ACID MINE DRAINAGE TREATMENT USING CHICKEN EGGSHELL WASTE

Tratamiento de drenaje ácido de mina usando residuos de cascarón de huevo

Mariana MARTÍNEZ-CASTREJÓN¹, Jonathan RAMIREZ-NAVA^{2,3}, Jazmin Alaide LÓPEZ-DÍAZ^{2,3}, Óscar TALAVERA-MENDOZA², Rocío Lley GARCÍA-MESINO³, Sergio Adrián SALGADO-SOUTO², Alejandro H. RAMÍREZ-GUZMÁN², Alicia SARMIENTO-VILLAGRANA⁴ and Giovanni HERNÁNDEZ-FLORES⁵*

¹Centro de Ciencias de Desarrollo Regional, Universidad Autónoma de Guerrero, Privada de Laurel 13, Col. El Roble, 39640 Acapulco, Guerrero, México.

² Escuela Superior de Ĉiencias de la Tierra, Universidad Autónoma de Guerrero, Exhacienda San Juan Bautista s/n, 40323 Taxco el Viejo, Guerrero, México.

³ Facultad de Ecología Marina, Universidad Autónoma de Guerrero, Gran Vía Tropical 20, Fracc. Las Playas, 39390 Acapulco, Guerrero, México.

⁴ Facultad de Ciencias Agropecuarias y Ambientales, Universidad Autónoma de Guerrero, Periférico Poniente s/n frente a la colonia Villa de Guadalupe, 40040 Iguala de la Independencia, México.

⁵ Consejo Nacional de Ciencia y Tecnología-Escuela Superior de Ciencias de la Tierra, Universidad Autónoma de Guerrero, Exhacienda San Juan Bautista s/n, Taxco el Viejo, 40323 Guerrero, México.

*Author for correspondance: ghernandez@uagro.mx

(Received: May 2021; accepted: January 2022)

Key words: acid mine drainage, chicken eggshell valorization, heavy metal removal, limestone, water pollution.

ABSTRACT

Acid mine drainage (AMD) is a source of soil and water resources pollution. Calcite is a mineral constituted of calcium carbonate (CaCO₃). The AMD interaction with calcite drives their natural neutralization. Calcite is the main component of the chicken eggshell (ES). This work aimed to evaluate the use of ES waste as a material to treat raw AMD. Five treatments (T1, T2, T3, T4, and T5) were carried out with concentrations of 1, 2, 3, 4, and 5 ES g/L AMD, respectively. Each treatment was performed for 3 h at room temperature without agitation. The response variables analyzed were pH, redox potential (Eh), electrical conductivity (σ), chlorides (Cl⁻), alkalinity, sulfates (SO4²⁻), nitrates (NO3⁻, and potentially toxic heavy metals and metalloids (PTHMM). Also, the removal efficiencies of SO₄²⁻, NO₃⁻, and PTHMM were analyzed. Additionally, the chemical and mineralogical composition of ES and precipitates were determined. The initial pH for AMD was 2.50 and it reached a final value of 5.50, 5.60, 5.80, 5.93, and 6.12 in T1, T2, T3, T4 and, T5, respectively. Moreover, the different treatments granted alkalinity to the treated effluents, reaching a maximum value of 124 CaCO₃ mg/L in T5. Finally, Al and Fe were completely removed from AMD, whereas Cu reached > 95 % removal, especially in T3, T4, and T5. Ba, Cr, and Pb showed an average removal of ~65 %. The ES concentration that showed the best results of neutralization and PTHMM removal efficiency was 5 ES g/L. The results showed that ES is a biocompatible waste material with an added value because it can be used as a sustainable material to treat raw AMD.

Palabras clave: calizas, contaminación del agua, drenaje ácido de mina, remoción de metales pesados, valorización del cascarón de huevo.

RESUMEN

El drenaje ácido de mina (DAM) es un efluente peligroso que representa una fuente de contaminación del recurso hídrico y el suelo. La calcita es un mineral formado a base de carbonato de calcio (CaCO₃) y su interacción con el DAM conduce a la neutralización natural de este peligroso efluente. La calcita es el principal mineral componente del cascarón de huevo (CH). Por esta razón, el objetivo de este trabajo fue evaluar el uso potencial de residuos de CH como material para tratar DAM crudo. Cinco tratamientos T1, T2, T3, T4 y T5 fueron llevados a cabo, donde las concentraciones fueron 1, 2, 3, 4 y 5 g CH/L de DAM, respectivamente. Cada tratamiento se realizó durante 3 horas a temperatura ambiente y sin agitación. Las variables de respuesta analizadas fueron pH, potencial redox (Eh), conductividad eléctrica, cloruros, alcalinidad y eficiencia de remoción de sulfatos, nitratos y metales pesados y metaloides potencialmente tóxicos (MPMPT). Adicionalmente, la composición química y mineralógica del CH y precipitados recuperados de los diferentes tratamientos fue determinada. El pH inicial del DAM fue de 2.50 y alcanzó un pH final de 5.50, 5.60, 5.80, 5.93 y 6.12 en T1, T2, T3, T4 y T5, respectivamente. Adicionalmente, los diferentes tratamientos otorgaron alcalinidad a los efluentes tratados alcanzando un valor máximo de 124 CaCO₃ mg/L en T5. Finalmente, Al y Fe fueron removidos completamente en el DAM mientras que Cu alcanzó una remoción > 95 %, especialmente en los tratamientos T3, T4 y T5. Ba, Cr y Pb mostraron una remoción promedio de ca. 65 %. La concentración que mostró los mejores resultados de neutralización y remoción de MPMPT fue la del T5, 5 g CH/L de DAM. Los resultados señalan que el CH es un residuo biocompatible que presenta un valor agregado debido a su potencial para ser usado como material sostenible para tratar DAM crudo.

