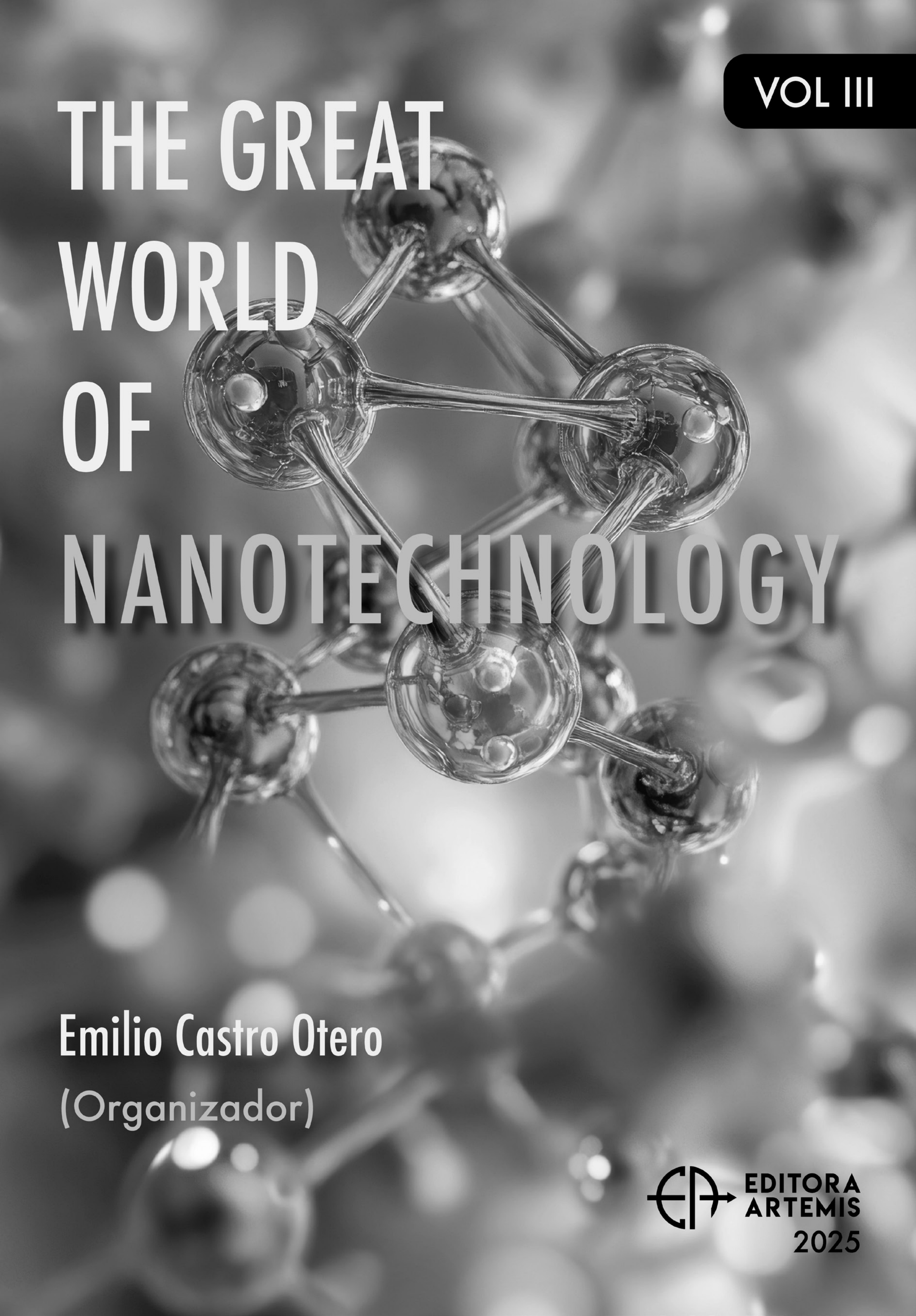
VOL III

THE GREAT WORLD OF NANOTECHNOLOGY

Emilio Castro Otero
(Organizador)

EDITORA ARTEMIS
2025



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FOREWORD

We are thrilled to present the third installment of ***The Great World of Nanotechnology***, a volume dedicated to exploring the cutting edge of nanotechnology applications, from the fundamental science of materials to their tangible impact on health, industry, and the environment. This book is meticulously structured into four thematic blocks, designed to guide the reader through the latest innovations that seek to solve crucial challenges in modern society.

The first pillar of this volume, ***Fundamentals of Nanomaterial Manufacturing and Characterization***, delves into the critical methodologies for creating high-quality nanostructures. Chapter 1 offers systematic research on the Effects of the Transfer Process on the Structure of Graphene Synthesized by Chemical Vapor Deposition. Complementing this, Chapter 2 examines Polymer Nanofibers via Airbrushing.

In ***Nanomaterials for Surface Engineering and Smart Sensors****, the chapters* explore how these nanostructures can be applied in functional devices and material protection. Chapter 3 presents advances in the development of sensors based on graphene functionalized with nanoparticles. Similarly, Chapter 4 addresses the electrodeposition of nanostructured metal coatings.

