TERRA LATINOAMERICANA

Physicochemical Analysis of Sulfide Groundwater in the Ejido Puente Negro in Coahuila, Mexico, Community Diagnosis and Proposal for Sulfide Desorption
Análisis Fisicoquímico de Agua Subterránea Sulfurosa en el Ejido Puente Negro en Coahuila, México, Diagnóstico Comunitario y Propuesta de Desorción de Sulfuros

Diego Martínez-Carrillo[1,2], Cynthia Guerrero-Bermea[3‡], Guadalupe Esmeralda Alcalá-González[3], Rubí Alcalá-González[3], Hilda Cristina Martínez-Tovar[3], Perla Mayara Alcalá-González[3], José Caín Hernández-Rodríguez[1], Juan Josué Enciso-Cárdenas[1], and Carlos Alberto Ávila-Orta[2]

[1] Centro de Investigación en Geociencias Aplicadas UAdeC. Calle 5 de febrero esq. con Boulevard Simón Bolívar No. 303-A, Colonia Independencia. 26830 Nueva Rosita, Coahuila, México; (D.M.C.), (J.C.H.R.), (J.J.E.C.).
[2] Centro de Investigación en Química Aplicada (CIQA). Boulevard Ingeniero Enrique Reyna Hermosillo No. 140, Colonia San José de los Cerritos. 25294 Saltillo, Coahuila, México; (D.M.C.), (C.A.A.O.).
[3] Tecnológico Nacional de México, ITES de la Región Carbonífera. Carretera 57 km 120. Colonia Villa de Agujita. 26950 Sabina Coahuila, México; (C.G.B.), (G.E.A.G.), (R.A.G.), (H.C.M.T.), (P.M.A.G.).
[‡] Corresponding author: 2157@rcarbonifera.tecnm.mx

SUMMARY

The Ejido Puente Negro is characterized by the economic activities of farming and agriculture, despite having extensive periods of drought. Access to groundwater through dug wells is one of the main alternatives to meet the living needs of its inhabitants. However, poor practices have resulted in groundwater degradation, compromising phreatic mantles. The generation of treatment methods results in a good option to supply the population and ensure its quality. However, it is essential that residents are informed and have sufficient knowledge to implement these practices. The present work shows a physicochemical study of groundwater from different wells located in the Ejido. A kinetic analysis of the desorption of sulfides was also carried out, concluding that their natural desorption is sufficient to reduce more than 70% of their concentration in a period of 6 days. Additionally, the geology of the area is assessed in search of possible influence on groundwater contamination. Finally, a social study is presented about contaminated groundwater, the health implications involved in its consumption, and the understanding of purification and reuse processes.

Index words: *desulfurization, hydroxide sulfur, water quality.*

RESUMEN

El Ejido Puente Negro se caracteriza por las actividades económicas de ganadería y agricultura, a pesar de que se tengan épocas extensas de sequía. El acceso al agua subterránea mediante pozos excavados es una de las principales alternativas para cubrir necesidades de vida de sus pobladores. Sin embargo, las malas prácticas han resultado en la degradación de los mantos freáticos, comprometiendo la calidad del agua. La generación de métodos de tratamiento resulta en una buena opción para abastecer a la población y asegurar su calidad. Sin embargo, es indispensable que los habitantes estén informados y cuenten con los conocimientos suficientes para implementar dichas prácticas. El presente trabajo muestra un estudio fisicoquímico del agua subterránea proveniente de diferentes pozos ubicados en el ejido. Asimismo, se realizó un análisis cinético de la desorción de sulfuros concluyendo que su desorción natural es suficiente para reducir más del 70% de su concentración en

Recommended citation:

Martínez-Carrillo, D., Guerrero-Bermea, C., Alcalá-González, G. E., Alcalá-González, R., Martínez-Tovar, H. C., Alcalá-González, P. M., ... & Ávila-Orta, C. A. (2025). Physicochemical Analysis of Sulfide Groundwater in the Ejido Puente Negro in Coahuila, Mexico, Community Diagnosis and Proposal for Sulfide Desorption. *Terra Latinoamericana, 43*, 1-11. e2098. https://doi.org/10.28940/terra.v43i.2098

Received: September 27, 2024.
Accepted: February 25, 2025.
Article, Volume 43.
August 2025.

