

Synthesis of magnetite and her used by AgNO₃ remove from aqueous system**Síntesis de magnetita y su uso en la remoción de AgNO₃ de sistemas acuosos**

MÁRQUEZ-VALDEZ, Clara†, SALAZAR-HERNÁNDEZ, Mercedes*, ELORZA-RODRÍGUEZ, Enrique and LÓPEZ-BAEZ, Israel

Departamento de Ingeniería en Minas, Metalurgia y Geología, Universidad de Guanajuato. México.

ID 1st Author: Clara, Márquez-Valdez / ORC ID: 0000-0001-8039-8124, Open ID Author: 56182864800

ID 1st Co-author: Mercedes, Salazar-Hernández / ORC ID: 0000-0001-8633-6063, Open ID Author: SC1141798600

ID 2nd Co-author: Enrique, Elorza-Rodríguez / ORC ID: 0000-0001-8633-6063, Open ID Author: 14621850400

ID 3rd Co-author: Israel, López-Baez / Open ID Author: 14621850400

DOI: 10.35429/EJB.2023.19.10.1.6

Received July 10, 2023; Accepted December 30, 2023

Abstract

Today pollution is an important problem that must be addressed, in this sense adsorption processes are a methodology that is usually used to remove different pollutants such as anions, cations and organic compounds. There is a great diversity of adsorbents ranging from porous oxides, metallic networks and polymeric membranes; magnetite and its composites have been shown to be adsorbent materials for the removal of various contaminants. The present work shows the study of the removal of Ag(I) from aqueous systems with Fe₃O₄ synthesized from precipitation processes. The magnetite showed an adsorption capacity of 19.84 mgg⁻¹ according to the Langmuir adsorption model, a K_L of 0.143 Lmg⁻¹, the partition coefficient showed a favorable adsorption with values between 0.1-0.01 and an endothermic Gibbs free energy. of 4.8 KJmol⁻¹. The kinetics of adsorption is carried out using a second order system, observing a decrease in the magnitude of the rate constant (K₂) with the initial concentration of Ag(I), which suggests that the adsorption process at concentrations elevated is limited by the intra-particle diffusion of the system.

Resumen

Hoy en día la contaminación, es un problema importante que debe de atenderse, en ese sentido los procesos de adsorción son una metodología que usualmente se utiliza para remover diferentes contaminantes como aniones, cationes y compuestos orgánicos. Existe una gran diversidad de adsorbentes que van desde óxidos porosos, redes metálicas y membranas poliméricas; la magnetita y compósitos de esta, se han mostrado como materiales adsorbentes para la remoción de diversos contaminantes. El presente trabajo muestra el estudio de la remoción de Ag(I) de sistemas acuosos con Fe₃O₄ sintetizada a partir de procesos de precipitación. La magnetita mostró una capacidad de adsorción de 19.84 mgg⁻¹ de acuerdo con el modelo de adsorción de Langmuir, una K_L de 0.143 Lmg⁻¹, el coeficiente de reparto mostró una adsorción favorable con valores entre 0.1-0.01 y una energía libre de Gibbs endotérmica de 4.8 KJmol⁻¹. La cinética de adsorción se lleva a cabo mediante un sistema de segundo orden, observándose una disminución de la magnitud de la constante de velocidad (K₂) con la concentración inicial de la Ag(I), lo que sugiere que el proceso de adsorción a concentraciones elevadas es limitada por la difusión intraparticular del sistema.

Magnetite, Adsorption, AgNO₃**Magnetita, Remoción, AgNO₃**

Citation: MÁRQUEZ-VALDEZ, Clara, SALAZAR-HERNÁNDEZ, Mercedes, ELORZA-RODRÍGUEZ, Enrique and LÓPEZ-BAEZ, Israel. Synthesis of magnetite and her used by AgNO₃ remove from aqueous system. ECORFAN Journal-Bolivia. 2023. 10-19:1-6.

* Correspondence to Author (E-mail: merce@ugto.mx)

† Researcher contributing first author.