Nanotechnology in Biomedical and Pharmaceutical Applications brings three chapters focusing on the use of nanotechnology to improve human health. Chapter 5 evaluates the Cytotoxic Effect of Nanoemulsion with Pumpkin Seed Oil on Breast Cancer Cell Lines. In the field of tissue engineering, Chapter 6 describes the development of Alginate/Collagen Structures Enhanced with Conductive Nanoparticles (PEDOT) for the Regeneration of Small-Diameter Blood Vessels. Finally, Chapter 7 discusses the development of an antiseptic gel based on bioactive compounds encapsulated in nanoparticles.

Concluding our exploration, ***Nanotechnological Solutions for Environmental Remediation*** addresses the water pollution crisis. The final chapter describes the Removal of Arsenic from Groundwater Using Recycled Iron Nanoparticles through the development of a low-cost filter that uses iron nanoparticles.

We invite you to immerse yourself in reading The Great World of Nanotechnology. Vol. III, where science on the smallest scale translates into large-scale solutions. We sincerely hope that this compilation of advanced research will not only be of utmost interest to you, but also inspire new directions of study and application in this infinitely promising field.

Emilio Castro Otero

PRÓLOGO

É com grande entusiasmo que apresentamos a terceira edição de ***The Great World of Nanotechnology***, um volume dedicado a explorar a vanguarda das aplicações nanotecnológicas, desde a ciência fundamental dos materiais até o seu impacto tangível na saúde, na indústria e no ambiente. Este livro está meticulosamente estruturado em quatro eixos temáticos, concebidos para guiar o leitor através das mais recentes inovações que procuram resolver desafios cruciais na sociedade moderna.

O primeiro eixo deste volume, ***Fundamentos da Fabricação e Caracterização de Nanomateriais***, aprofunda as metodologias críticas para a criação de nanoestruturas de alta qualidade. O Capítulo 1 oferece uma investigação sistemática sobre os Efeitos do Processo de Transferência na Estrutura do Grafeno Sintetizado por Deposição Química de Vapor e o segundo capítulo examina as Nanofibras Poliméricas via Aerografia.

Em seguida, o eixo ***Nanomateriais para Engenharia de Superfícies e Sensores Inteligentes***, explora como essas nanoestruturas podem ser aplicadas em dispositivos funcionais e proteção de materiais. O Capítulo 3 apresenta os avanços no desenvolvimento de Sensores Baseados em Grafeno Funcionalizado com Nanopartículas. Paralelamente, e o Capítulo 4 aborda a Eletrodeposição de Revestimentos Metálicos Nanoestruturados.

O eixo ***Nanotecnologia em Aplicações Biomédicas e Farmacêuticas***, centra-se na utilização da nanotecnologia para melhorar a saúde humana. O Capítulo 5 avalia o Efeito Citotóxico da Nanoemulsão com Óleo de Semente de Abóbora em Linhagens de Células de Cancro da Mama. No campo da engenharia de tecidos, o Capítulo 6 descreve o desenvolvimento de Estruturas de Alginato/Colagénio Melhoradas com Nanopartículas Condutoras (PEDOT) para a regeneração de Vasos Sanguíneos de Pequeno Diâmetro. Finalmente, o Capítulo 7 expõe a Elaboração de um Gel Antisséptico Baseado em Compostos Bioativos Encapsulados em Nanopartículas.

Concluindo a nossa exploração, o eixo ***Soluções Nanotecnológicas para Remédios Ambientais,*** aborda a crise da contaminação da água. Este último capítulo descreve a Eliminação de Arsénico das Águas Subterrâneas Usando Nanopartículas de Ferro Reciclado, através do desenvolvimento de um filtro de baixo custo que utiliza nanopartículas de ferro.

Convidamo-lo a mergulhar na leitura de The Great World of Nanotechnology Vol. III, onde a ciência na escala mais pequena se traduz em soluções em grande escala. Esperamos sinceramente que esta compilação de pesquisas avançadas não só seja do seu interesse, mas também inspire novos rumos de estudo e aplicação neste campo infinitamente promissor.

Emilio Castro Otero

TABLE OF CONTENTS

CHAPTER 8

ARSENIC REMOVAL FROM GROUNDWATER USING RECYCLED IRON NANOPARTICLES: DEVELOPMENT AND EVALUATION OF A LOW-COST FILTER FOR RURAL COMMUNITIES

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ABSTRACT: The presence of geogenic arsenic in groundwater poses a serious threat to public health in regions such as the Lake Poopó basin in Oruro, Bolivia. This study developed and evaluated a low-cost experimental filter using metallic iron (Fe^0) and iron oxide (Fe_3O_4) nanoparticles obtained from recycled iron shavings using top-down and bottom-up filtration technologies. The nanoparticles were integrated into a homemade filtration system along with readily available materials such as sand, charcoal, and ground brick. Kinetic and adsorption tests were performed under controlled conditions, achieving arsenic removal rates exceeding 97% with Fe^0 nanoparticles and 91% with Fe_3O_4. These results best fit the Freundlich isotherm model and second-order kinetics, which describe the arsenate adsorption behavior on both nanoparticles. The filter proved effective for up to 13 consecutive treatment cycles, reducing arsenic concentrations to levels ≤ 0.01 mg/L. This approach represents a sustainable, economical, and technically viable alternative for rural communities affected by this contaminant.