Section Editor:
Dr. Fernando Ayala Niño

Technical Editor:
M. C. Ayenia Carolina Rosales Nieblas

un periodo de tiempo de 6 días. Adicionalmente, se evalúa la geología de la zona en busca de posible influencia en la contaminación de las aguas subterráneas. Por último, se presenta un estudio social sobre el conocimiento de la población acerca de aguas subterráneas contaminadas, las implicaciones en la salud que involucra su consumo y comprensión sobre procesos purificación y reutilización.

Palabras clave: *desulfuración, sulfuro de hidrógeno, calidad del agua.*

INTRODUCTION

Groundwater is an essential resource for human survival and economic development in regions with dry or arid climates (Bosch, 2000), which is characteristic of most of the Coahuila territory. Access to groundwater through dug wells is one of the main initiatives to meet certain needs. Globally, approximately 70% of extracted groundwater is used for agricultural production of food, livestock, and industrial crops (Milera-Rodríguez, 2021; Díaz-González, Rosales, and Chávez, 2023). Despite the numerous social and economic benefits derived from the use of this resource, poor management practices have resulted in the overexploitation and degradation of groundwater (Rodríguez-Orozco, Ruiz, and Fajersson, 2010).

According to a study carried out (Gleeson, Wada, Bierkens, and Van Beek, 2012), groundwater reserves are decreasing; approximately 20% of the aquifers in the world are overexploited. Additionally, the National Water Information System (CONAGUA, 2019) indicates that approximately 24% of Mexico's aquifers are in this condition. On the other hand, the quality and availability of groundwater face the pressure exerted by anthropogenic pollution mainly caused by the discharge of urban, industrial, and agricultural effluents (FAO, 2015), as well as natural origin that can be caused by the incorporation of substances present in metalliferous, non-metalliferous, radioactive and hydrocarbon deposits (Auge, 2006), as well as coal mining (Wang, Gao, Jiang, Zhang, and Liu, 2021; Zhang, Xu, Sun, Gao, and Zhu, 2022; Chen, Feng, and Gong, 2023). Regardless of the contamination source, the well water characterization is important for determining the remediation method or technique to be used (Abed, Ștefan, and Ștefan, 2024).

The World Health Organization (WHO), in its document "Guidelines for the Quality of Drinking Water" (WHO, 2011), establishes the reference parameters for measuring the permissible concentrations of the most common contaminants found in water. Similarly, in Mexico, the Official Mexican Regulation NOM-127-SSA1-2021 (SSA, 2021) establishes the permissible limits of pollutants in water for human use and consumption. It is important to note that in none of the documents is hydrogen sulfide considered a primary contaminant.

Sulfur pollution has gained significant global attention (Li, Masuda, Kusakabe, Yanagisawa, and Zeng, 2006; Satapathy *et al*., 2017; Hinckley, Crawford, Fakhraei, and Driscoll, 2020). The effects of sulfur on water quality are mainly caused by the presence of compounds such as hydrogen sulfide (H_2S) and sulfates (SO_4^{2-}), which cause effects focused on the liquid's acceptability due to odor and taste characteristics, possible laxative and corrosive effects (Figure 1) that prevent its domestic use (WHO, 2011).

Figure 1. Metal pipe used in water extraction corroded by H2S.

There are studies worldwide that characterize water contaminated by sulfides to determine the source of contamination or to propose remediation (Wilson, Litvinenko, and Obukhov, 2020). Mexico is not the exception in this case; different types of groundwater contamination have been studied in the Mexican Republic (Sánchez, Álvarez, Pacheco, Carrillo, and González, 2016; Guerrero and Castañeda, 2017; Cruz *et al*., 2022), but it has not been considered whether the population near the study sites is aware of this problem and their availability as a community to support remediation or water treatment.

Important coal deposits in Mexico are well-known and are primarily located in Coahuila, Oaxaca, and Sonora. The so-called Región Carbonífera in Coahuila (Figure 2) is the most significant in the country (Campos, 2022), comprising two important sub-regions: the Sabinas Basin and the Fuentes-Rio Escondido Basin (Corona-Esquivel, Tritlla, Benavides, Piedad, and Ferrusquía, 2006). Within the territory of the Sabinas Basin, small and medium-sized coal producers generate wastewater with contaminants such as hydrocarbons, ammonia and amines, oxygenated compounds, acids, inorganic salts, and heavy metals in ionic form. Furthermore, the area has a depth at the shallow static level, which varies from 5 to 30 meters (CONAGUA, 2015). On the border of the basin, there are underground waters that are contaminated by sulfides, as is the case of the Ejido Puente Negro.