Introduction

Adsorption processes have been shown to be a good alternative for the removal of various contaminants in aqueous systems (metals, drugs, dyes, pesticides and others). This process has great advantages such as its simplicity, since they basically consist of placing the adsorbent with the aqueous system to be treated, either in bulk or in column [1,2], in addition to a wide range of adsorbents, such as polymeric membranes, mesoporous silica, metal oxides, MOFs, among others.

In this sense, the use of magnetite in various processes of adsorption of contaminants in aqueous systems has been published, for example Uranium (VI), Chunhui Luo et al. reported that the metal removal capacity improves with the presence of metal-reducing bacteria, associating the removal of uranium to the formation of FeUO₄ species [3], the use of this metal oxide and its composites for the removal of various contaminants such as organic matter, dyes and other heavy metals such as Ni, Pb, Cd and Cr among others, both in aqueous systems and in soil, have also been reported [4-9].

The present work shows the study of the removal of Ag(I) in aqueous systems with magnetite synthesized by precipitation and hydrothermal treatment, the adsorption of the metal is evaluated using the Langmuir adsorption model, the effect of pH on the adsorption of the metal and the kinetics of adsorption of the same.

Experimental Section

Synthesis and characterization of Fe₃O₄

The synthesis of magnetite was carried out by precipitation techniques according to equation 1, with a 2Fe³⁺:Fe²⁺ ratio [10,11]. In a 250 mL flask, 5.27 g of FeSO₄ and 2.7 g of FeCl₃ were dissolved in 200 mL of water under constant stirring, then the pH was adjusted to 10-11 with NH₄OH and the system was placed at reflux for 24 h. At the end of this time, the magnetite was recovered by filtration and dried at 75°C for 12 h [10,11].



Reaction 1

The magnetite was characterized by powder XRD, which was carried out on a RIGAKU ULTIMA IV X-ray diffractometer.

Adsorption studies of Ag(I) from aqueous systems

The evaluation of silver(I) adsorption capacity was performed by determining the adsorption kinetics at 10 min intervals for 1 h with standard solutions of AgNO₃ at different concentrations (100-500 ppm). 0.1 g of the material was placed with 10 mL of a solution at 57, 123, 192, 319 and 694 mgL⁻¹ of Ag and the residual concentration of silver in the solution was determined at the aforementioned times by atomic absorption spectrometry.

The adsorption capacity of silver was determined by equation 1, where q_t is the loading at time t , C_0 and C_t are the concentrations of silver in the initial solution and at time t in mgL⁻¹, V the volume of sample used (L) and m the mass of material used in g.

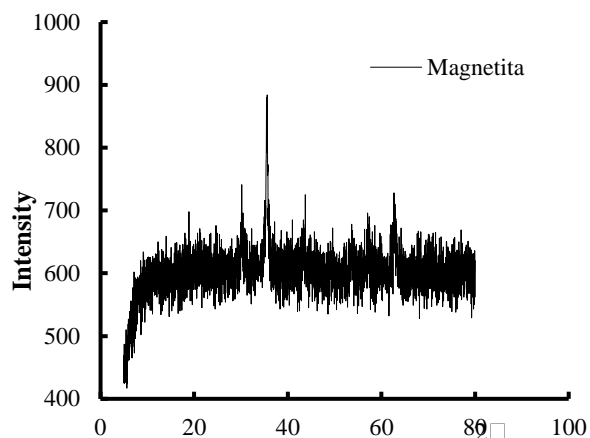
$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Effect of pH on Ag (I) Adsorption

The effect of pH on the adsorption capacity of magnetite was evaluated by determining the adsorption capacity of magnetite at pH 3, 4.5, 6 and 10. 0.1 g of the material was placed with 10 mL of Ag(I) solution at the pH under study for 20 minutes and the concentration of residual Ag in the solution was determined.