KEYWORDS: arsenic; iron nanoparticles; iron oxide; groundwater; low-cost filter; adsorption.

1. INTRODUCTION

Arsenic is an inorganic contaminant naturally present in aquifers of volcanic origin, especially in Andean regions. In Bolivia, its presence in groundwater has been little studied, despite representing a significant health risk. The World Health Organization (WHO) establishes a maximum limit of 10 µg/L for arsenic in drinking water. However, concentrations of up to 112 µg/L have been detected in the community of San Agustín de Puñaca. In groundwater bodies, arsenic is found as hydrogen arsenate and arsenic acid, which, under oxidizing or reducing conditions, can release As $^{+5}$ or As $^{+3}$ ions, respectively. The availability and transport of these compounds in the environment are mainly determined by the pH of the groundwater and by interaction with soil minerals through adsorption and desorption processes. In this context, an experimental filter based on recycled nanomaterials was developed as an accessible and effective solution for arsenic removal. The behavior of Fe^0 and Fe_3O_4 nanoparticles was evaluated using kinetic models and adsorption and equilibrium isotherms for arsenic removal in groundwater samples, allowing the determination of whether the mechanism corresponded to physisorption or chemisorption.

2. MATERIALS AND METHODS

Water samples were collected at five sampling points. Analyses included pH, conductivity, turbidity, and anions. (Bicarbonates, phosphate, nitrates, sulfates), cations (silicon, iron), and total arsenic. To determine the initial arsenic concentration, Atomic Absorption Spectrophotometry (AA500) was used. Samples were microfiltered through a 0.45 µm membrane (Hawach Scientific) using a vacuum pump and then acidified with 2–3 drops of 1% (w/v) HNO_3 (trace metal grade). All samples were stored at low temperature (4°C). Arsenic concentrations were measured using an Atomic Absorption Spectrophotometer to assess the filter's adsorption efficiency.

Metallic iron (Fe^0) and iron oxide (Fe_3O_4) nanoparticles were synthesized from iron shavings using top-down and bottom-up physical and chemical methods. (Torres Espada, 2020) The resulting particles ranged in size from 20–200 nm. The filter consisted of a 5 × 20.6.cm PVC column with 12 layers of filter materials: Fe^0 and Fe_3O_4 nanoparticles, sand, charcoal, and ground brick. (TorresEscalera, 2024) The downward flow was gravity-fed at 0.16 L/h. Batch tests were performed with different concentrations of nanoparticles (10–100 mg), contact times (10–240 min), pH of the natural water solution and 250 RPM. To determine the percentage of arsenic removal. To study the adsorption kinetics of arsenate on metallic iron and iron oxide particles, jar tests were performed at 250 RPM for predetermined intervals (10, 20, 30, 60, 120 and 240 min) during stirring, using 10 and 100 mg of nanoparticles at a pH of 7.86. The best-fitting isothermal and kinetic models were determined according to the coefficient of determination (R^2 value).

Finally, for the isotherm study, experiments were conducted with an initial arsenate concentration of 112 µg/L, using a dosage of 10–100 mg for both nanoparticles at 250 RPM for different times (10, 20, 30, and 60 min). An aliquot was taken from each batch and filtered for arsenic concentration analysis of the filtrate. Several fitting models (Langmuir, Freundlich, and Dubinin) were tested to find the best fit between the experimental data and the theoretical behavior.

3. RESULTS

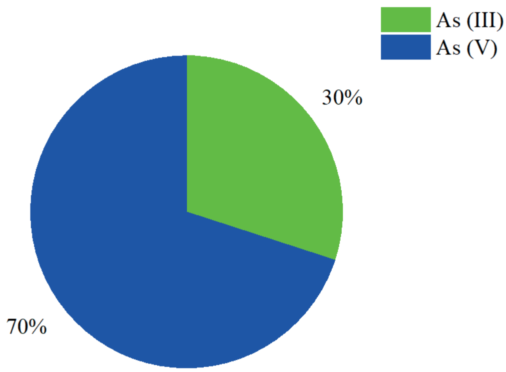
Table 1 shows the results of the physical and chemical parameters of the well located in the community of San Agustín de Puñaca, northeast of Lake Poopó, in the department of Oruro. The water quality meets the Bolivian standard NB 512 for drinking water, except for the arsenic content. The arsenic content is 112 µg-As/L, significantly higher than the limit established by the Bolivian standard NB 512 of 10 µg-As/L. The contents of competitive anions – sulfates, nitrates, chlorides, and phosphates – are relatively low, with the exception of silicates.

Table 1. Physical-chemical characterization of the San Agustin de Puñaca community.

