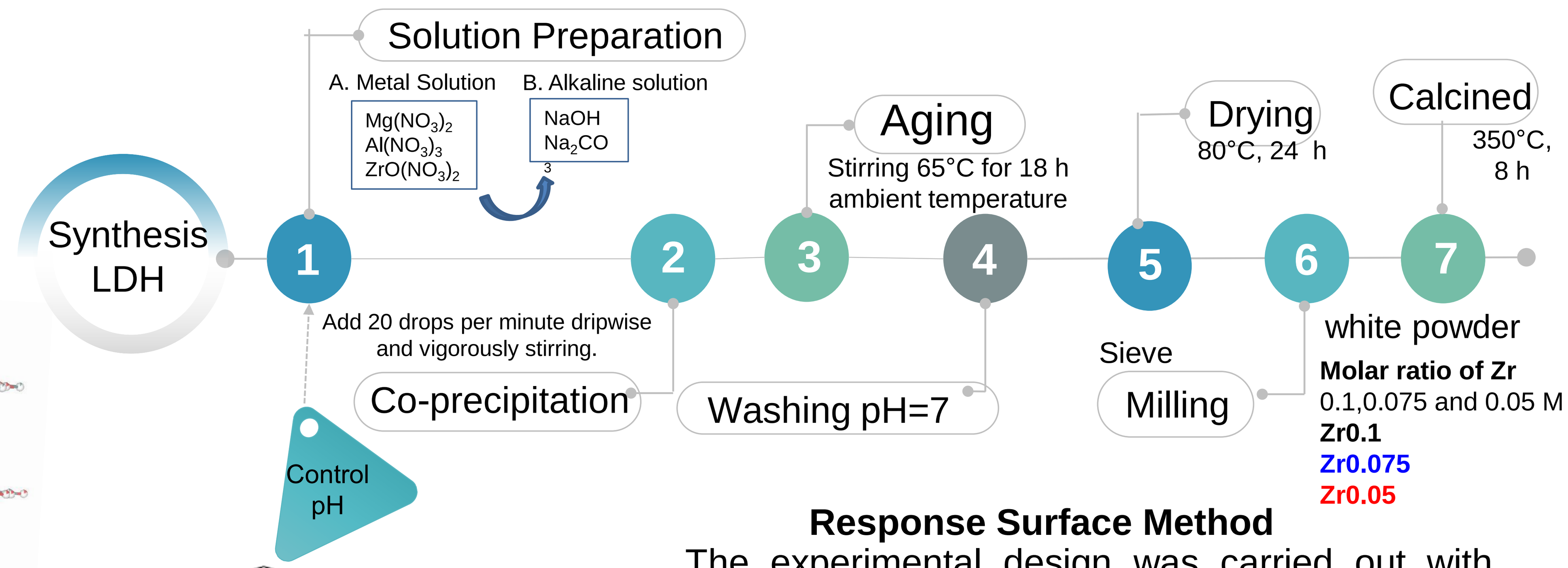
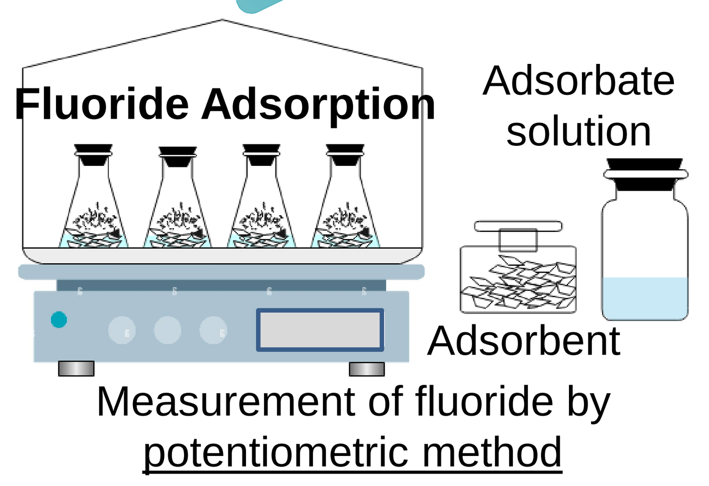


Figure 1. Hydrotalcite structure

METHOD





Response Surface Method

The experimental design was carried out with three independent factors (Table 2) and the percent (%) removal as the dependent variable.