Results and discussion

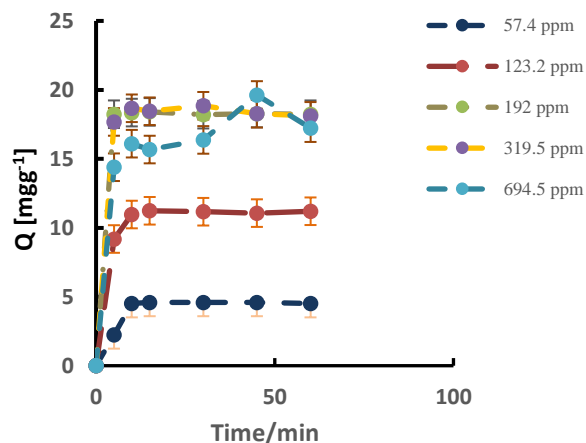
Figure 1 shows the diffractogram of the synthesized magnetite, corroborating the obtaining of this phase. The planes are observed at 2θ at 30.1, 35.4, 43.1, 54.5, 57.6, 62°, which correspond to the magnetite according to Mohammadi et al].



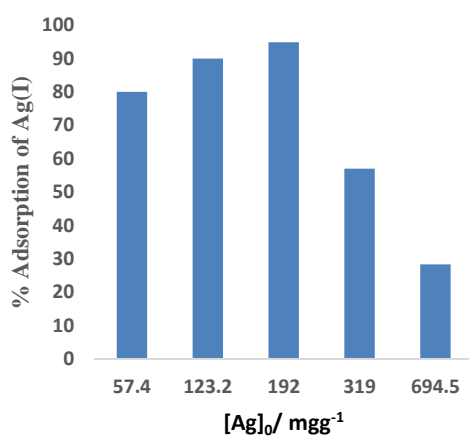
Graphic 1 XRD Synthesized magnetite

Adsorption studies of Ag(I) from aqueous systems

Figure 2 shows the adsorption isotherms of Ag(I) with the synthesized Fe₃O₄, observing an adsorption equilibrium after 20 minutes of contact. A removal of 80 to 95% was observed at moderate concentrations of 57 to 200 mgL⁻¹ Ag, decreasing to 28% at high concentrations of 700 mgL⁻¹ Ag (Figure 3).



Graphic 2 Adsorption isotherms of Ag(I) with Fe₃O₄



Graphic 3 Adsorption capacity of Ag(I) with Fe₃O₄

The fit of the experimental data to the Langmuir and Freundlich adsorption models showed a poor fit to the Freundlich model (Figure 4b), fitting the experimental data only to the Langmuir model (Equation 2, Figure 4a), where C_e and q_e refer to the concentration and charge at equilibrium of the system, K_L represents the Langmuir constant and Q_0 the maximum charge for the formation of the monolayer. This model assumes that adsorbate-adsorbate interactions are weak (physisorption) and that there are no adsorbate-adsorbate interactions [13, 14].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (2)$$

Figure 4a, shows the fit of the experimental data to the Langmuir model, showing a maximum loading capacity (Q_0) of 19.84 mgg⁻¹ of Ag(I) and a Langmuir constant (K_L) of 0.143 Lmg⁻¹. The Gibbs free energy was determined from Equation 3, where R is the gas constant (8.314 JK⁻¹ mol⁻¹), T the absolute temperature and K_L the Langmuir constant; an endothermic adsorption process was observed with a magnitude of 4.8 KJmol⁻¹. The partition coefficient (R_L), was determined according to Equation 4, where K_L is the Langmuir constant and C_0 the initial concentration of sorbate (Ag(I)); the magnitude of R_L , is a parameter that allows identifying if the adsorption process is favorable or not; when the system presents values of $R_L=1$, the adsorption process is linear, while values of $R_L=0$ imply an irreversible adsorption process and for values of $0 < R_L < 1$, the adsorption process is favorable. The adsorption system of Ag(I) on Fe₃O₄, showed R_L magnitudes in the range of 0.1-0.01, suggesting a favorable adsorption process.

$$\Delta G = -RT \ln K_L \quad (3)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