Parameters	Units	Analytical Method	Results	Permissible limit NB 512
pH		SM 4500-H / 1992 Potentiometric	7.86	6.5-9.0
Temperature	°C	SM 2550/1992	18.8	-
Electrical Conductivity	µS/cm	SM 2510 / 1992 Conductimetric	970	1500
Potential Oxidation-Reduction	mV	Potentiometric	98	-
Turbidity	NTU	2130-B-SM Turbidimeter	3.19	5
Alkalinity	mg/L	ASTM D 1057-02	150	370
Bicarbonates	mg/L	ASTM D 3875-03	94	370
Chlorides	mg/L	SM 3030-F / 1992	0.45	250
Sulfates	mg/L	ASTM D 516-02	103.1	400
Nitrates	mg/L	DIN 38405 T10 mod.	7.05	45
Phosphates	mg/L	Photometric	0.20	-
Silicates	mg/L	ASTM D 859-05	22.77	-
Iron	mg/L	ASTM D 1068-05A	<0.018	0.3
Arsenic	mg/L	SM 3030-F / 1992 EAA	0.12	0.01

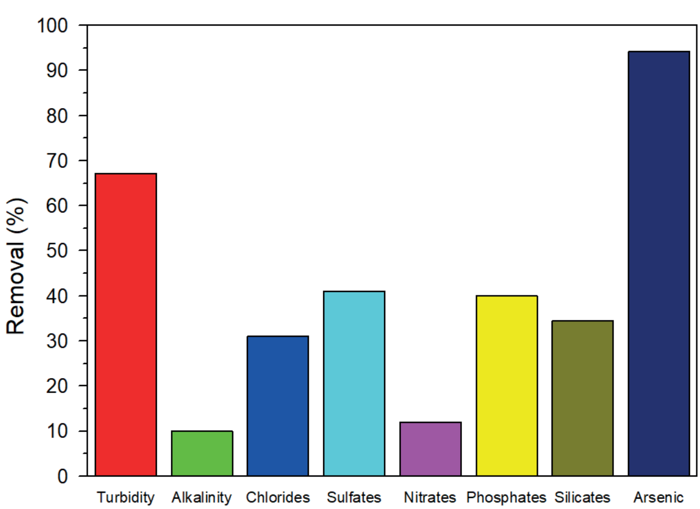
Arsenic speciation in groundwater was determined by analyzing the redox potential (Eh) versus pH diagram, which established that under oxidative conditions it has an Eh of 98 mV and a natural pH of 7.86 (Figure 1). Arsenate As^{+5} is the dominant species, having an anionic product of HAsO42- , which favors its removal through adsorption processes, since it is negatively charged. Neutral H_3AsO_3 at natural pH values (between 6 and 9) is not easily removed. Since arsenic is present as $HAsO_4^{2-}$, it is not necessary to increase the oxidation-reduction potential, Eh, of the contaminated well by aeration, or by the use of chemical reagents to modify the pH, since if the pH is decreased, arsenite As^{+3} will be present as the dominant species, being more toxic, which explains a lower efficiency in arsenic removal systems.

Figure 1. Speciation of arsenic in groundwater.



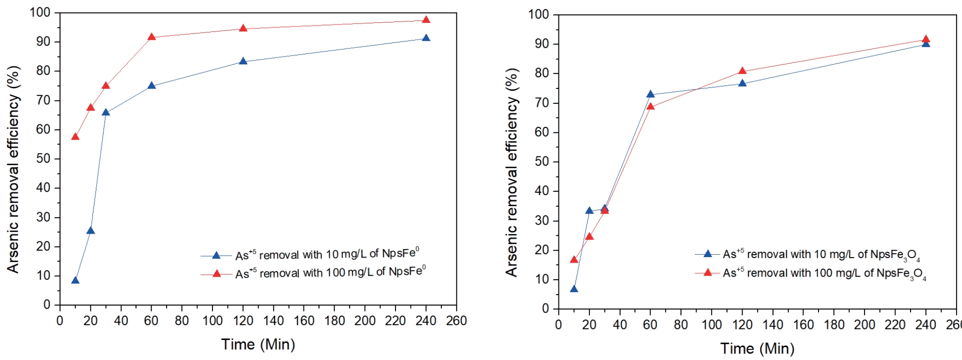
The filter reduced arsenic to 0.007 mg/L in 13 filtration cycles of 10 L, complying with Bolivian standard NB512 and WHO guidelines. Figure 2 shows the physicochemical characterization of the groundwater sample from the community of San Agustin de Puñaca after filtration, reducing turbidity by 67.08%, Aa by 10%, chlorides by 31.11%, sulfates by 41%, nitrates by 12%, phosphates by 40%, and silicates by 34.46%.

Figure 2. Removal of physicochemical parameters.



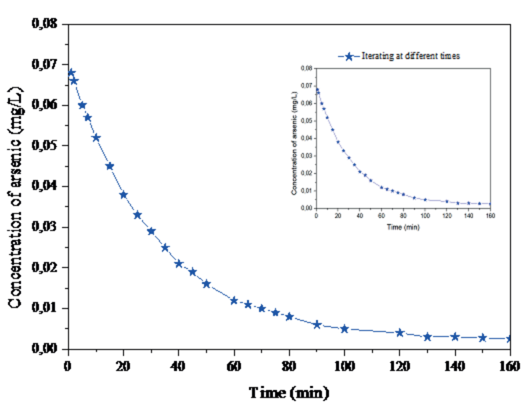
The arsenic removal process under these conditions was optimal, achieving a removal rate of 97.5% for ($Fe^{0)}$ zero valent nanoparticles and 91.7% for Fe_3O_4 iron oxide nanoparticles. The sample was collected directly from its natural environment and contains not only arsenic but also other minerals, organic compounds, and other physicochemical properties, including nitrates, silicates, phosphates, sulfates, etc. All these factors, among others, interfere with the adsorption process, making it less efficient.

