

Reduction of fluorides present in drinking water in the municipality of Calera de Víctor Rosales Zacatecas, using chitosan gel beads

Disminución de fluoruros presentes en agua potable del municipio de Calera de Víctor Rosales Zacatecas, usando perlas de gel de quitosano

GONZÁLEZ-MARTÍNEZ, Enrique Iván[†]¹, GARCÍA-GONZÁLEZ, Juan Manuel¹, CONEJO-FLORES, Ricardo¹ and GUZMÁN-PANTOJA, Javier^{*2}

¹Universidad Autónoma de Zacatecas, Unidad Académica de Ciencias Químicas, Programa Académico de Ingeniería Química, Campus UAZ Siglo XXI

²Gerencia de Refinación de Hidrocarburos, Instituto Mexicano del Petróleo

ID 1st Author: *Enrique Iván, González-Martínez* / ORC ID: 0000-0001-9885-6496

ID 1st Co-author: *Juan Manuel, García-González* / ORC ID: 0000-0001-7259-5021

ID 2nd Co-author: *Ricardo, Conejo-Flores* / ORC ID: 0000-0002-8513-1821

ID 3rd Co-author: *Javier, Guzmán-Pantoja* / ORC ID: 0000-0003-2103-3488

DOI: 10.35429/JANRE.2022.10.6.1.8

Received March 25, 2021; Accepted June 30, 2021

Abstract

The quality of water distributed to the population in Zacatecas shows a deficit due to contaminants such as fluorinated compounds that exceed the limits allowed in the volumes of water used as a source of public supply. The objective of this work is to reduce the concentration of fluorides present in the drinking water of the municipality of Calera de Víctor Rosales, Zac., by using PVA cross-linked chitosan gel beads. An initial sample from a public supply was characterized, showing a fluoride concentration of 5.3 ppm, a value higher than the limit set in NOM-127-SSA1-1994. Batch experimentation was carried out at different degrees of sample dissolution with stirring conditions temperature of 450 rpm and 18.5 °C, respectively, in volumes of 150 mL and 0.3 g of chitosan gel beads. The adjustment of the experimental data to the various models of isotherms and adsorption kinetics was carried out; of these, the Freundlich isotherm and the pseudo-second order kinetic model are the models with the highest correlation to the experimental data. In addition, an average fluoride decrease of 80.08% was achieved in the samples with the established conditions.

Fluorides, Adsorption, Chitosan

Resumen

La calidad del agua distribuida a la población en el estado de Zacatecas muestra un déficit debido a contaminantes como compuestos fluorados que superan los límites permitidos en los volúmenes de agua empleados como fuente de abastecimiento público. El objetivo del presente trabajo es disminuir la concentración de fluoruros presentes en el agua potable del municipio de Calera de Víctor Rosales, Zac., mediante el uso de perlas de gel de quitosano reticuladas con PVA. Se caracterizó una muestra inicial proveniente de pozo de abastecimiento público, arrojando una concentración de fluoruros de 5.3 ppm, valor mayor al límite marcado en la NOM-127-SSA1-1994. Se realizó experimentación por lotes a diferentes grados de disolución de la muestra con condiciones de agitación y temperatura de 450 rpm y 18.5 °C, respectivamente en volúmenes de 150 mL y 0.3 g de perlas de gel de quitosano. Se realizó el ajuste de los datos experimentales a los diversos modelos de isotermas y cinéticas de adsorción; de estos, resultan la isoterma de Freundlich y el modelo cinético de pseudo-segundo orden como los modelos con mayor correlación a los datos experimentales. Además se logró una disminución de fluoruros promedio del 80.08% en las muestras con las condiciones establecidas.