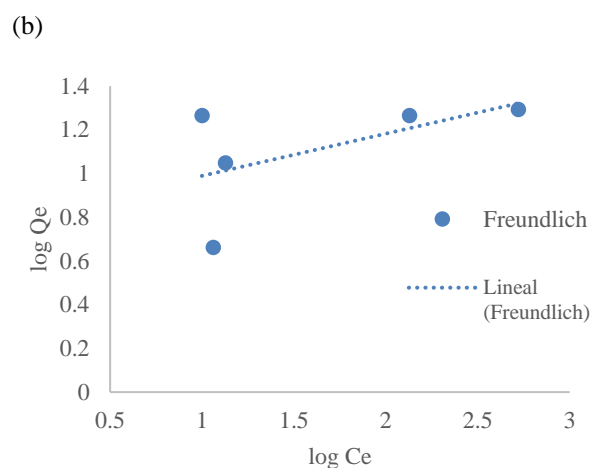
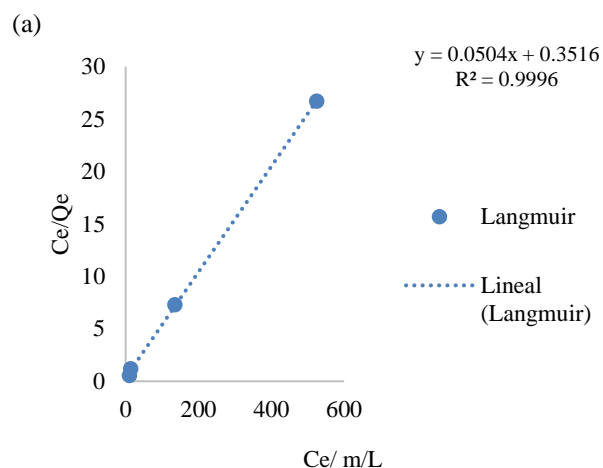


Figure 4 Fit of experimental data to the model of (a) Langmuir and (b) Freundlich.

The adsorption kinetics was adjusted to the pseudo-second order model (Equation 5 and 6), where q_e and q_t , are the charges at equilibrium and at time t and K_2 the velocity constant of the system. The velocity constant of the system, values from 0.22 to 0.057 $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ were observed. The rate constant decreases as the initial Ag(I) concentration of the system increases (Figure 5), suggesting that at high concentrations the adsorption mechanism is limited by intraparticle diffusion [13, 14].

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

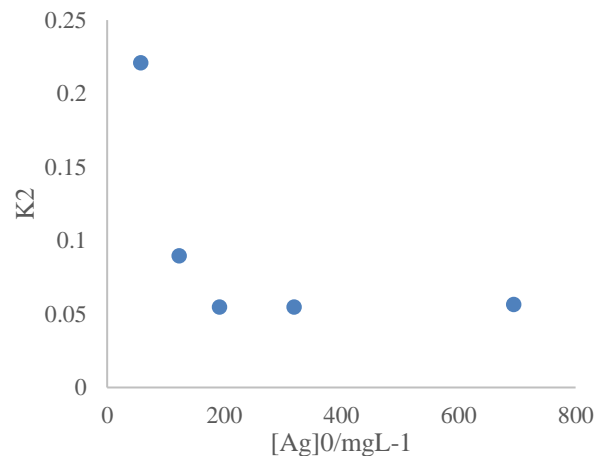


Figure 5 Dependence of K_2 on the initial Ag(I) concentration

Effect of pH on the adsorption of Ag(I) from aqueous systems with Fe_3O_4

Figure 6 shows the effect of pH on the adsorption of $[Ag(H_2O)_2]^+$ with magnetite, a decrease in the adsorption capacity of the material is observed as the pH of the system increases, with 78% removal at acidic pH (3) and decreasing as the pH increases in the system, with only 51% removal at pH 6.0. This decrease is due to the change of the magnetite surface charge at pH higher than 3.0, which disfavors the Fe-Ag interactions and the adsorption process, at basic pH (3.0).