Figure 3. Effect of contact time on arsenic removal efficiency with different doses 10-100 mg a) iron nanoparticles Fe^{0} b) iron oxide nanoparticles Fe_3O_4.



Because the adsorption process was too rapid, exceeding 57.5% efficiency in the first 10 minutes, an equation was developed to describe the adsorption process in such a way that the data could be iterated and the removal efficiency obtained every 2 min, 3 min, 4 min, 5 min, 6 min, etc. It can be seen in Figure 4, that just one minute of contact of the iron nanoparticles with the contaminant, an efficiency of 52% is achieved, thus confirming that the use of metallic iron nanoparticles is effective in the removal of arsenic thanks to their surface area ranging from 60-200 nm, high capacity and high reactivity characteristics of the magnetic material used.

Figure 4. Exponential fit describing the concentration of arsenic in zero valent nanoparticles (Fe^{0}).

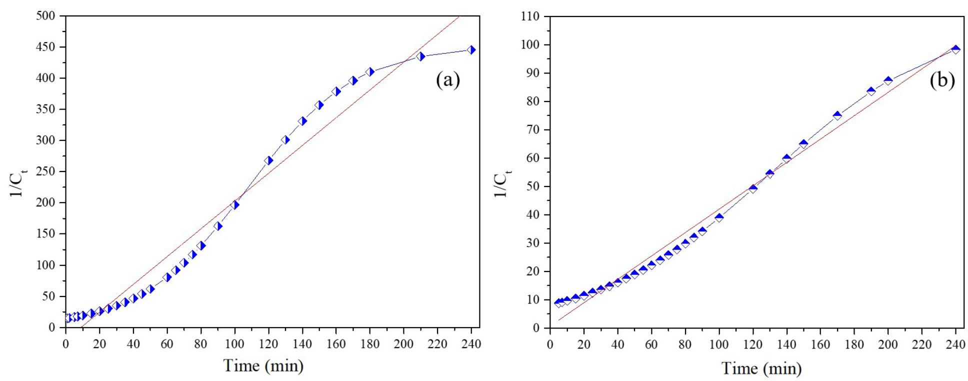


To understand the adsorption mechanism and efficiency of both nanoparticles, the experimental data were analyzed using first-order and second-order kinetic models. The correlation coefficient (R^2) was used to evaluate the best kinetic model (Table 2). Of all the models, the second-order model showed a good correlation coefficient and best fit the experimental data (Figure 5).

Table 2. Kinetic parameters for arsenic removal using metallic iron nanoparticles and iron oxide.

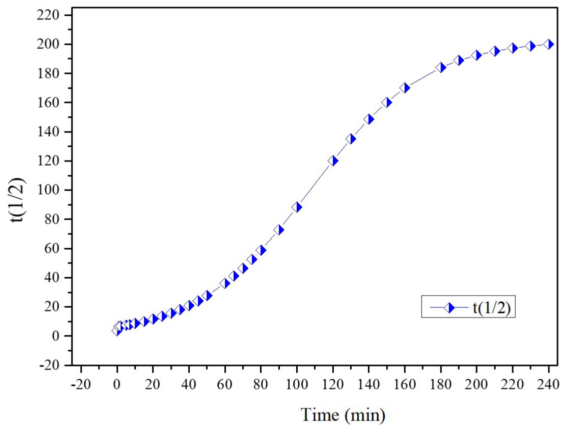
Kinetic Model	Constant	Worth
First Order with NpsFe ^{0}	K	-0.0169
	R^2	0.8971
Second Order with NpsFe ^{0}	K	2,2288
	R^2	0.9607
First Order with NpsFe$_3$O$_4$	K	-0.0115
	R^2	0.9526
Second Order with NpsFe$_3$O$_4$	K	0.4127
	R^2	0.9841

Figure 5. Second-order kinetic model for arsenic removal (a) metallic iron nanoparticles (b) iron oxide nanoparticles.



The half-life with respect to contact time, as shown in (Figure 6), shows that after 180 minutes the nanoparticles no longer adsorb more arsenic, so they begin to saturate and the half-life tends to be constant.

Figure 6. Half-life vs. contact time with NpsFe ^{0}.



Adsorption isotherm models are fundamental to describing the equilibrium between the adsorbate and the adsorbent. To evaluate the adsorption behavior of the nanoparticles, some well-known isotherms such as the Langmuir, Freundlich, and Dubinin-Radushkevich constants were considered. The fitting results are shown in Figure 7. Table 3 shows the linear regression results according to the Langmuir model. The dimensionless factor R_{$_{L}$} is less than one; therefore, applying the Langmuir isotherm is unfavorable. The calculated Langmuir constant Kf $_{,}$ which can be interpreted as the enthalpy of adsorption, showed negative values. This suggested the exothermic nature of the process and indicated that the surface of the metallic iron and iron oxide nanoparticles was energetically favorable for reacting with the ions.

Table 3. Langmuir model results for arsenic adsorption on nanoparticles.