Fluoruros, Adsorción, Quitosano

Citation: GONZÁLEZ-MARTÍNEZ, Enrique Iván, GARCÍA-GONZÁLEZ, Juan Manuel, CONEJO-FLORES, Ricardo and GUZMÁN-PANTOJA, Javier. Reduction of fluorides present in drinking water in the municipality of Calera de Víctor Rosales Zacatecas, using chitosan gel beads. Journal-Agrarian and Natural Resource Economics. 2022. 6-10: 1-8

* Correspondence to Author (e-mail: jguzmanp@imp.mx)

† Researcher contributing as first author.

1. Introduction

Water is an indispensable resource for human development. Of the total water present on the planet, only 2.5% is available as fresh water, suitable for consumption. Only small amounts of freshwater from the shallow rivers, lakes and aquifers that are the Earth's main water resources can be easily exploited. However, these resources are not exempt from containing contaminating substances or species of a natural or anthropogenic nature, which implies a latent risk to human health, examples of which are arsenic and fluorine, the latter being found in various minerals, such as topaz, fluorite and fluorapatite, to name a few.

Given the poor solubility of these rocks and minerals, the concentration of F⁻ in natural waters does not usually exceed mg/L on average, and may be much higher in volcanic areas rich in fluorinated rocks and in some mineral waters. In the state of Zacatecas, located in central Mexico, groundwater naturally contains high amounts of arsenic and fluoride. Studies carried out by Martínez et al. (2016), show that approximately 90% of samples taken in public supply intakes exceeded the levels established by the WHO and 43% exceeded the limits allowed by NOM-127-SSA1-1994 in terms of As content and 43% exceeded the limits for fluorides set in the same standard.

The intake of high doses of F⁻ in constant periods can result in the formation of dental and skeletal lesions, as well as negative effects in the endocrine, renal and even neurological fields (Alarcón-Herrera *et al.*, 2020).

The study area has as its main hydrological source of supply the Calera aquifer, which is located in the central zone of the State, in an area of low availability of surface water, in which the largest industrial and agricultural activity of the State is located, for what is of the utmost importance is to ensure that the parameters are within the regulatory limits to guarantee an optimal quality of the water that is used to cover the demand of the productive sectors and in the same way to cover the supply in homes.

Its center-south area is made up of the municipalities of Enrique Estrada, Calera and Morelos, with an area of 766,447 km², which represents 33.97% of the total area of the aquifer.

It borders to the north with the municipality of Fresnillo, to the east with Pánuco and Vetagrande, to the south with Zacatecas and to the west with Jerez. In this area, the temperate semi-dry climate predominates with average annual temperatures of 14.6 to 16.6 °C, average rainfall of 425 mm per year and evapotranspiration of 2,263 mm per year (Flores-Rodarte, Cristobal-Acevedo, & Pascual-Ramírez, 2019).

The objective of the present is to reduce the concentration of fluorides present in the drinking water of the municipality of Calera de Víctor Rosales, Zacatecas, through the adsorption process using chitosan gel beads as adsorbent material, as well as to determine the possible adsorption load that may occur per gram of adsorbent. Being a current and constant problem, several conventional methods have been proposed for the removal of fluorides present in water, examples of which are electrocoagulation, reverse osmosis or the use of ion exchange resins to mention a few, however, there are certain drawbacks within its application such as operating costs, sludge generation or resin selectivity.

Examples of the most recent work on fluoride removal within the country are the application of the batch adsorption process using natural Mexican zeolites by (Sampedro Duran, 2018), which were obtained from the states of Oaxaca and Guanajuato and were later modified with Ca⁺, Mg⁺ and Fe⁺ ions, obtaining removal percentages of 83% when dealing with the iron-modified zeolite from Guanajuato (ZCSF-Fe) after a stirring process at 120 rpm for 72 hours, the maximum adsorption load reported in said work with the zeolite ZCSF-Fe is 0.19mg of F⁻/g of adsorbent. Despite being a method that contemplates the prior management of a national natural resource, the drawback is the contact time necessary with the medium to be treated to achieve a considerable decrease in the fluorides present.