At basic pH (10), the quantitative removal of silver from the system is observed, this is due to the precipitation of $Ag(OH)$ ($K_{ps} = 1.5 \times 10^{-8}$), which favors the removal of the metal by precipitation and not adsorption processes.

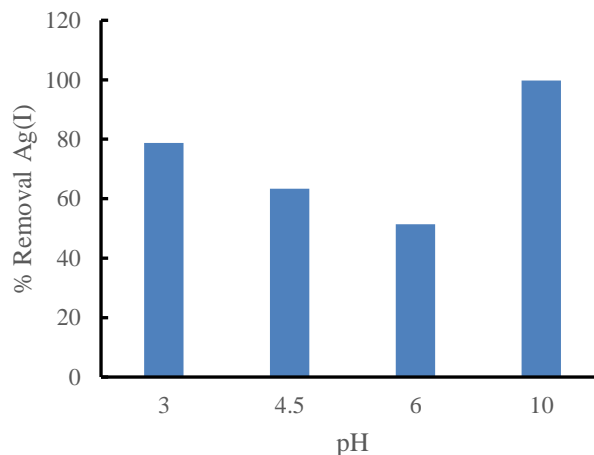


Figure 6 Effect of pH on the adsorption process of Ag(I)

Conclusions

The removal of Ag(I) in aqueous systems with Fe₃O₄, is favorable at acidic pH <3, where the highest metal removal is observed at 78 %. The removal capacity of silver with magnetite is moderate, according to the Langmuir model, the maximum loading capacity for the formation of the monolayer on the surface is 19.84 mgg⁻¹, the KL is 0.143 Lmg⁻¹. The adsorption kinetics is carried out by a second pseudo-order model, the rate constant decreases with respect to the initial concentration of silver in the system, suggesting that intra-particle diffusion governs the adsorption process at high concentrations, while external diffusion is the main resistance at low concentrations.

Acknowledgment

The authors would like to thank the national laboratory LICAAM for the technical support for the characterization of the synthesized magnetite, as well as the University of Guanajuato and the IPN for the financial support provided.

Financing

Financial support for this project was provided by the UG-DAIP [CII 142-2023].

Acknowledgments

The authors would like to acknowledge the technical support of the national laboratory LICAMM for the characterization of the materials.

References

- [1] Warren-Vega, W.M.; Campos-Rodríguez, A.; Zárate-Guzmán, A.I.; Romero-Cano, L.A. A Current Review of Water Pollutants in American Continent: Trends and Perspectives in Detection, Health Risks, and Treatment Technologies. *Int. J. Environ. Res. Public Health* 2023, 20, 4499. <https://doi.org/10.3390/ijerph20054499>
- [2] Peibo Du, Jinping Zhang, Zaisheng Cai, Fengyan Ge, High adsorption of cationic dyes from aqueous solution using worm-like porous nanosilica: Isotherm, kinetics and thermodynamics, *Materials Today Communications* (2023), 35: 105697. <https://doi.org/10.1016/j.mtcomm.2023.105697>.
- [3] Chunhui Luo, Tingting Zhang, Zongdi Yuan, Zheng Fu, Shuo Lv, Chengcai Huang, Baowei Hu, Yuling Zhu, Bin Zheng “Removal of hexavalent uranium [U(VI)] by magnetite in the presence of metal-reducing bacteria from rice soil” *Environmental Technology & Innovation* (2022) 28: 102616-102627. <https://doi.org/10.1016/j.eti.2022.102616>.
- [4] Yangfan Yuan, Changai Zhang, Chenhao Zhao, Bing Wang, Xiaozhi Wang, Bin Gao, Shengsen Wang, Jörg Rinklebe, “One-step preparation of a novel graphitic biochar/Cu⁰/Fe₃O₄ composite using CO₂-ambiance pyrolysis to activate peroxydisulfate for dye degradation” *Journal of Environmental Sciences* (2023) 125: 26-36. <https://doi.org/10.1016/j.jes.2021.10.030>.
- [5] Guang Yang, Zhiyang Cheng, Huanzhong Bao, Lianbao Zhang, Hongwei Zhang, Hui Jia, Jie Wang “Mechanistic insight of weak magnetic field trigger transformation of amorphous Fe(III)-(oxy)hydroxide for enhanced ferrate (VI) towards selective removal of natural organic matter” *Chemosphere* (2022)303: 134967. <https://doi.org/10.1016/j.chemosphere.2022.134967>.
- [6] Zeinab Rahmani, Mousa Ghaemy, Ali Olad, “Removal of heavy metals from polluted water using magnetic adsorbent based on κ-carrageenan and N-doped carbon dots” *Hydrometallurgy* (2022), 213: 105915. <https://doi.org/10.1016/j.hydromet.2022.105915>.