This work includes an analysis of various water quality parameters, such as pH, electrical conductivity, total dissolved solids, temperature, salinity, heavy metals (Fe, Pb, As, Cd, Al, Mg), and total sulfide concentration. The latter is evaluated using the iodometric method defined in the NMX-AA-084-SCFI-2008 standard (SE, 1982), which involves the kinetics of sulfide desorption as a basis for a remediation proposal for contaminated water. Additionally, possible sources of contamination are examined, as well as societal perspectives on this issue.

MATERIALS AND METHODS

Physicochemical Characterization of Water from Underground wells

Seven water wells were located and visited under the supervision and guidance of the Ejido Puente Negro Commissionerate. The location of each point of interest was obtained using GPS equipment in the WGS 84 UTM 14N coordinate system. The wells were identified numerically from one to seven based on the order in which they were inventoried. Each of them was described through observations of their physical appearance and characteristics, such as color, odor, and taste, provided by the inhabitants.

A preliminary *in-situ* physicochemical characterization was carried out, considering only the pH, electrical conductivity, total dissolved solids, temperature, and salinity values for each sample using the HANNA HI98194 multiparameter equipment.

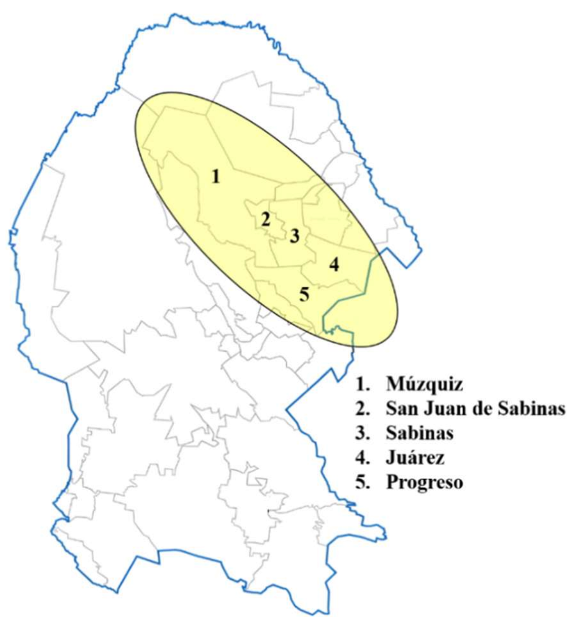

Figure 2. Location of the municipalities that make up the Región Carbonífera in the state of Coahuila, Mexico.

Once the preliminary physicochemical results were evaluated, one well whose analysis values were outside or close to the permissible limits reported for human consumption was selected. Water samples were collected for a complementary physicochemical analysis to determine the total concentration of sulfides and heavy metals (Fe, Pb, As, Cd, Al, Mg), following preservation procedures following Mexican standards for NMX-AA-084-1982 “Determination of Sulfides” (SE, 1982) and NMX-AA-051-SCFI-2001 “Determination of Metals by Atomic Absorption in Natural, Drinking, Wastewaters and Wastewaters Treated” (SE, 2001)

Hydrogen Sulfide Desorption Kinetics

One of the sulfur water treatment techniques is natural aeration of the water to remove the hydrogen sulfide present. The sulfide desorption kinetics were developed from a standard solution of 50 mg L^{-1} sulfide (S^{2-}). Sodium sulfide (Na_2S) was used as a sulfide generator based on the following chemical reaction:

$$Na_2S + 2H_2O \rightarrow H_2S + 2NaOH \quad (1)$$

From a 500 mL sample in an open beaker, promoting natural aeration at 23 °C, aliquots were taken at different time intervals (initial, 1 day, 6 days, and 14 days) to analyze sulfide content using the iodometric method defined in the NMX-AA-084-SCFI-2008 standard (SE, 2008). To describe the desorption, the following kinetic model was used:

$$\frac{dC}{dt} = -kC \quad (2)$$

Where C is the sulfide concentration, *t* is the natural aeration time in days, *k* is the desorption kinetic constant in s^{-1}. Integrating and evaluating for an initial time (t_i, 0 days) at an initial concentration (C_i) up to any time (t) and its corresponding concentration (C_t), we have Equation 3:

$$C_t = C_i exp^{(-kt)} \quad (3)$$

However, since there will never be a sulfide concentration equal to zero, an additional concentration that represents the minimum expected sulfide concentration (C_a) will have to be considered in Equation 3. Equation 4 would represent the mathematical model of the desorption kinetics. It should be noted that in the second member of Equation 4, Ci was changed to C_b, which will be equal to the difference between the initial concentration (C_i) and the minimum concentration reached (C_a).