(Robledo-Peralta, López-Guzmán, Morales-Amaya, & Reynoso-Cuevas, 2021) tested removal methods such as electrocoagulation using aluminum and steel electrodes, in addition to varying the pH in two scenarios: pH=3 and pH=5, for which removal percentages of 41.51% and 55.50%, respectively, were obtained using only aluminum electrodes.

These results show a considerable improvement by reaching 93.16% removal when using the steel and aluminum electrodes together in an environment conditioned at a pH of 3. The improvement is due to the fact that there is a greater release of Al^{+3} within the solution to be treated, so there is a greater number of coagulating species within the medium. It should be noted that, although the scene is more favorable in terms of the percentage of fluoride decrease, it also implies a greater generation of sludge, which is considered an inconvenience due to the impact they can have on the environment and also on the cost of operation of the process due to its treatment or disposal.

Similarly, these authors tested the use of bioadsorbents obtained from the peel of apple (*Citrus senesis*) and orange (*Malus domestica*), but impregnating them with zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$); for pH of 3, removal percentages were obtained in a range of 69-85% after 60 minutes of contact under stirring conditions at 320 rpm and 93-95% after 1440 minutes under the same stirring conditions and pH.

(Wang *et al.*, 2017) carried out modifications with lanthanum to bone debris in order to improve the adsorption capacity of fluorides in a batch process at 200 rpm, which lasted 24 hours, thus obtaining removals of more than 91% under pH conditions, 2.5-10, and decreasing to 81.9% when reaching a pH of 11.5, which may be due to a higher affinity of hydroxide ions towards adsorption sites compared to fluoride ions.

In the use of chitosan as a fluoride adsorbent molecule, (Pamila Tecuatzin, 2019) developed hydrogels synthesized with gamma radiation and grafted with dimethylacrylamide with the purpose of reducing the presence of fluorinated compounds and arsenic in the groundwater of Chihuahua, achieving better results for arsenic and reporting a decrease percentage of F^- of 14% under its operating conditions.

The work carried out in comparison to those previously described uses a bioadsorbent in the same way however, the advantage of this lies in issues such as the use of waste from the fishing sector to obtain chitosan from chitin present in the exoskeletons of crustaceans.

In addition to offer better results when cross-linking the gel beads with polyvinyl alcohol (PVA) since a better mechanical resistance to impacts by the magnetic bullet is obtained within the batch process and removal percentages are higher than those shown by the study already carried out with chitosan in the form of a modified hydrogel in shorter periods of time.

2. Chitosan as bioadsorbent

Chitosan is a compound derived from chitin which comes from the exoskeleton of industrially processed crustaceans; as a natural polymer, it has great potential in different applications ranging from the area of health to agriculture, they have a wide advantage in the market for benefits provided by this polymer such as: its biodegradability, its non-toxicity and its biocompatibility (Romero, Sánchez, & Benavente, 2018).

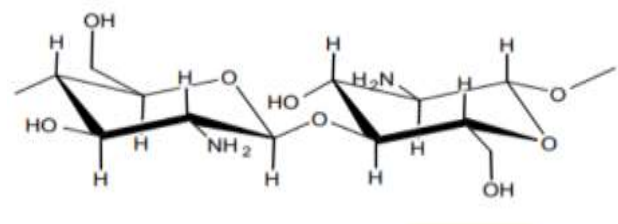


Figure 1 Chitosan structure. (Vera, 2020)

Various techniques have been used to physically modify chitosan and thereby condition the shape of the polymer, such as powder, nanoparticles and gels, the latter as beads, membranes, sponges, honeycombs, etc. The mixture of chitosan with PVA has been reported as a good option to improve the mechanical and chemical properties of the material. PVA is a non-toxic, water-soluble, biocompatible and biodegradable synthetic polymer that offers good tensile strength and flexibility. Some of its applications have been in the field of biomedicine and biochemistry. On the other hand, it has also been used to remove lead in aqueous solution. However, the chitosan/PVA mixture has rarely been studied (Flores Alamo, 2016).