LANGMUIR MODEL				
PARAMETER	Quantity of NpsFe ^{0} 0.01 g	Quantity of NpsFe ^{0} 0.1 g	Quantity of NpsFe $_{3}$O $_{4}$ 0.01 g	Quantity of NpsFe $_{3}$O $_{4}$ 0.1 g
Adsorption capacity of a monolayer Q_{or} (mg/g)	1,0683	0.7088	1,0243	0.1789
Langmuir constant K_{f} (L/mg)	-33.5520	-26.7710	-30.9536	-32.8267
Adsorption capacity q_{e} (mg/g)	9,0000	1,1000	8,7500	0.8250
Regression coefficient $^{R^2}$	0.5863	0.7537	0.3499	0.6984
R_{L}	-0.3305	-0.4520	-0.3684	-0.3402

Table 4 shows the results of the Freundlich model; a higher Kf value indicates a greater adsorption capacity of the adsorbent. Furthermore, a Kf value greater than one indicates the spontaneous nature of the process (Mandal et al., 2014) lanthanum diethanolamine hybrid material is synthesized by co-precipitation method and used for the removal of Cr(VI. However, for all adsorption isotherms for different quantities of nanoparticles, the regression coefficient R^2 was more reliable for the Freundlich model, fitting the experimental data better than for the Langmuir model.

The value of n is related to the distribution of ions bound to the active sites on the surface of the nano-adsorbent. The negative values of n for the different quantities of nanoparticles indicate that the ions of the species present are unfavorable, making it impossible to determine whether the process is by physisorption or chemisorption.

Table 4. Freundlich model results for arsenic adsorption on nanoparticles.

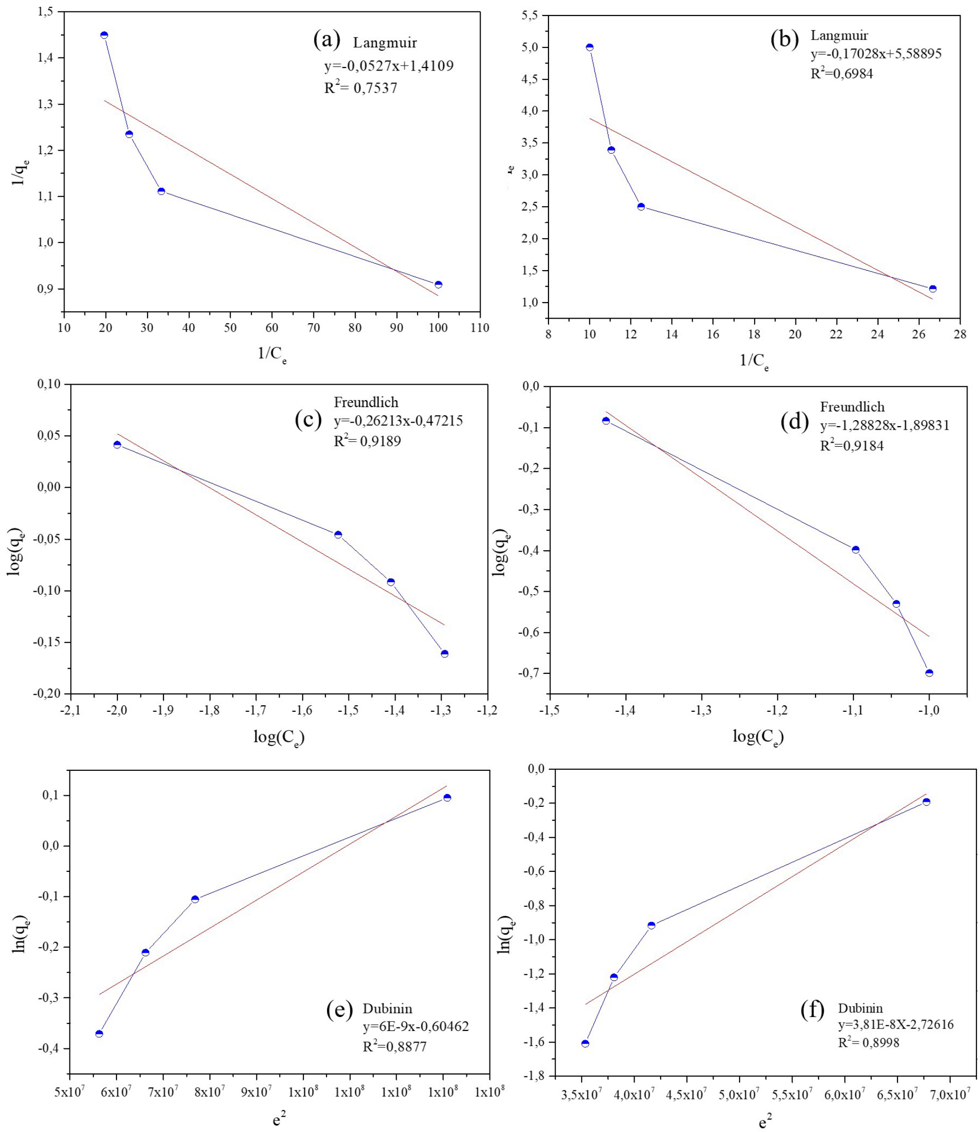
FREUNDLICH MODEL				
PARAMETER	Quantity of $NpsFe^{0}$ 0.01 g	Quantity of $NpsFe^{0}$ 0.1 g	Quantity of $NpsFe_3O_4$ 0.01 g	Quantity of $NpsFe_3O_4$ 0.1 g
Freundlich constant K_f (L/mg)	0.0492	0.3372	0.0440	0.0126
Adsorption capacity of a monolayer Q_e (mg/g)	0.2145	0.6237	0.2576	0.1498
Adsorption capacity q_e (mg/g)	9,0000	1,1000	8,7500	0.8250
Regression coefficient $^{R^2}$	0.8777	0.9189	0.7253	0.9184
n	-0.6496	-3.8149	-0.6199	-0.7762