$$C_t = C_a + C_b exp^{(-kt)}$$

$$if\ t \rightarrow 0\ then\ C_t = C_a + C_b = C_i, if\ t \rightarrow \infty\ then\ C_t = C_a \quad (4)$$

Where the *k* value of the kinetic model were calculated using the method used by González-Barraza, Martínez, Moreno, and López (2022).

Contamination of Groundwater Due to the Dissolution of Sulfides from Mineral Coal (Pyrite)

Sulfide dissolution tests were conducted in batch using coal samples extracted from the Región Carbonífera to evaluate the concentration of sulfides provided by this mineral directly in contact with water (specifically pyrite, FeS_2). The methodology used for the dissolution tests was as follows: a coal sample was conditioned to a particle size of less than 60 mesh, in accordance with the ASTM D4239 standard, and its sulfur content (in percentage) was analyzed using a Leco SC analyzer. -144DR. Four mixtures, each consisting of 50 g of conditioned carbon and 500 mL of deionized distilled water, were prepared, confined in 4 Nalgene bottles of 1 L capacity, and labeled for identification as MA, MB, MC, and MD.

Before preparing the mixtures, the physicochemical properties of the deionized distilled water were analyzed using a HANNA HI98194 multiparameter device (pH, electrical conductivity, total dissolved solids, and salinity). These mixtures were kept at rest; after the first month of rest, the MA mixture was taken and filtered to separate the carbon from the solution. The physicochemical properties of the solution and the sulfur content of the coal were analyzed. After the second month of rest, the MB mixture was taken, and the same analyses were carried out on the MA mixture. The same procedure was followed for the MC and MD mixtures in the third and fourth months, respectively.

Additionally, a bibliographic study was conducted to describe the geology of the study area and its relationship with the natural contamination of water by sulfides present in the stratigraphy of the Región Carbonífera.

Social Perspective

Simultaneously with the previously mentioned physicochemical analyses, a survey was designed as a support instrument to evaluate community knowledge about the existence of water contaminated by sulfides, the health problems that can arise from its consumption, as well as treatments and reuse options for sulfurous groundwater. The survey was conducted among 1000 individuals, both male and female, aged 15 to 75 years, including residents of the study area and surrounding municipalities.

RESULTS AND DISCUSSION

Physicochemical Characterization of Water from Underground Wells

The seven wells of interest were located in collaboration with the inhabitants of the Ejido Puente Negro to collect samples. Figure 3 shows the location of each of them, as well as the name with which they were labeled according to their characteristics.

The physical characteristics of each well were registered to make inferences about the possible chemical properties of water. The water from the Azufroso well had a foul odor, dark color, visual turbidity, and had evidence of causing diarrhea in cattle when they drink it shortly after it was extracted. The water from the Escolar well and the Dulce 1 and 2 wells had no odor or color, nor were any suspended particles observed with the naked eye. On the other hand, the water from the Salado 1 and 2 wells also had no smell or color but was brackish. The water from the Privado well is slightly salty or brackish, odorless, and a little cloudy, and it is used to water livestock.

Once the study wells were described, a preliminary *in-situ* physicochemical characterization was carried out, obtaining the results shown in Table 1.