INTRODUCTION

Mining is a worldwide industrial activity that plays a transcendental role in the economic development of nations with mineral resources (Abinandan et al. 2017). Latin America has the first position in mining exploration projects, with approximately 30 % of the worldwide investment in this area. Chile, Peru, and Mexico are the outstanding Latin American countries with greatest inversion in mining exploration projects (CEPAL 2006). On the other hand, China, the USA, Russia, Australia, and India have the highest percentages of active mineral extraction (Abinandan et al. 2017). The Servicio Geológico Mexicano (Mexican Geological Survey) reported that Mexico is within the top 10 mineral-producing countries (SGM 2019). Mexico is recognized for its worldwide production of silver and fluorite; however, despite the economic benefits produced by the mining industry, this activity generates waste which deteriorates the quality of the surrounding environment and natural resources, such as water (Jiménez-Rodríguez et al. 2009, Sánchez-Montoya et al. 2019, Vélez-Pérez et al. 2020).

Acid mine drainage (AMD) is one of the hazardous wastes generated mainly from the interior of mines and by the oxidation of residual pulverized rock (mining tailings) deposited outdoors without any treatment. However, some rocks with a sulfur composition in the oxidation process generate an acid effluent with similar characteristics to AMD (Smith and Skema 2001, Krauskopf and Bird 2003). The presence of sulfur minerals, mainly pyrite (FeS₂), exposed to an atmosphere rich in oxygen, water (such as humidity, rainwater, surface or underground water), and microorganisms favor oxidation. The oxidation of sulfur minerals by anthropic activities is the primary source of AMD generation (Kalyoncu-Ergüler 2015). AMD has the following characteristics: (i) pH values < 4, (ii) high potentially toxic heavy metals and metalloids (PTHMM) concentrations, and (iii) high levels of sulfates. When the AMD reaches the water reservoirs, water quality is affected negatively as well as the health of the different ecosystems that inhabit or consume it (Park et al. 2007, Espinosa-Rodríguez et al. 2010, Kalyoncu-Ergüler 2015, Vélez-Pérez et al. 2020). As a consequence of AMD dispersion in mining areas, PTHMM are usually

found in water reservoirs because they are soluble in acid conditions and non-biodegradable. PTHMM in drinking water can produce adverse effects on the population's health, and this situation can persist for decades and even hundreds of years (Méndez-Ortiz et al. 2012, Carreto-Morales et al. 2021).

Some rocks, such as limestone and dolomites, have a high carbonates composition, such as calcite, which is a mineral formed mainly by calcium carbonate (CaCO₃) whose chemical compound has a natural ability to neutralize acidic aqueous solutions (e.g., AMD) (Krauskopf and Bird 2003, Ferral-Pérez and Galicia García 2020). However, this neutralizing effect is inhibited during long interaction periods or by the generation of large amounts of AMD (Bai et al. 2009, Muliwa et al. 2018). Rice husks and green algae (Dipak et al. 1993), shrimp shells (Cho 1994), oak sawdust (Yu et al. 2000), basalt slag (Nugteren et al. 2002), crab shells (Lee et al. 2004), coconut shell (Amuda et al. 2007), and eggshell (ES) (Park et al. 2007, Kalyoncu-Ergüler 2015, Zhang et al. 2017) are some natural materials that have been evaluated to treat AMD and prevent environmental deterioration. Most of these materials are considered waste. ES is a worldwide waste generated from one edible product in the basic basket: the chicken egg (Kinoshita et al. 2002, Lesnierowski and Stangierski 2018).