Table 5 shows the results obtained after applying the Dubinin model. The regression coefficient was almost the same as those calculated by the Freundlich model.

Table 5. Results of the Dubinin model for the adsorption of arsenic on nanoparticles.

DUBININ-RADUSHKEVICH MODEL				
PARAMETER	Quantity of $NpsFe^{0}$ 0.01 g	Quantity of $NpsFe^{0}$ 0.1 g	Quantity of $NpsFe_3O_4$ 0.01 g	Quantity of $NpsFe_3O_4$ 0.1 g
Dubinin constant K_f (L/mg)	$4.47x10^{-8}$	$6.00x10^{-9}$	$4.57x10^{-8}$	$3.18x10^{-8}$
Adsorption capacity of a monolayer Q_e (mg/g)	0.3559	0.5463	0.3745	0.06547
Adsorption capacity q_e (mg/g)	9,0000	1,1000	8,7500	0.8250
Regression coefficient $^{R^2}$	0.8492	0.8877	0.6712	0.8998

Figure 7. Equilibrium adsorption isotherm for arsenic on metallic iron nanoparticles and iron oxide. (a) Langmuir isotherm with 100 mg of NpsFe ^{0}. (b) Langmuir isotherm with 100 mg of NpsFe $_{3}$O $_{4}$. (c) (d) Freundlich isotherm with 100 mg of NpsFe ^{0}. (e) Freundlich isotherm with 100 mg of NpsFe $_{3}$O $_{4}$. (f) Dubinin model with 10 mg of NpsFe ^{0}. (f) Dubinin model with 100 mg of NpsFe $_{3}$O $_{4}$.



Thermodynamic parameters, such as Gibbs free energy (ΔG), can help determine the likelihood, spontaneity, or exothermic or endothermic states of a reaction – critical aspects of an adsorption process. The energy required to transfer one mole of metallic iron nanoparticles to iron oxide was greater than 40 kJ/mol for arsenic. These results confirmed that the interactions between the adsorbate and the adsorbent were chemical, i.e., a chemisorption process.

4. DISCUSSION

The use of recycled nanoparticles represents a technological innovation with a positive environmental and social impact. Despite the small quantities used, the system achieved results comparable to more expensive commercial technologies. Its combination with locally sourced materials facilitates community implementation. The filter also demonstrated the removal of other contaminants (phosphates, silicates, nitrates), increasing its versatility.

5. CONCLUSIONS

- The presence of geogenic arsenic in the community's groundwater was confirmed, in concentrations dangerous to human health.
- The experimental filter developed effectively removed arsenic to levels below that established by the Bolivian standard NB 512 of 10 µg-As/L, making it an accessible solution for rural areas.
- The adsorption fit the Freundlich model and showed second-order kinetics, indicating a chemisorption process and occurring spontaneously.
- The system is replicable, economical and sustainable, with potential for application in other regions with similar problems.

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ABOUT THE ORGANIZER

Emilio Castro Otero é professor da área de Bioengenharia na *Universitat Internacional de Catalunya*, Barcelona, Espanha. Pesquisador com ampla trajetória científica nas áreas de biomateriais, nanotecnologia, química física de polímeros e sistemas nanoestruturados aplicados à medicina regenerativa e à liberação controlada de fármacos. Sua produção abrange estudos fundamentais sobre auto-organização molecular, interações entre copolímeros e surfactantes, estabilidade proteica e desenvolvimento de nanopartículas e hidrogéis inteligentes, contribuindo de maneira significativa para a compreensão dos mecanismos físico-químicos que governam materiais avançados e sua aplicabilidade biomédica. Seu trabalho mais recente, publicado em Acta Biomaterialia (2023), aborda o papel angiogênico e imunomodulador de íons nas fases iniciais da regeneração óssea, consolidando sua atuação no campo dos biomateriais bioativos. Ao longo de sua carreira, publicou artigos de impacto em periódicos como Langmuir, Biomacromolecules, Journal of Biomedical Nanotechnology, Macromolecular Bioscience, Journal of Physical Chemistry B, Chemical Physics e Journal of Colloid and Interface Science, além de contribuir com capítulo de livro na área de nanomedicina, ampliando sua presença internacional na literatura científica.