3. Adsorption

Adsorption is a method of mass transfer by which a substance is concentrated at the interface where the interfacial composition is different from the corresponding compositions within the phases.

GONZÁLEZ-MARTÍNEZ, Enrique Iván, GARCÍA-GONZÁLEZ, Juan Manuel, CONEJO-FLORES, Ricardo and GUZMÁN-PANTOJA, Javier. Reduction of fluorides present in drinking water in the municipality of Calera de Víctor Rosales Zacatecas, using chitosan gel beads. Journal-Agrarian and Natural Resource Economics. 2022

The process can be batch, semi-continuous and continuous. At molecular level, adsorption is primarily due to attractive interfaces between a surface and the adsorbing group. All adsorption processes rely on equilibrium and mass transfer rates. Depending on the type of intermolecular attractive forces, the adsorption could be physical or chemical (Baby Abrarunnisa, Devanna, & Chari, 2019).

There are two aspects that must be considered in the adsorption process: the effect of adsorption on the interfacial energy of the system in equilibrium and the speed of the adsorption process.

In the analysis of adsorption processes, equilibrium data are usually expressed as adsorption isotherms.

In recent years, linear regression analysis has been one of the most applied tools to define the most suitable adsorption model since it analyzes the adsorption system and verifies the consistency of theoretical assumptions of the adsorption isotherm model (Ayawei, Ebelegi, & Wankasi, 2017).

The type II isotherm is the Freundlich isotherm, in which it is assumed that the surface of the adsorbent is energetically heterogeneous, made up of groups of adsorption sites with characteristic energies.

It is also considered that there are no lateral interactions between the adsorbed molecules and that only one monolayer is adsorbed. It is used to describe the adsorption of aqueous solutions, although this type of isotherm cannot define the linear interval at very low concentrations or the effect of saturation at very high concentrations, which is why intermediate concentrations are used (Ureña Gómez, 2017). The mathematical expression is as follows:

$$q = K * C_{eq}^{\frac{1}{n}} \quad (1)$$

where K is the adsorption capacity constant, where the higher the value of K, the higher the adsorbent load that can be achieved; and is the adsorption intensity constant, which factor is related to the energetic heterogeneity of the adsorbent surface and isotherm and if $n = 1$, the graph becomes linear; isotherms with $n > 1$ are considered unfavorable.

The linearized equation is expressed normatively in its logarithmic form:

$$\text{Log } q = \text{Log } K + \frac{1}{n} \text{Log } C_{eq} \quad (2)$$

One of the most important factors for the design of an adsorption system is to predict the rate at which adsorption will occur, the residence time of the adsorbate and the dimensions of the reactor, which will depend on the kinetics of the adsorption system.

Adsorption kinetics is expressed as the rate of solute removal that controls the residence time of the solute at the solid-solution interface. In adsorption studies, it is important to identify the involved mechanisms, which may include external diffusion, internal diffusion and chemical reactions. For this, there are kinetic models that are based on the reaction surface as the kinetic step that controls the rate of adsorption. These models include the pseudo-first-order kinetics, pseudo-second-order kinetics, and the intraparticulate diffusion equation.

The pseudo-second order kinetic model was proposed by Ho and McKay in 1999. In this model, the adsorbate is assumed to be adsorbed on two active sites. Since then, better fits of the experimental data to this model have been reported with respect to its predecessors (Carbonel Ramos, 2018).

The equation of this kinetic model is the following:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

By integrating the expression from $t=0$ to $t=t$ and rearranging the expression to make the graphic form, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 is the adsorption rate constant for pseudo-second order ($\text{g/mg} \cdot \text{min}$), q_t and q_e remain the amount of adsorbate at time t and at equilibrium, respectively.