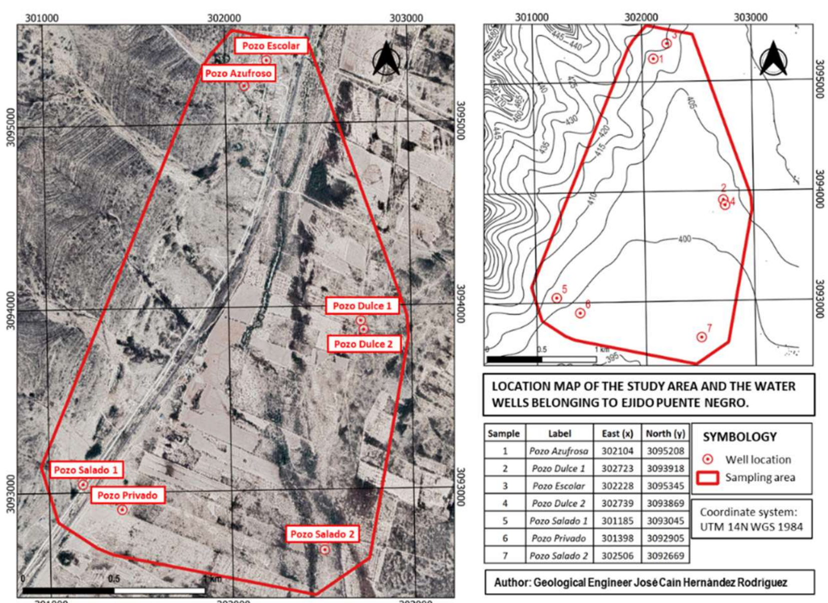

Figure 3. Location plan of the study wells with UTM coordinates.

Table 1. Physicochemical analysis of water samples from underground wells in Ejido Puente Negro.

Sample	Well Label	pH	Conductivity	Absolute conductivity	Total dissolved solids	Temperature	Salinity
			µS cm^{-1}	µS cm^{-2}	mg L^{-1}	°C	PSU
1	Azufroso	7.35	3621.00	3834.00	1809.00	28.00	1.89
2	Dulce 1	7.90	1777.00	1944.00	890.00	29.85	0.89
3	Escolar	7.40	1346.00	1400.00	673.00	27.67	0.67
4	Dulce 2	7.60	1513.00	1644.00	758.00	29.00	0.75
5	Salado 1	8.09	3520.00	3716.00	1760.00	27.90	1.84
6	Privado	7.41	2258.00	2599.00	1129.00	32.90	1.14
7	Salado 2	7.03	1742.00	1856.00	872.00	28.38	0.88

The values of total dissolved solids and pH of the groundwater in the seven study wells were analyzed (Figure 4), comparing them with the permissible limits outlined in NOM-127-SSA1-2021 (SSA, 2021). These two parameters generally present the least variation over time, providing information on water quality, such as the amount of dissolved material, including inorganic salts and organic matter.

The Azufroso, Salado 1, and Privado wells exceed the permissible limit of total dissolved solids for human consumption, while the pH for all wells remains within the permissible range. The increase in the amount of total dissolved solids is directly related to an increase in the conductivity and salinity of the samples (Calderon y Pulgar, 2023[1]), as reflected in Table 1.

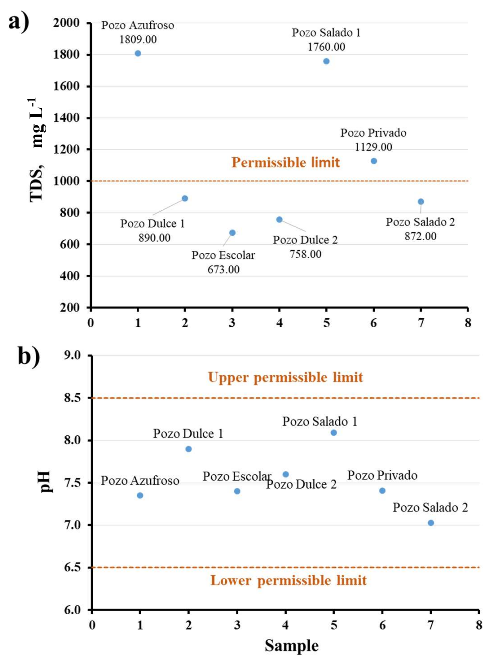

Figure 4. Graph of (a) total dissolved solids and (b) pH of the groundwater of the study wells, with reference to the permissible limits according to NOM-127-SSA1-2021(SSA, 2021).

[1] Calderon-Nieves, J. B., & Pulgar-Gonzalez, A. F. (2023). *Efecto de la conductividad eléctrica a partir de la salinidad y sólidos disueltos en los procesos biológicos de nitrificación y desnitrificación para la remoción de compuestos nitrogenados en aguas residuales domésticas*. Tesis para obtener el grado de Doctor en Ciencias. Universidad de la Costa, Corporación Universidad de la Costa. Disponible en: https://hdl.handle.net/11323/10205

As a reference to the physicochemical results shown above, the Azufroso well exhibits higher electrical conductivity and total dissolved solids values than the other wells. According to the classification based on the diagram of the United States Salinity Laboratory (Richards, 1954), the water from this well is classified as very highly saline (C4) because it has electrical conductivity greater than 2250 µS cm^{-1}, and total dissolved solids values above 1440 mg L^{-1}, being considered water of limited use. This well was selected as a case study, with the intention of improving water quality for possible agricultural or industrial use.