In 2017, eight countries contributed to the global production of chicken eggs. China ranked first with 39 % and Mexico fourth with 3 %, as well as Japan, Russia, and Brazil. However, Mexico has been positioned as the leading egg consumer internationally, with an annual per capita egg consumption of 23 kg (UNA 2018), which makes it the largest producer of ES waste. On the other hand, ES waste management has become an environmental problem worldwide (Muliwa et al. 2018). Nevertheless, due to its chemical composition (with a high content of of CaCO₃), ES can mitigate the environmental problems caused by AMD. Therefore, ES could be valorized as a recyclable material with environmental benefits (Oliveira

et al. 2013). ES composition is a combination of organic fibers and inorganic crystals of calcium minerals distributed as follows: 95.1 % minerals (93.6 % calcium carbonate/calcite, 0.8 % magnesium carbonate, and 0.73 % tricalcium phosphate), 3.3 % organic matter, and 1.6 % water (Fernández and Arias 2000). ES represents around 10 % of the egg's total weight, and its structure is permeable due to its high porosity (7000-10 000 pores). Due to the ES physical and chemical characteristics, it has been used in some studies to evaluate its potential as a PTHMM scavenger and AMD neutralizer. Most studies have used ES with diluted synthetic acid solutions, or AMD that has undergone some pretreatment. The techniques using synthetic acid solutions or AMD previously treated are not practical to apply in real situations. The complexity of an actual system, e.g., raw AMD, is greater than the synthetic acid solutions previously evaluated (Muliwa et al. 2018). Therefore, the objective of this work was to evaluate the potential use of ES as a material to treat raw AMD.

MATERIALS AND METHODS

The experimental phase consisted of the AMD treatment using different concentrations of ES. The experiment was divided into three stages: (1) sampling and characterization of AMD and ES, (2) AMD treatment using ES, and (3) analysis of the AMD treatment efficiency using ES.

Sampling and characterization of acid mine drainage and eggshell

The sampling site is located in the municipality of Taxco de Alarcón, northern zone of Guerrero State, between coordinates 18° 30-18° 47' N, and 99° 33'-99° 46' W. The AMD used for this research was collected from outside of a mine (437284 E-2049242 N) in the Xochula community. The AMD was collected from a deposit in the principal exit of the mine (**Fig. 1**).



Fig. 1. Acid mine drainage deposit outside the Guerrero mine.

The samples were collected in Nalgene polypropylene bottles previously treated with diluted HNO3 (8 N) and deionized water. The bottles were conditioned in situ with three AMD rinses. Subsequently, 2.5 L of AMD were collected, and temperature, pH, redox potential (Eh), and electrical conductivity (σ) were determined. Temperature and pH were determined using an OAKTON pH/mV/°C Meter pH 11 Series potentiometer, while a Waterproof ORPTestr 10 (Oakton) was used for Eh. σ was measured using a Horiba model ES-14E conductivity meter. Subsequently, the AMD sample was transferred to the laboratory, where sulfates (SO_4^{2-}) , nitrates $(NO_3^{-} \text{ as } N)$, and chlorides (Cl⁻) were analyzed. The SO₄^{2–} and NO₃⁻ anions concentrations were determined by colorimetry using a HACH model DR/890 portable colorimeter (Sánchez-Montoya et al. 2019), while the Cl⁻ anion concentration was determined by the argentometric method (ASTM 1999). Additionally, 500 mL of AMD were collected and acidified with 2.5 mL of ultrapure concentrated HNO₃ (Ultrex II) for cation analysis (PTHMM concentration). At the laboratory, the acidified samples were filtered using cellulose acetate filters of 0.45 µm pore size. Afterward, the cation analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer optimal 3200 DV equipment. The following certified standards were used for calibration: CWW-TM-D; CWWTM-H; CWW-TM-A, CWW-TM-E, in addition to the Lg-Cal-A and Lg-Cal-C standards. The minimum concentrations established as detection limit (DL) were (in mg/L): Cd: 0.005; Ba, As, Pb, Se, Mo and Sb: 0.010; Fe, Mn, Co and Cu: 0.025.

On the other hand, ES, a household waste, used as raw material to carry out the AMD treatment was collected for one month from different households and self-service stores. Approximately 5 kg of ES were collected. A first in situ washing of ES was carried out using drinking water. Subsequently, it was dehydrated at room temperature. The material was transferred to the laboratory, where it was subjected to pretreatment before being analyzed and used to treat AMD. Manual grinding was carried out up to reach a relatively homogeneous size (Fig. 2a, b). Next, using a Sonicator ultrasonic test sieve cleaner (Haver USC 200), a wash was carried out for 2 h, placing 5 g of ES in 125 mL of deionized water in a beaker (Fig. 2c, d). During those 2 h, the volume of deionized water was replaced with a new water volume every 10 min. Then, ES was dehydrated using an acrylic box adapted with an air filter to produce a laminar flow. Also, the two lamps of the device were

used to warm the environment up to 63 ± 1.91 °C for 8 h (Fig. 2e). Finally, ES was crushed with a mortar with pistil until a fine and homogeneous powder (< 0.063 mm) was obtained (Fig. 2f). It was possible to determine the mineralogical composition of this sample by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer. The diffraction analysis was carried out for 1 h in a range of 5-70° at the 2 theta angle. Furthermore, a microanalysis was carried out through scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS) using a Jeol IT300-LV scanning electron microscope with a Bruker EDS (Quantax: XFlash 6/30). The sample was coated with graphite by thermal carbon evaporation using a Denton Desk Carbon Accessor vacuum coater. The SEM-EDS working conditions were as follows: the escape angle was set at 35° and all analyses were made at 20 keV, WD = 10 ± 0.5 mm. The chemical mapping of the samples was carried out for 50 min in an area ~3.5 mm². The elements considered representative in the analyses are those that presented an abundance higher than 0.5 %.