Entre suas contribuições relevantes, destacam-se estudos sobre auto-organização de elastina recombinante e copolímeros responsivos à temperatura, síntese e caracterização de nanopartículas funcionalizadas, incluindo magnetita peguilada e nanocápsulas multifuncionais, e sistemas poliméricos capazes de encapsular e liberar fármacos de forma controlada, com foco em aplicações oncológicas e terapêuticas avançadas. Sua pesquisa também inclui extensas investigações termodinâmicas envolvendo surfactantes, copolímeros e sistemas micelares complexos, bem como análises detalhadas de interações entre proteínas e fármacos anfifílicos, contribuindo para o entendimento de processos de dobramento, estabilidade e agregação proteica. Com forte perfil interdisciplinar, o pesquisador tem colaborado com grupos internacionais de renome em bioengenharia, físico-química de materiais, nanotecnologia e biotecnologia aplicada, contribuindo para o desenvolvimento de estratégias inovadoras em engenharia de tecidos, medicina regenerativa e materiais biomiméticos.

Ao longo de quase duas décadas de produção científica contínua, Emilio Castro Otero consolidou uma carreira marcada pela investigação rigorosa, inovação metodológica e abordagem integrada da ciência dos materiais, oferecendo contribuições relevantes tanto para o avanço do conhecimento fundamental quanto para o desenvolvimento de soluções tecnológicas com potencial translacional na área biomédica.

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INDEX

A

B

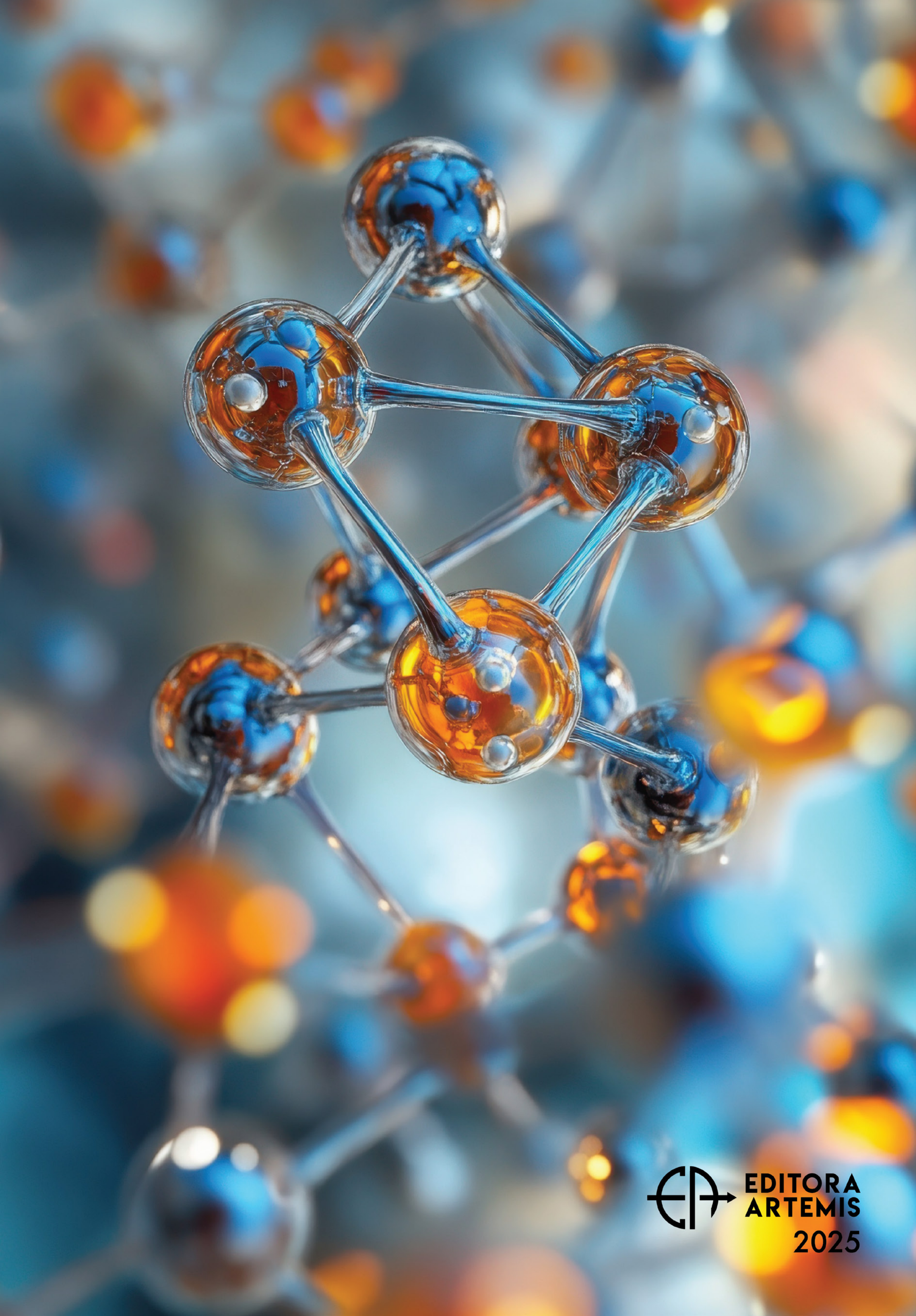
C

E

F

G

I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