Knowing that the total amount of dissolved solids is mainly the set of minerals, salts and metals dissolved in the water (Camacho-González y Quimis, 2022[2]), the concentration of some heavy metals and metalloids in the water from the Azufroso well was evaluated, comparing the results with the limits allowed for water for human use and consumption, in accordance with NOM-127-SSA1-2021(SSA, 2021). The results of the analysis are presented in Table 2, which shows that there is no problem of heavy metal contamination.

Hydrogen Sulfide Desorption Kinetics

First, the concentration of total sulfur in a solution of the Azufroso well (H_2S and HS^-) was evaluated according to the NMX-AA-084-1982 (SE, 1982) as reference, resulting in a concentration of 60.80 mg L^{-1} with a standard deviation of ±3.23 milligrams per liter.

According to the above, hydrogen sulfide desorption tests were conducted at various time intervals, starting from a standard sample with a concentration of 50 mg L^{-1}. The desorption kinetics of H2S are shown in Figure 5a.

Considering these results, the exponential kinetic model of H_2S desorption was adjusted giving the following equation:

$$[S^{2-}] = 12.22\frac{mg}{L} + 33.30\frac{mg}{L}exp^{\left(-0.85\frac{1}{day}t\right)} \quad (5)$$

Where the constant value *a* of concentration that we expected to reach was 12.22 mg L^{-1}, the difference between the initial concentration and value *a* was 33.30 mg L^{-1} (*b*). The best value of the kinetic constant (*k*) was 0.85 day^{-1}. The real concentration values of the sulfide ion (S^{2-}) were linearly related to those calculated with the kinetic model, obtaining a linear regression coefficient of 0.9994 (Figure 5b). These results enable us to accurately estimate the desorption time of hydrogen sulfide in groundwater for aeration treatment.

Contamination of Groundwater Due to the Dissolution of Sulfides from Mineral Coal (Pyrite)

According to the methodology, samples of the aqueous carbon solutions were taken at different times to measure pH, electrical conductivity, total dissolved solids, and salinity. Table 3 shows the results of some physicochemical analyses of the suspended water and the percentage of sulfur (% S) remaining in the coal.

Table 2. Concentration of metals and metalloids in the sample from the Azufroso well, with respect to the permissible limits according to NOM-127-SSA1-2021(SSA, 2021).

Metallic element	Concentration	Permissible limit NOM-127-SSA1-2021
	- - - - - - - - - - - - - - - - mg L^{-1}	- - - - - - - - - - - - - - - -
Aluminum	0.083	0.200
Arsenic	< 0.02	0.025
Cadmium	< 0.02	0.005
Iron	< 0.05	0.300
Magnesium	32.000	50.000
Lead	< 0.05	0.010

[2] Camacho-González, A. J., & Quimis-Baque, O. F. (2022). *Estudios de la potabilización de fuentes subterráneas que contengan concentraciones de sólidos disueltos, que excedan a lo indicado por las normas INEN 1108*. Tesis para obtener el grado de Ingeniero Civil. Universidad de Guayaquil. Disponible en: http://repositorio.ug.edu.ec/handle/redug/60475