Acid mine drainage treatment using eggshell

Table I shows the conditions of the five treatments. Each treatment was carried out in duplicate using 200 mL of AMD (**Fig. 3**). All of them were carried out at room temperature (25 °C) without shaking for 3 h. During this time, pH was measured every 3 min during the first hour and in 10 min intervals thereafter. After 3 h, the effluent was separated by filtration for later analysis. A 10 mL sample of treated and previously filtered AMD was acidified with HNO₃ Ultrex II for PTHMM analysis. On the other hand, the precipitate was recovered and dehydrated.

In the case of the treatment used as duplicate (Tx'), the interaction time among ES and AMD in static conditions was extended to 261 h. Only the pH was monitored every 24 h in each treatment.

Efficiency analysis of acid mine drainage treatment using eggshell

The effect of the AMD treatment with ES was measured as follows. The initially analyzed parameters were again determined following the procedure described for raw AMD: pH, Eh, σ , SO₄^{2–}, NO₃[–], Cl[–], and PTHMM concentration. The alkalinity value was also analyzed based on the pH value reached with each treatment. The alkalinity was determined by titration using 0.02 N HCl as titrant and phenolphthalein, methyl red, and bromocresol green as colorimetric indicators (SE 2001). In addition, the



Fig. 2. Eggshell pretreatment. (a) Eggshell, (b) size of the manually crushed eggshell, (c) Haver USC 200 Ultrasonic Test Sieve Cleaner sonicator, (d) eggshell wash using a sonicator, (e) eggshell dehydration in a Cleanbox, (f) eggshell grinding in a porcelain mortar.

TABLE I. DESCRIPTION OF TREATMENTS FOR THE
REMOVAL FROM ACID MINE DRAINAGE AND
NEUTRALIZATION OF POTENTIALLY TOXIC
HEAVY METALS AND METALLOIDS.

Treatment	Concentration (g Es/L AMD)
T1	1
Τ2	2
Т3	3
Τ4	4
Т5	5

Es: eggshell; AMD: acid mine drainage.

sulfates removal efficiency ($\eta_{SO_4^{2-}}$), nitrates removal efficiency ($\eta_{NO_3^{-}}$), and PTHMM removal efficiency (η_{PTMM}) for each treatment was determined using equation 1 (Vélez-Pérez et al. 2020)

$$\eta_X(\%) = \left[\frac{X_i - X_f}{X_i}\right] *100\tag{1}$$

where η_X represents the *X* component removal efficiency expressed in %, X_i the SO₄^{2–}, NO₃[–] or PTHMM initial concentration, as appropriate, and X_f the final concentration of each component at the end of the ES treatment.



Fig. 3. Experimental design. ^aeggshell; ^bacid mine drainage; ^ctreatment X, where X = 1, 2, 3, 4, and 5 g/L and T_X' represent the duplicate of treatment X; ^dX-ray diffraction; ^escanning electron microscopy with X-ray energy dispersion spectroscopy; ^froom temperature; ^gredox potential; ^helectrical conductivity; ⁱinductively coupled plasma-atomic emission spectroscopy.

On the other hand, the generated and dehydrated precipitate was characterized by determining its chemical and mineralogical composition using SEM-EDS and XRD, respectively, following the methodology used for the ES.

RESULTS AND DISCUSSION

Acid mine drainage characteristics

The raw AMD presented extremely low pH and high Eh values of 2.50 and +541 mV, respectively. The World Health Organization (WHO 2011) and the Mexican Secretariat of Health have established the adequate physicochemical parameters for water used for human consumption. Mexican Official Standard NOM-127-SSA1-1994 (SSA 2000) sets the allowable pH range values for drinking water between 6.5-8.5. On the other hand, NOM-001-SEMARNAT-1996 (SEMARNAT 1996) establishes the maximum permissible limits of pollutants in wastewater discharges into national waters and assets. In this standard, the pH range allowed for the discharge of residual effluent into national waters and assets is between 5 and 10. The pH values shown by the raw AMD are completely different to the permissible values. Also, the raw AMD showed a σ of 3.5 mS/cm, and concentrations of 2.6 g/L and 19 mg/L of SO_4^{2-} and NO_3^{-} , respectively. The maximum limits established for