4. Methodology to be developed

Based on the CONAGUA, SEMARNAT and Official Mexican Standards, NOM-014-SSA1-1993 and NOM-230-SSA1-2002, the water was sampled at different points in the city of Calera, Zac.; the samples were mixed to homogenize them, combining a volume of 20 L. For the physicochemical analysis, the Official Mexican Standard NOM-127-SSA1-1994 was used as reference. The following properties were determined: Hardness (a HANNA-Instruments HI3812 equipment was used); pH and conductivity (a HANNA-Instruments HI98130 equipment was used); chlorides (a HANNA-Instruments HI3815 equipment was used) and fluorides (a HANNA-Instruments HI739 equipment was used). For arsenic sorption tests on chitosan gel beads, a series of experiments were performed in batches. For the batch regime 150-mL samples were used, the concentration of fluorides in the sampled water was varied by adding deionized water, 0.3 g of chitosan gel beads were placed in each flask, stirred at 450 rpm on a stirring grid at a temperature of $18.5\text{ }^{\circ}\text{C} \pm 0.5$ for 135 min to determine the adsorption model and the kinetic model.

5. Results

Table 1 shows the results obtained for the physicochemical characterization of the original sample collected in the supply well, as well as the standard deviation between the obtained data.

Parameter	Obtained value
Fluoride (ppm)	5.3 ± 0.0
Hardness (ppm CaCO_3)	46 ± 1.73
pH	8.19 ± 0.37
Free chlorine (ppm)	0.5 ± 0.0
Chlorine (ppm)	20 ± 0.0
Temperature ($^{\circ}\text{C}$)	18.46 ± 0.30
Conductivity (mS)	0.47 ± 0.025

Table 1 Characterization of drinking water from Calera, Zacatecas, from a supply well

Table 2 presents the results obtained from the sorption of arsenic in the cross-linked chitosan gel beads.

Knowing the concentration level of fluorides present at different times, the adsorption capacity of the beads can be calculated using the following expression:

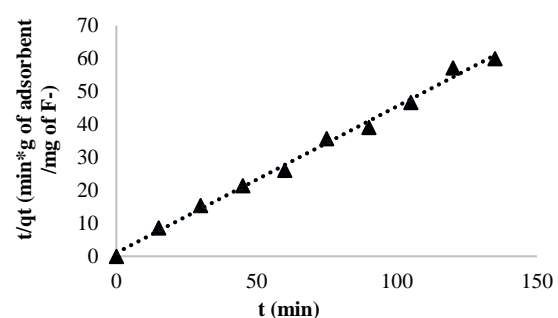
$$q = \frac{C_0 - C_t}{m} * V \quad (5)$$

where q is the adsorption capacity, C_0 is the initial concentration of fluorides in the untreated water (mg F-/L), C_t is the concentration of fluorides at a time "t" of stirring of the treated water (mg F-/ L), m is the mass of the adsorbent (g chitosan beads) and V is the control volume (L).

Time (min)	Fluoride (ppm)	q_t (mg F/ g)
0	5.30	0
15	1.80	1.75
30	1.40	1.95
45	1.10	2.1
60	0.70	2.3
75	1.10	2.1
90	0.70	2.3
105	0.80	2.25
120	1.10	2.1
135	0.80	2.25

Table 2 Results of the fluoride sorption process on chitosan gel beads

The batch process was considered stable after 135 minutes, since in subsequent measurements, the fluoride concentration values ranged between 1.10 and 0.8 ppm, so it was considered that the maximum adsorption capacity of the beads had been reached. It should be noted that the pH of the treated sample was in a range of 8.4-8.7 during the adsorption-desorption process and it was not necessary to acidify the sample. The sorption data of the process and its fitting to the pseudo-second order kinetic model are shown in Graphic 1.