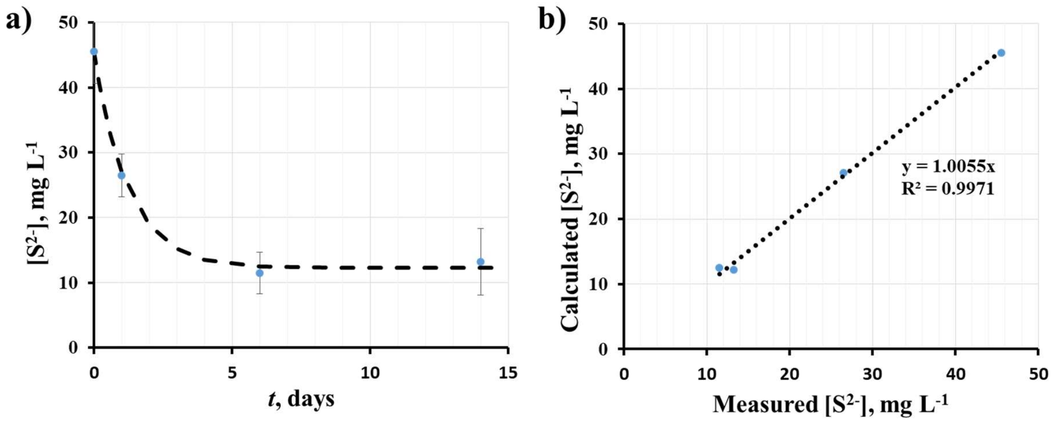

Figure 5. Graph of a) S2- desorption kinetics and b) linear regression of S2- desorption between the experimental data and the kinetic model.

The results demonstrate how the pH of the solution and the percentage of sulfur in the coal decrease, while the conductivity, total dissolved solids, and salinity increase over time, as reported in mine water analysis (Brown *et al*., 2024). This behavior is attributed to the fact that when FeS_2 dissociates, it produces H^+ (Equation 6), thereby providing acidity to the solution, promoting the activity of ions, facilitating electron transfer, and increasing conductivity (Pardo-Carrasco, Suárez-Mahecha, and Pertuz, 2009).

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (6)$$

The findings highlight the importance and concern of the geology near the study area, where its previously reported stratigraphic sequence (Sánchez, Solís, Partida, and Camprubí, 2007; Eguiluz de Antuñano, 2011), classifies the Sabinas Basin as a coal and hydrocarbon field (Figure 6). Within these fields, one of the most abundant sulfides associated with biological activity with coal during its formation is pyrite (FeS_2), and there is a possible cause of the presence of sulfides in the groundwater of the Región Carbonífera (Pavetti, Conesa, Faz, Arnaldos, and García, 2006; Senese, Negrelli, and Hidalgo, 2021).

Social Perspective

The survey was conducted in the study area and its surrounding municipalities, primarily in Sabinas (41.82%), San Juan de Sabinas (29.09%), and Melchor Múzquiz (8.18%). Most of the surveyed population is under 46 years old (61.11%) and predominantly female (55.86%). 52.29% of the surveyed population were professionals, while 42.20% were students, and the remaining 5.51% had other occupations.

The results revealed that respondents lack knowledge about sulfur as a chemical substance (58.4%) and about its behavior in contact with water (76.10%). Likewise, most (70.80%) of those surveyed are unaware of the health effects of consuming water contaminated with sulfides.

Table 3. Physicochemical analysis of suspended water and percentage of sulfur remaining in the coal at different times.

Time (months)	pH	Conductivity	Absolute conductivity	Total dissolved solids	Salinity	Sulfur in coal
		μS cm^{-1}	μS cm^{-2}	mg L^{-1}	PSU	%
0	6.70	3.00	*	1.00	*	3.45
1	6.21	1003.00	1043.00	502.00	0.49	3.24
2	6.00	1134.00	1228.00	567.00	0.56	3.13
3	5.55	1253.00	1374.00	630.00	0.62	3.03
4	3.34	1374.00	1415.00	687.00	0.68	2.95

*Values below the detectable scale.