 SO_4^{2-} and NO_3^{-} as N are 400 and 10 mg/L, respectively, i.e., raw AMD has 6.5 times higher SO_4^{2-} than the maximum limit established, whereas NO₃⁻ as N are ~ 2 times higher than the maximum limit established (SSA 2000). NOM-001-SEMARNAT-1996 does not consider SO_4^{2-} or conductivity as part of the parameters to be evaluated, but it does consider total nitrogen concentration. Depending on the receiving water body, a maximum allowable concentration for total nitrogen is established for this parameter. Considering that raw AMD would be discharged into a river or stream, the maximum permissible concentrations (monthly average) would be 40, 40, and 15 mg/L depending on whether the river water is used for agricultural irrigation, urban public use, or protection of the aquatic life, respectively. The AMD concentration (19.6 mg/L of NO₃⁻) exceeds the allowed value for this effluent to be discharged into a river destined for the protection of aquatic life. Furthermore, AMD collected from the Guerrero mine showed several chemical elements such as Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Sr, V, Zn, Al, As, and Pb (Vélez-Pérez et al. 2020). NOM-127-SSA1-1994 (SSA 2000) contemplates 11 PTHMM within its regulation: Ba, Cd, Cr, Cu, Fe, Mn, Zn, Al, As, Pb, and Hg, whereas NOM-001-SEMAR-NAT-1996 contemplates eight PTHMM (As, Cd, Cu, Cr, Hg, Pb, Ni, and Zn). Hg was not analyzed in this work. Table II shows the identified PTHMMs,

Potentially toxic	Concentration (mg/L) -	Permissible limits (mg/L)					
heavy metals and metalloids		NOM-127-	NOM-001	NOM-001-SEMARNAT-1996			
		SSA1-1994	А	В	С		
Ba	0.14	0.70	NCS	NCS	NCS		
Cd	2.91	0.005	0.2	0.1	0.1		
Cr	0.04	0.05	1.0	0.5	0.5		
Cu	1.34	2.00	4.0	4.0	4.0		
Fe	42.53	0.30	NCS	NCS	NCS		
Mn	36.48	0.15	NCS	NCS	NCS		
Zn	412.38	5.00	10	10	10		
Al	51.50	0.20	NCS	NCS	NCS		
As	2.90	0.05	0.2	0.1	0.1		
Pb	0.02	0.01	0.5	0.2	0.2		
Ni	0.25	NCS	2.0	2.0	2.0		
Sr	1.04	NCS	NCS	NCS	NCS		
Mg	248	NCS	NCS	NCS	NCS		
Co	0.11	NCS	NCS	NCS	NCS		
K	4.69	NCS	NCS	NCS	NCS		
Ca	352	NCS	NCS	NCS	NCS		
V	< DL	NCS	NCS	NCS	NCS		

TABLE II.	CONCENTRATIONS OF POTENTIALLY TOXIC HEAVY METALS AND MET-
	ALLOIDS FROM ACID MINE DRAINAGE AND THEIR COMPARISON WITH
	PERMISSIBLE LIMITS ESTABLISHED BY NOM-127-SSA1-1994 AND NOM-
	001-SEMARNAT-1996.

NCS: not considered by the standard; DL: detection limit.

A: river for agricultural irrigation; B: river for urban public use; C: river for protection of the aquatic life.

their determined concentrations, and the allowable limits established by NOM-127-SSA1-1994 (SSA 2000) the NOM-001-SEMARNAT-1996 (SEMAR-NAT 1996). The raw AMD analysis showed that Cd, Fe, Mn, Zn, Al, As, and Pb exceeded the maximum concentration established according to NOM-127-SSA1-1994 (SSA 2000). On the other hand, considering NOM-001-SEMARNAT-1996, Cd, Zn, and As concentrations exceed the permissible limits so that this effluent can not be discharged into a river, regardless of the water use.

Therefore, the raw AMD is a risk to the biological environment at surroundings (Chapman et al. 2003, Akcil and Koldas 2006, Lottermoser 2010). In the case of Ba, Cr, and Cu, concentrations were found to be lower than the permissible limits, therefore they do not represent any risk to public health or environmental contamination (**Table II**). Additionally, elements such as Ni, Sr, Mg, K, and Ca were identified in raw AMD, nevertheless these elements are not considered in NOM-127-SSA1-1994 (SSA 2000). Although treated AMD is not intended for human consumption, the comparison with NOM-127-SSA1-1994 (SSA 2000) allows evaluating the treatment's efficiency in terms of the safety degree that can be achieved according to the physical and chemical parameters evaluated in this work. In the case of Ni, this element is considered in NOM-001-SEMARNAT-1996, but the quantified concentration in the AMD is lower than the maximum permissible limits set by regulations.

It is evident that due to the physical and chemical characteristics analyzed, the use or disposition of AMD towards a recipient body without any prior treatment represents a risk for the environment and society. Additionally, it was observed that the raw AMD used in this study had similar physical and chemical characteristics as previously reported AMDs (**Table III**).

Acid mine drainage alkalinization by eggshell

Even though AMD samples were treated with different concentrations of ES, all of them showed a significant neutralization effect after 3 h of interaction between ES and raw AMD (**Table IV**, **Fig. 4a**).

The pH values reached with treatments T1 and T2 were one unit below the limit established by WHO, whereas treatment T5 (5 g ES/L of AMD) reached a pH remarkably close to the WHO reference value.