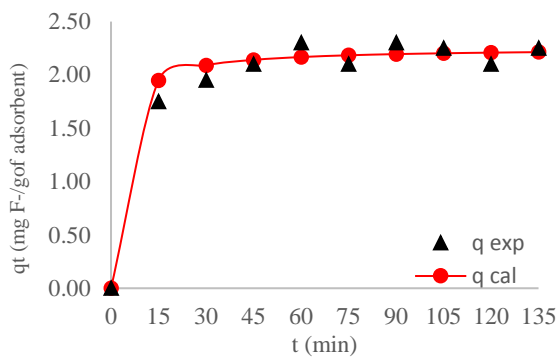
Graphic 1 Fitting of sorption data based on a pseudo-second order kinetic model

Compared to other kinetic models, this fitting shows a Pearson correlation coefficient (R^2) of 0.9943. With the equation in the graph, it was possible to calculate the values of k_2 , q_e and h , the latter being the initial adsorption rate (mg/g*min) and whose equivalence is:

$$h = k_2 q_e^2 \quad (6)$$

The values obtained for these parameters were: $q_e = 2.25 \text{ mg F}^- / \text{g}$ of adsorbent, $k_2 = 0.19 \text{ g/mg} \cdot \text{min}$ and $h = 0.96 \text{ mg F}^- / \text{g}$ of adsorbent $\cdot \text{min}$.

Graphic 2 shows the relation of the values obtained experimentally with respect to those calculated based on the theory of the pseudo-second order kinetic model, for which an average error percentage of 4.69% was obtained according to the adjustment of the data.



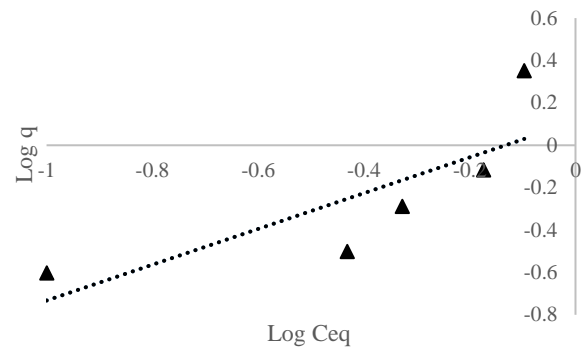
Graphic 2 Comparison of experimental data (q_{exp}) vs pseudo-second order model (q_{cal})

For the modeling of the adsorption process, dilutions of the sample to be treated were made, for which 0.3 grams of chitosan pearls were used in each system; in the same way, a time of 135 minutes was taken as necessary to achieve equilibrium. The results obtained are shown in Table 3.

Sample (ml) + deionized water (ml)	C_o (ppm)	C_{eq} (ppm)	q (mg F ⁻ /g)
150 +0	5.3	0.8	2.25
120+30	2.2	0.67	0.76
90+ 60	1.5	0.47	0.51
60+90	1	0.37	0.31
30+120	0.6	0.1	0.25

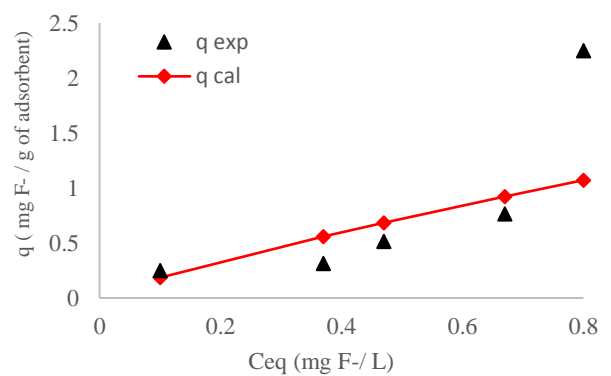
Table 3 Results obtained by varying the dissolution range of the sample

With the obtained values, the adjustment was made to the various models of adsorption isotherms, resulting in the Freundlich model, which presents a Pearson coefficient of 0.6395, the values obtained for K and n are $1.29 \text{ mg F}^- / \text{g}$ of adsorbent and 1.18, respectively.