Table 2. Experimental design variables

Dependent Variable	High	Center	Low
Initial concentration (mg/L)	5	10	15
Adsorbent doce (g/L)	0.5	0.75	1.0
pH	4	5	6

The adsorption kinetics were carried out with the optimal conditions of the experimental design.

RESULTS & DISCUSSION

Characterization

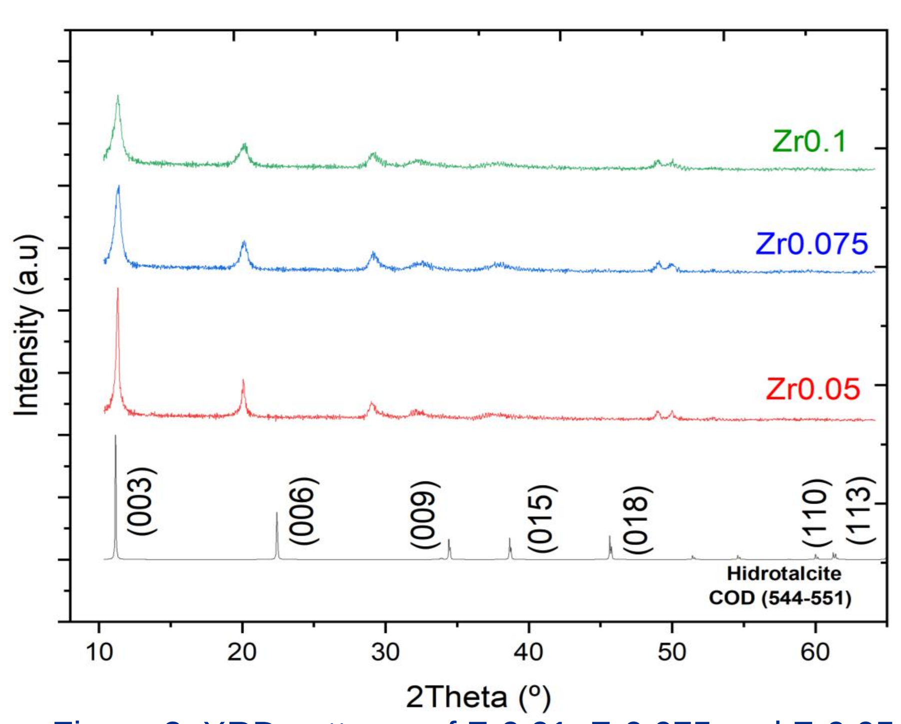


Figure 2. XRD patterns of Zr0.01, Zr0.075 and Zr0.05

The XRD patterns of the absorbents, when compared with the crystallographic chart of the LDH, exhibited the characteristic reflections at the angles 2Ө ≈11°-60° (Arhzaf *et al*,. 2020).