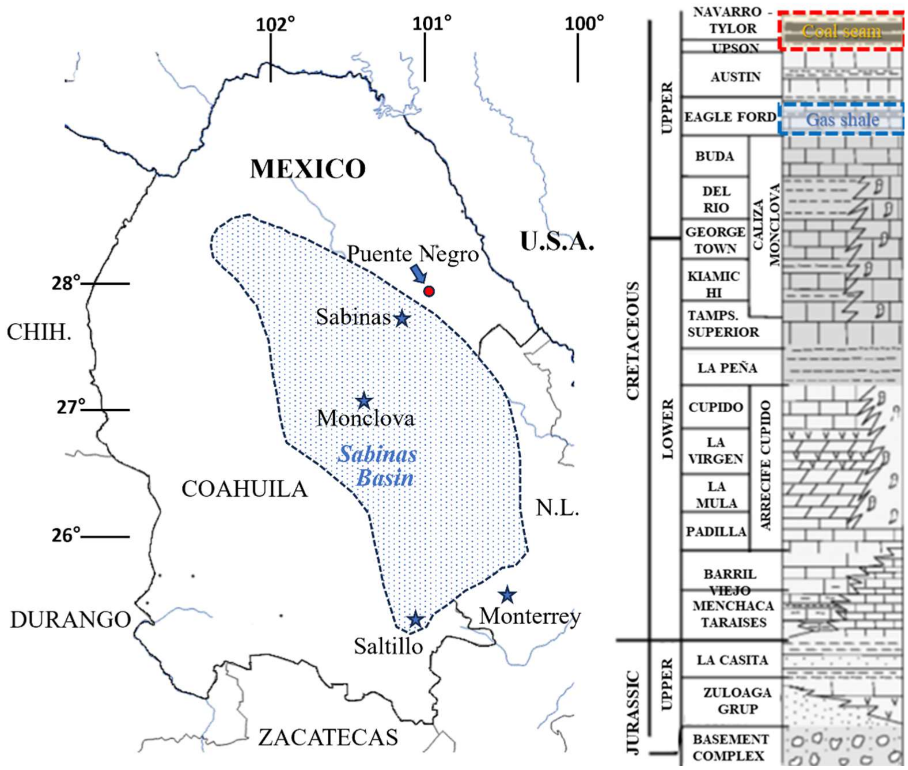

Figure 6. Puente Negro location and stratigraphic section of the Sabinas Basin area.

On the other hand, the community's knowledge and openness about the purification or reuse of contaminated water were evaluated. It was found that 80.53% are unaware of the purification methods, with a majority also evidently uninformed about the costs involved (74.34%) and the time required for the process (86.73%). Consequently, it was identified that 73.45% of those surveyed were unaware of the possibility of using treated water.

The study highlights a worrying lack of knowledge about a national problem related to the socio-natural water cycle, which is why it is recommended to develop a community monitoring plan based on reported references (Perevochtchikova and Sandoval, 2020; Ulloa, Godfrid, Damonte, Quiroga, and López, 2021).

CONCLUSIONS

The physicochemical properties detected in three different wells located in the Puente Negro ejido classify them as highly saline, which is why their use is limited. The water well called "Sulfuroso" was characterized by having greater conductivity and a greater amount of total dissolved solids, also having the characteristic of emitting a foul odor (like a rotten egg). Its possible source of contamination is the shale strata rich in hydrocarbons.

An exponential kinetic model of H_2S desorption was developed. It was observed that after the seventh day, the variation in H_2S desorption is minimal, reaching a S^{2-} concentration of 12.22%, equivalent to 73.15% sulfur removal.

It was demonstrated that the sulfide present in the coal of the Región Carbonífera dissociates when in contact with water, causing the water to become acidic and leading to the leaching of other metallic minerals in the area, which generates H_2S. However, a general problem of heavy metal contamination was ruled out.

From a social perspective, the need to consolidate an action plan for the area's inhabitants was detected. This plan would involve information regarding contaminated groundwater, a proposal for desulfurization, and its reuse to satisfy the community's personal and economic needs.

ETHICS STATEMENT

Not applicable.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF SUPPORTING DATA

Not applicable.

COMPETING INTERESTS

The authors declare that they have no competing interests.

FINANCING

Not applicable.

AUTHORS' CONTRIBUTIONS

Conceptualization, D.M.C.; investigation, D.M.C., G.E.A.G., R.A.G., H.C.M.T., P.M.A.G., J.C.H.R., J.J.E.C., and C.C.A.O. Data curation: C.G.B. Formal analysis: C.G.B., G.E.A.G., R.A.G., H.C.M.T., P.M.A.G., and J.C.H.R. Methodology, J.C.H.R.; writing - original draft, D.M.C.; writing - review & editing, D.M.C., C.G.B., and C.C.A.O.; validation, J.J.E.C., and C.C.A.O.; funding acquisition, J.J.E.C.

ACKNOWLEDGMENTS

The authors of this work thank CONAHCYT for the support received for this study. Additionally, we thank the Universidad Autónoma de Coahuila (UAdeC) for the facilities granted for this project. Likewise, we thank the Centro de Investigación en Geociencias Aplicadas UAdeC, the Tecnológico Nacional de México/ITES de la Región Carbonífera and the Centro de Investigación de Química Aplicada (CIQA), for facilitating the use of equipment and laboratories for water analysis. We also thank Eng. José Antonio Dávila Paulin and CONAMP Sabinas for the support and equipment provided. In addition, we thank Dr. Raúl Herrera Mendoza from CIQA chemical analysis laboratory.

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