Graphic 3 Adjustment of the data with respect to the Freundlich adsorption model

With the obtained parameters, it was possible to calculate the theoretical adsorption capacity for each system. Graphic 4 presents the comparison between the experimental adsorption load values in relation to the theoretical load predicted by the Freundlich model. When adjusting the experimental data with respect to the theoretical data, there was an error of 45%.



Graphic 4 Comparison of experimental data (q_{exp}) vs the Freundlich adsorption model (q_{cal})

6. Conclusions

The established process conditions yielded favorable results in the reduction of fluorinated compounds through adsorption, with average efficiencies of 80%; this result opens the way to a new stage of experimentation in which the adsorption process through chitosan will be carried out continuously, with the implementation of the continuous process it is expected to minimize the contact times necessary to achieve the adsorption of fluorides at the levels obtained at the batch stage or even to improve the removal efficiency achieved so far.

The pseudo-second order kinetic model fitted very adequately to the adsorption process that occurred in the chitosan beads, in addition to the fact that the maximum adsorption capacities obtained by this model and experimentally do not present a significant variation. On the other hand, it can be said that when coupling the data to the Freundlich model, being in an alkaline medium of pH 8-9, the adsorption sites may have been occupied by OH⁻ ions instead of F⁻ ions, so the adsorption capacity of F⁻ in most of the dilutions was lower than expected according to the theory.

References

- Alarcón-Herrera, M. T., Martín-Alarcon, D. A., Gutiérrez, M., Reynoso-Cuevas, L., Martín-Domínguez, A., Olmos-Márquez, M. A., & Bundschuh, J. (2020). Co-occurrence, possible origin, and health-risk assessment of arsenic and fluoride in drinking water sources in Mexico: Geographical data visualization. *Science of the Total Environment*, 698, 134–168. Recovered from: <https://eprints.usq.edu.au/38007/7/2019.03.01%20STOTEN%20final%20proof.pdf> el 26 de marzo 2022 DOI:<https://doi.org/10.1016/j.scitotenv.2019.134168>
- Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry, 2017*. Recovered from: <https://www.hindawi.com/journals/jchem/2017/3039817/> el 24 de febrero 2022 DOI: <https://doi.org/10.1155/2017/3039817>
- Baby Abrarunnisa, B., Devanna, N., & Chari, M. A. (2019). Low-Cost Adsorbents procedure by means of Heavy Metal Elimination from Wastewater. *Preprints*. Recovered from: <https://www.preprints.org/manuscript/201902.0013/v1> el 24 de febrero 2022 DOI:<https://doi.org/10.20944/preprints201902.0013.v1>
- Carbonel Ramos, D. (2018). Cadmium , Copper and Lead Adsorption on Natural and Modified Bentonite , Kaolin and Zeolite : A Review of Process Parameters, Isotherms and Kinetics. *Ingeniería*, 23(3), 252–273. Recovered from: <https://www.redalyc.org/jatsRepo/4988/498858250004/html/index.html> el 26 de febrero 2022 DOI: <https://doi.org/10.14483/23448393.13418>
- Flores-Rodarte, A., Cristobal-Acevedo, D., & Pascual-Ramírez. (2019). Agricultural water productivity in the central zone of the Calera aquifer, Zacatecas. *Ingeniería Agrícola y Biosistemas*, 11(2), 181–199. Recovered from: https://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S2007-40262019000200181DOI:https://doi.org/10.5154/r.inagbi.2019.03.040 el 20 de febrero 2022
- Flores Alamo, N. (2016). *Estudio de adsorción de Zn(II) y Cu(II) mediante esferas del hidrogel quitosano-pva en sistemas por lote y continuo*. Universidad Autónoma del Estado de México. Recovered from: <http://ri.uaemex.mx/bitstream/handle/20.500.11799/65403/TESIS%20DOCTORADO%2002%20FEB%202016.pdf?sequence=1> el 13 de marzo 2022
- Martínez-Acuña, M. I., Mercado-Reyes, M., Alegría Torres, J. A., & Mejía Saavedra, J. J. (2016). Preliminary human health risk assessment of arsenic and fluoride in tap water from Zacatecas , México. *Environmental Monitoring and Assessment*, 476–489. Recovered from: <http://ricaxcan.uaz.edu.mx/jspui/bitstream/20.500.11845/561/1/Preliminary%20Human%20Health.pdf> el 28 de febrero 2022 DOI:<https://doi.org/10.1007/s10661-016-5453-6>
- Pamila Tecuatzin, I. (2019). “Remoción De Arsénico Y Flúor Del Agua Subterránea De Chihuahua Mediante Hidrogeles De Quitosano Sintetizados Con Radiación Gamma”. *Repositorio De Tesis -Universidad Autonoma De Chihuahua Con Grado De Maestro*. Universidad Autónoma de Chihuahua. Recovered from: <http://repositorio.uach.mx/242/1/REMOCI%C3%93N%20DE%20ARS%C3%89NICO%20Y%20FL%C3%9AOR%20DEL%20AGUA%20SUBTERR%20C3%81NEA%20DE%20CHIHUAHUA%20MEDIANTE%20HIDROGELES%20DE%20QUITOSANO%20SINTETIZADOS%20CON%20RADIACION%20GAMMA.pdf>