Reference	Turkey (Kalyoncu- Ergüler 2015)	Germany (Meschkea et al. 2015)	Spain (Macías et al. 2017)	China (Zhang et al. 2017)	USA (Pozo et al. 2017)	China (Li et al. 2017)	South Africa (Muliwa et al. 2018)	Iran (Esmaeili et al. 2019)	Turkey (Yilmaza et al. 2019)	Mexico (Vélez-Pérez et al. 2020)
Parameter					Val	res				
Hd	3.79	2.50	2.98	2.40	2.70	2.75	2.43	4.60	1.94	2.50
Eh (mV)	NR	NR	485	NR	NR	NR	NR	NR	NR	541
σ (mS/cm)	3.18	NR	16.80	NR	10	NR	12.41	1,795	NR	3.50
TDS (g/L)	2.30	NR	NR	NR	NR	NR	10.27	NR	NR	NR
Nitrates (g/L)	NR	NR	NR	NR	0.04	0.014	137	NR	NR	18.62
Sulfates (g/L)	3.59	1.70	87	2.0-4.5	3.50	10	29	NR	3.36	2.60
Al (mg/L)	NR	NR	628	NR	472	NR	506	NR	NR	52
K (mg/L)	1.66	NR	ę	NR	41	NR	10	NR	NR	NR
Na (mg/L)	64	NR	124	NR	1451	NR	150	NR	NR	NR
Ca (mg/L)	324	NR	455	110	547	109	909	NR	NR	NR
B (mg/L)	0.20	NR	NR	NR	NR	NR	NR	NR	NR	NR
Li (mg/L)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Fe (mg/L)	44	220	2231	5-195	564	205	6120	NR	400	43
Mn (mg/L)	50	NR	881	49-62	58	322	155	NR	50	37
Mg (mg/L)	155	NR	1825	128 -140	590	152	648	NR	NR	248
Cd (mg/L)	<0.05	NR	NR	0.39	NR	NR	NR	NR	NR	С
Cu (mg/L)	0.2	NR	398	6.30	5.80	177	NR	NR	200	1.34
Co (mg/L)	1.18	NR	NR	NR	2.70	NR	NR	NR	50	0.13
Mo (mg/L)	<0.05	NR	NR	NR	NR	NR	NR	NR	NR	NR
Ni (mg/L)	0.57	NR	NR	0.4-0.5	4.3	2.04	NR	1	50	NR
Zn (mg/L)	9.19	NR	2075	98 -102	145	45	NR	13	50	412
Cr (mg/L)	<0.05	NR	NR	0.05-0.07	0.4	NR	NR	80	NR	0.039
Pb (mg/L)	0.11	NR	NR	1.2	0.6	NR	NR	NR	NR	0.022
Ba (mg/L)	<0.05	NR	NR	NR	NR	NR	NR	NR	NR	0.14
Sr (mg/L)	1.62	NR	NR	NR	NR	NR	NR	NR	NR	1.04
Hg (mg/L)	<0.005	NR	NR	NR	NR	NR	NR	NR	NR	NR
As (mg/L)	<0.01	NR	NR	0.03-0.04	1.4	0.004	NR	NR	NR	2.90
Se (mg/L)	<0.01	NR	NR	NR	NR	NR	NR	NR	NR	NR

TABLE III. CHARACTERISTICS OF ACID MINE DRAINAGE FROM DIFFERENT COUNTRIES.

418

M. Martínez-Castrejón et al.

NR: not reported; σ electrical conductivity; TDS: total dissolved solids.

Parameters	AMD			Treated AMD		
		Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
рН	2.50 ± 0.1	5.48 ± 0.2	5.60 ± 0.2	5.79 ± 0.2	5.93 ± 0.2	6.12 ± 0.2
EH (mV)	541 ± 22	349 ± 14	264 ± 11	257 ± 10	252 ± 10	246 ± 10
σ (mS/cm)	3.50 ± 0.1	3.17 ± 0.1	3.26 ± 0.1	3.26 ± 0.1	3.30 ± 0.1	3.33 ± 0.1
Alkalinity (mg CaCO ₃ /L)	ND	24.4 ± 1	87.84 ± 4	92.72 ± 4	112.24 ± 4	124.44 ± 5
Chlorides (mg/L)	ND	40 ± 2	44 ± 2	46 ± 2	54 ± 2	56 ± 2
Sulfates (g/L)	2.60 ± 0.1	2.60 ± 0.1	2.60 ± 0.1	2.70 ± 0.1	2.70 ± 0.1	2.60 ± 0.1
Nitrates (mg/L)	19 ± 1	0	0	0	0	0
Temperature (°C)	25 ± 1					

TABLE IV. EFFECT OF THE DIFFERENT TREATMENTS ON ACID MINE DRAINAGE.

AMD: acid mine drainage; EH: redox potential; σ : electrical conductivity; ND: not determined. Data are presented as mean \pm standard deviation (n = 2).



Fig. 4. Modification of acid mine drainage pH as a function of different eggshell concentrations: (a) at the first 3 h and (b) after 3 h.