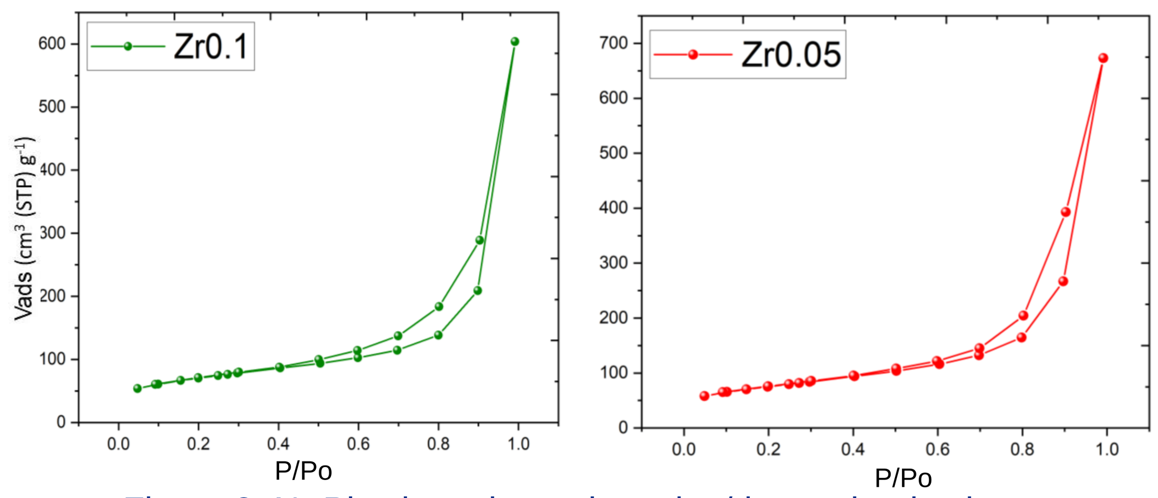


Figure 3. N_2 Physisorption, adsorption/desorption isotherms

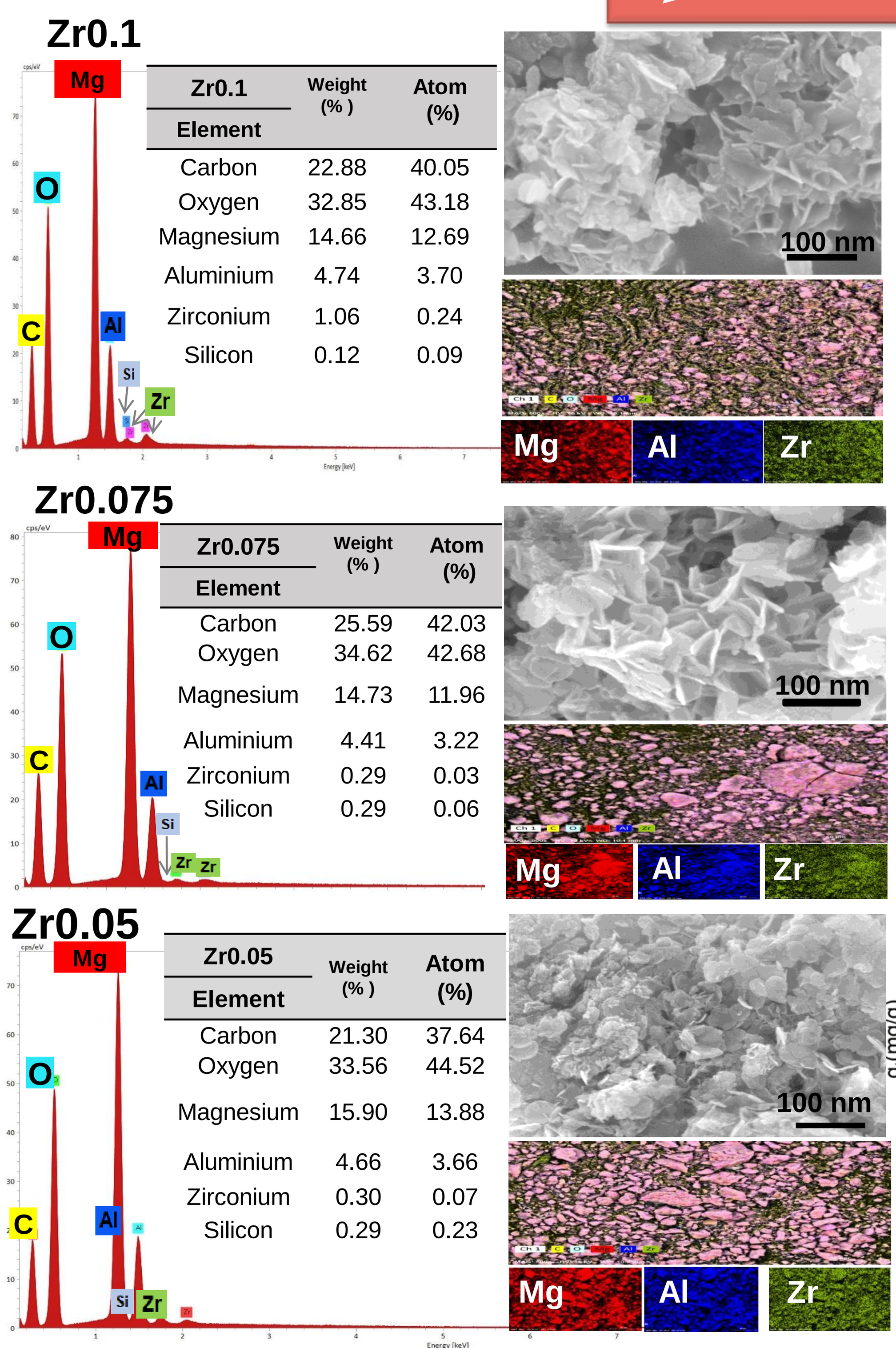


Figure 4. SEM-EDS, Elemental mapping of adsorbents

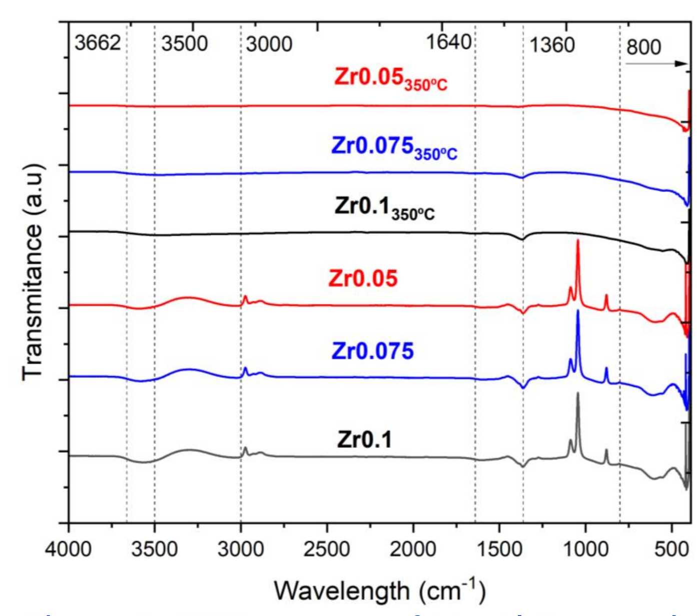


Figure 5. FTIR spectra of Mg-Al-Zr materials before and after calcination

Response Surface Method

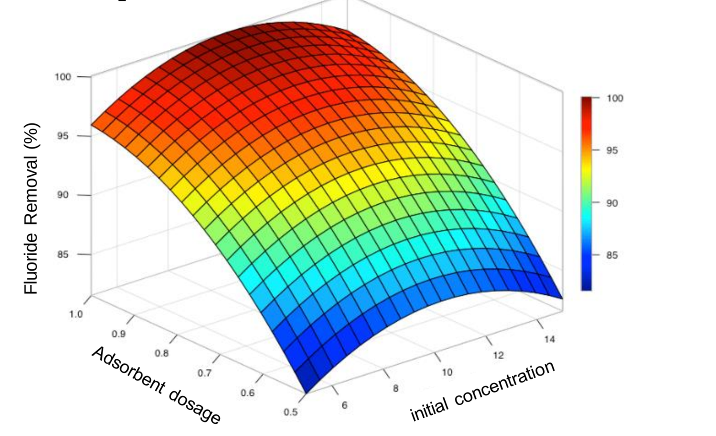


Figure 6. Response surface graph
Conditions: contact time: 6 h, 150 rpm, 25ºC

Optimal point

Initial concentration	12 mg/L
Adsorbent dosage	1 g//L
pH	5

Fluoride removal 98 %

Adsorption Kinetics

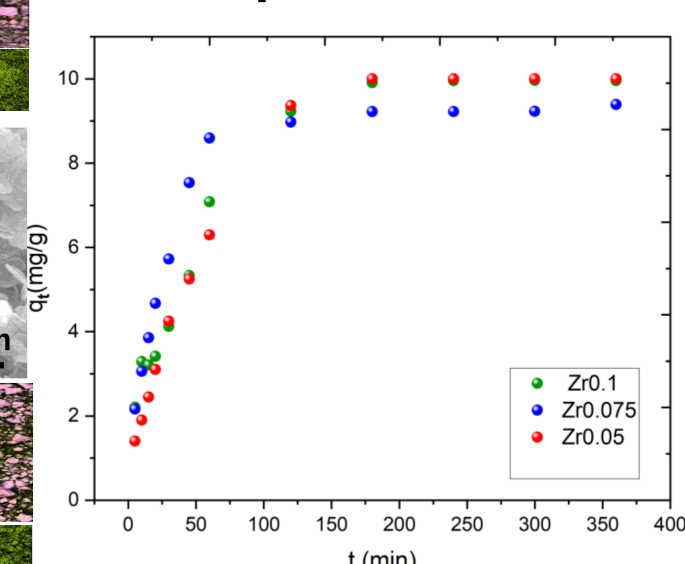


Figure 7. Fluorides adsorption kinetics studies of mixed Mg-Al-Zr oxides.

The data were fitted to the Pseudo-second order models

Zr0.05 R^2_{ajus}= 98%

K2=0.015 (g/mg·min); q_e= 12.58 mg/g

Adsorption follows a chemisorption process.

Fluoride removal >99%

Table 3. Textural properties of the samples.

Adsorbent	Specific surface area (m^2/g)	Volume (cm^3/g)	Diameter (nm)
Zr0.1	243	0.94	15.40
Zr0.05	261	1.04	16.0

Figure 3 shows that the Zr0.05 material has a 7% higher surface area compared to Zr0.1. This is related to the EDS results, which show a lower zirconium content (by weight %) in Zr0.05. A lower Zr content directly impacts the adsorption efficiency, leading to higher efficiency