Robledo-Peralta, A., López-Guzmán, M., Morales-Amaya, C. G., & Reynoso-Cuevas, L. (2021). Arsenic and fluoride in groundwater, prevalence and alternative removal approach. *Processes*, 9(7), 1–15. Recovered from: <https://www.mdpi.com/2227-9717/9/7/1191> el 28 de febrero 2022 DOI: <https://doi.org/10.3390/pr9071191>

Romero, M., Sánchez, S., & Benavente, S. (2018). De Aguas Residuales De Tenerías Application of Modified Chitosan in Tannery Wastewater Treatment. *Revista Científica Nexo*, 31(02), 104–119. Recovered from: <https://www.camjol.info/index.php/NEXO/article/view/6834> el 20 de febrero 2022 DOI:<http://dx.doi.org/10.5377/nexo.v31i2.6834>

Sampedro Duran, J. (2018). *Remoción de flúor en agua con zeolitas naturales mexicanas*. Universidad Autónoma Metropolitana. Recovered from: http://zaloamati.azc.uam.mx/bitstream/handle/11191/6725/Remocion_de_fluor_en_agua_Sampedro_Duran_J_2018.pdf?sequence=1&isAllowed=y el 22 de febrero 2022

Ureña Gómez, D. (2017). *Diseño de un sistema de adsorción para la eliminación de contaminantes emergentes presentes en disoluciones*. Universitat Politècnica de Valencia. Recovered from: [https://riunet.upv.es/bitstream/handle/10251/97809/UREÑA - Diseño de un sistema de adsorción para la eliminación de contaminantes emergentes present....pdf?sequence=1&isAllowed=y](https://riunet.upv.es/bitstream/handle/10251/97809/UREÑA_Diseño_de_un_sistema_de_adsorción_para_la Eliminación_de_contaminantes_emergentes_present....pdf?sequence=1&isAllowed=y) el 26 de febrero 2022

Vera, A. (2020). *Actividad enzimática digestiva y Composición química de juveniles de tilapia roja (Oreochromis sp.) alimentados con quitosano en dieta*. Universidad técnica estatal de Quevedo. Recovered from: <https://repositorio.uteq.edu.ec/handle/43000/5311> el 18 de febrero de 2022

Wang, L., Xie, Y., Yang, J., Zhu, X., Hu, Q., Li, X., & Liu, Z. (2017). Insight into mechanisms of fluoride removal from contaminated groundwater using lanthanum-modified bone waste. *RSC Advances*, 7(85), 54291–54305. Recovered from: <https://pubs.rsc.org/en/content/articlehtml/2017/ra/c7ra10713g> el 28 de febrero 2022 DOI:<https://doi.org/10.1039/c7ra10713g>