However, despite a relatively short interaction time (3 h) between ES and AMD, the pH levels reached in the five treatments were low enough to comply with this parameter according to NOM-001-SEMAR-NAT-1996 (SEMARNAT 1996). Moreover, the initial Eh in the AMD showed a highly oxidizing environment. The different treatments showed a significant diminution of pH and Eh, which indicates that ES can modify the environment to a less oxidizing level, reaching a maximum value of +246 mV with T5.

In all treatments, σ remained practically unchanged. In the case of alkalinity and Cl⁻, both parameters were not determined in raw AMD due to the low pH measured. These parameters' values began to increase from T1 to T5. The maximum alkalinity value and Cl⁻ concentration (124 mg CaCO₃/L and 56 mg Cl⁻/L, respectively) were reached in T5. Alkalinity is an important parameter because it shows the buffering capacity of treated AMD. The Cl⁻ value for treated AMD was within the limit of 250 mg/L established by NOM-127-SSA1-1994 (SSA 2000). The three parameters not considered in NOM-001-SEMARNAT-1996 (SEMARNAT 1996) are σ , alkalinity, and Cl⁻.

Once the 3 h of the different treatments had elapsed, the duplicate of each treatment (T_X ') was submitted to an additional 261 h to evaluate the effect on pH. At this time (11 days), a slight increase in the pH of the treated AMD was observed in each treatment (**Fig. 4b**). Final pH values of 5.97, 6.02, 6.22, 6.35, and 6.81 were reached for treatments T1, T2, T3, T4, and T5, respectively. This means that a longer interaction between ES and AMD increased the pH in all treatments; however, only T5 managed to reach a value within the limits established by WHO and NOM-127-SSA1-1994 (SSA 2000).

Removal efficiency of nitrates, sulfates, and potentially toxic heavy metals and metalloids

The results showed that the AMD treatment carried out with ES did not contribute to SO_4^{2-} removal (**Table IV**). On the other hand, NO_3^- as N detected in the raw AMD (19 mg NO_3^-/L) was removed successfully with a $\eta_{NO_3^-}$ of 100 %. Thus, treated AMD met the nitrates value (10 mg NO₃^{-/}L) established by NOM-127-SSA1-1994 (SSA 2000) and NOM-001-SEMARNAT-1996 (SEMARNAT 1996) regardless of the final disposal site or receiving water body.

Table V shows that the different treatments with ES managed to decrease the concentration of elements considered in NOM-127-SSA1-1994 (SSA 2000) and NOM-001-SEMARNAT-1996 (SEMARNAT, 1996), and also of those not considered (except Ca, Ni, and V), even for cations that were initially within the permissible limits, such as Ba, Cr, and Cu. This indicates that the treatment with ES for effluents with concentrations higher than those allowed by NOM-127-SSA1-1994 (SSA 2000) regarding Ba, Cr, and Cu can be considered an option for removing these PTHMM. In the case of elements that exceed the concentration established by NOM-127-SSA1-1994 (SSA 2000), only Fe, Al, and Pb reached a concentration lower or equal to the limit established by the Official Mexican Standard as an effect of treatment with ES. The concentration of elements such as Cd, Mn, Zn, and As decreased; however, the final concentration did not meet the limits established by NOM-127-SSA1-1994 (SSA 2000). On the other hand, for those PTHMM considered by NOM-001-SEMARNAT-1996 (SEMARNAT 1996) that exceed the permissible concentration (Cd, Zn, and As), it was possible to reduce the final concentration in most of the treatments. However, the effect of the different treatments was insufficient for the AMD to meet with the maximum permissible limits established by NOM-001-SEMARNAT-1996 for PTHMM (Table V). On the contrary, Ca, Ni, and V concentrations increased at the end of the treatment. The increase in the Ca^{2+} concentration was due to the composition of ES, mainly calcite (CaCO₃), and its dissociation into Ca^{2+} and HCO₃⁻ ions in the presence of an acid medium such as raw AMD (Krauskopf and Bird 2003).

The treatment with ES showed a decrease in the PTHMM final concentration measured in the treated AMD (**Table V**). However, η_{PTMM} was different for each PTHMM. Al and Fe were the only PTHMM in which a total removal was achieved (100 %), while a reduction > 95 % was reached for Cu, especially in T3, T4, and T5. On the other hand, an average removal of ~65 % was reached for Ba, Cr, and Pb. In the case of Sr, a removal > 50 % was achieved only in T3 and T4. Overall, the other PTHMM showed a η in the range of 20-40 %, except for Ni and Ca, in which no removal was observed. Unlike all the metal cations reported, the Ca²⁺ concentration increased in treated AMD, from an initial 352 to 556.3 mg/L after the treatment in T5 (**Table V**).