for Zr0.05 compared to the other adsorbents. The distribution of metals in the elemental mapping can be attributed to the fact that Zr is not entirely intercalated into the structure. While the intensities and widths of the XRD peaks suggest the probable formation of some amorphous phases (to a limited extent), reflections attributed to laminar LDH materials are still present, as confirmed by the SEM micrographs. However, Zr0.05 in the RSM experiment shows removals greater than 98% of an initial concentration of 12 mg/L at 180 min, confirmed by adsorption kinetics.

CONCLUSION

Zr-modified LDHs with a molar ratio of 0.05M (Mg-Al-Zr) are effective in removing fluorides from water, achieving an efficiency greater than 99% (q_e= 12.58 mg/g). The intercalation of Zr (0.05M) does not significantly affect the structural properties, as evidenced by the presence of laminar compounds and a homogeneous distribution of Mg-Al metals. However, Zr appears dispersed, suggesting the possible formation of a secondary zirconium oxide (ZrO_2) phase. Despite this, a portion of Zr remains intercalated within the LDH structure, contributing to a greater electrostatic charge and consequently impacting the adsorption efficiency. .

FUTURE WORK / REFERENCES

Additionally, we will investigate the formation of beads from the most effective LDH material for packing it into a column and creating a continuous flow system.

Arhzaf, S., Bennani, MN, Abouarnadasse, S., Ziyat, H. y Qabaqous, O. (2020). Efecto de la relación molar Mg/Al sobre la basicidad del óxido mixto Mg-Al derivado de hidrotalcita Mg-Al. Revista Mediterránea de Química
Gautam, R. K., Singh, A. K., & Tiwari, I. (2022). Nanoscale layered double hydroxide modified hybrid nanomaterials for wastewater treatment: A review. Journal of Molecular Liquids, 350, 118505.
Huo, Huo ,J., Min, X., Dong, Q., Xu, S., & Wang, Y. (2022). Comparison of Zn–Al and Mg–Al layered double hydroxides for adsorption of perfluorooctanoic acid. Chemosphere, 287, 132297. Podgorski, J., & Berg, M. (2022). Global analysis and prediction of fluoride in groundwater. Nature Communications, 13(1), 4232
Podgorski, J., & Berg, M. (2022). Global analysis and prediction of fluoride in groundwater. *Nature Communications*, *13*(1), 4232.
Wei, Y., Wang, L., Li, H., Yan, W. y Feng, J. (2022). Adsorción sinérgica de fluoruro mediante adsorbentes compuestos sintetizados a partir de diferentes tipos de materiales: una revisión. *Fronteras en Química* , *10* , 900660.

Acknowledgments This work was supported by CONAHCYT, CINVESTAV Saltillo Unit for the use of the facilities to carry out this project