- [7] Nasim Naini, Hossein Sid Kalal, Mohammad Reza Almasian, Danial Niknafs, Mohmmad Taghiof, Hassan Hoveidi, "Phosphine-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ /composites as efficient magnetic nanoadsorbents for the removal of palladium ions from aqueous solution: Kinetic, thermodynamic and isotherm studies" *Materials Chemistry and Physics* (2022), 287: 126242. <https://doi.org/10.1016/j.matchemphys.2022.126242>.
- [8] Xiang Ji, Chuanye Zhou, Liangxi Chen, Yanzhang Li, Tianci Hua, Yan Li, Changqiu Wang, Song Jin, Hongrui Ding, Anhuai Lu "Reduction, mineralization, and magnetic removal of chromium from soil by using a natural mineral composite" *Environmental Science and Ecotechnology* (2022), 11: 100181. <https://doi.org/10.1016/j.ese.2022.100181>
- [9] Fan Wang, Rongrong Ma, Jinling Zhan, Wenshuo Shi, Yuanyuan Zhu, Yaoqi Tian, "Superhydrophobic/superoleophilic starch-based cryogels coated by silylated porous starch/ Fe_3O_4 hybrid micro/nanoparticles for removing discrete oil patches from water" *Separation and Purification Technology* (2022), 291: 120872. <https://doi.org/10.1016/j.seppur.2022.120872>
- [10] Jae H. Kwon, Lee D. Wilson, R. Sammynaiken "Synthesis and characterization of magnetite and activated carbon binary composites" *Synthetic Metals* (2014) 197: 8-17. <https://doi.org/10.1016/j.synthmet.2014.08.010>
- [11] Jos J. M. Lenders, Guilia Mirabello, Nico A. J. Sommerdijk "Bioinspired magnetite synthesis via olid precursor phases" *Chem. Sci.* (2016) 7: 5624-5634. DOI: 10.1039/c6sc00523c
- [12] Mohammadi HR, Nekobahr E, Akhtari J, Saeedi M, Akbari J, Fathi F. "Synthesis and Characterization of Magnetite Nanoparticles by Co-precipitation Method Coated with Biocompatible Compounds and Evaluation of In-Vitro Cytotoxicity" *Toxicology Reports* (2021). Doi: <https://doi.org/10.1016/j.toxrep.2021.01.012>.
- [13] Feng-Chin Wu, Ru-Ling Tseng, Shang-Chieh Huang, Ruey-Shin Juang "Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: Amini-review" *Chemical Engineering Journal* (2009) 151: 1-9. <https://doi.org/10.1016/j.cej.2009.02.024>.
- [14] Gutiérrez-Valtierra Moises, Salazar-Salazar-Hernández Carmen; Mendoza-Miranda Juan Manuel; Elorza-Rodríguez Enrique; Puy-Alquiza María de Jesús; Caudillo-González Martín; Salazar Hernández, Mercedes;"Silica Rice Husk, amine modified SHR, Cr(III) removal, industrial waste effluents" *Desalination and Water Treatment* (2019) 158: 152-163. doi: 10.5004/dwt.2019.24184.