Chemical composition of eggshell waste sludge

The ES and eggshell waste sludge (recovered after the treatments) were analyzed by XRD to determine their mineralogical composition. We observed a typical peak in calcite at angle 20 at 30° (Figure 5a), as previously reported by Kalyoncu-Erguler (2015). Other peaks were observed, but within the patterns reported for calcite. No other important patterns were present. The mineralogical data indicates that ES is practically synthetized by calcite (CaCO₃). On the other hand, the eggshell waste sludge (precipitate recovered after the AMD treatment) showed a similar mineralogical composition (CaCO₃), except for T1 and T2 (Fig. 5b, c), where the presence of gypsum $(CaSO_4 \cdot 2H_2O)$ was observed. The source of this mineral is attributed to the high concentration of SO_4^{2-} present in the raw AMD and the incorporation of Ca^{2+} cations into the aqueous medium by the dissociation of CaCO₃ (**Table V**), favoring the formation and precipitation of gypsum (equation 2):

$$SO_{4 (aq)}^{2-} + Ca^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow CaSO_4 \cdot 2H_2O$$
 (2)

In addition to the XRD analysis, the SEM-EDS analyses allow to determine semi-quantitatively the presence of Ca in major proportions, and Al, Fe, Na, S, and Zn in minor proportions as part of the composition of the materials. A chemical map showed that Ca was found in abundance in the ES, whereas Al, Fe, Na, S, and Zn were identified in trace amounts (**Table VI**, **Fig. 6**). The presence of Ca in relative abundance is mainly attributed to the presence of CaCO₃ as the main mineral constituent of ES (**Fig. 6**). Ca, S, K, P, I, Zn, Mg, and S are part of the chemical composition of ES (Fernández and Arias 2000, Valdés-Figueroa 2009); however, in addition to what was reported by several authors, in this study, the presence of Al and Fe was observed in trace amounts (**Fig. 6**).

On the other hand, the chemical analysis of the precipitates formed after the five treatments with AMD showed a similar chemical composition. The map corresponding to the precipitate of T1 showed a relative increase in the concentrations of Al, Fe, Na, and Zn, indicating that the ES had a removal effect from the aqueous phase. In addition, an increase in the relative concentration of S related to gypsum precipitation was observed (**Table VI, Fig. 7**). Na and S showed higher concentrations in the precipitates (**Fig. 7**).

The increase of Al and Fe in the precipitates is due to the elimination of these cations from the aqueous phase (raw AMD), where the removal reached 100 %, while for Zn (initially present in high concentrations in the AMD), the removal was in the range of 11-41 %.

 TABLE V. CONCENTRATIONS OF POTENTIALLY TOXIC HEAVY METALS AND METALLOIDS ACCORDING TO NOM-127-SSA1-1994 AND NOM-001-SEMAR-NAT-1996.

			PTHI	MM concentration			ł	Allowable limi	it (mg/L)	
PTHMM				(mg/L)			NOM-127-	0-MON	01-SEMARN	AT-1996
	AMD	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5	SSA1-1994	А	В	С
Ba	0.14	0.045	0.056	0.037	0.043	0.051	0.70	NCS	NCS	NCS
Cd	2.91	2.555	3.053	1.752	2.075	2.324	0.005	0.2	0.1	0.1
Cr	0.04	0.012	0.017	0.011	0.014	0.015	0.05	1.0	0.5	0.5
Cu	1.34	0.484	0.121	0.038	0.062	0.063	2.00	4.0	4.0	4.0
Fe	42.53	0.020	0.030	0.007	0.008	0.007	0.30	NCS	NCS	NCS
Mn	36.48	29.21	36.17	24.55	25.35	36.71	0.15	NCS	NCS	NCS
Zn	412	306	365	245	255	336	5.00	10	10	10
Al	51.50	0.59	< DL	< DL	< DL	< DL	0.20	NCS	NCS	NCS
\mathbf{As}	2.90	2.544	3.042	1.746	2.069	2.317	0.05	0.2	0.1	0.1
$^{\mathrm{Pb}}$	0.02	0.010	0.010	0.010	0.005	0.004	0.01	0.5	0.2	0.2
Ni	0.25	0.285	0.352	0.224	0.268	0.321	NCS ¹	2.0	2.0	2.0
Sr	1.04	0.898	0.952	0.485	0.227	0.678	NCS	NCS	NCS	NCS
Mg	248	151	211	144	154	218	NCS	NCS	NCS	NCS
Co	0.11	0.087	0.109	0.071	0.083	0.099	NCS	NCS	NCS	NCS
K	4.69	4.57	5.50	2.44	0.97	3.78	NCS	NCS	NCS	NCS
Ca	352	345	508	354	374	556	NCS	NCS	NCS	NCS
V	<dl< td=""><td>0.024</td><td>0.046</td><td>0.022</td><td>0.030</td><td>0.035</td><td>NCS</td><td>NCS</td><td>NCS</td><td>NCS</td></dl<>	0.024	0.046	0.022	0.030	0.035	NCS	NCS	NCS	NCS
PTHMM: pc B: river for u	tentially to trban publi	xic heavy metal c use; C: river f	ls and metalloids; or protection of th	AMD: acid mine c he aquatic life.	lrainage; DL: detect	tion limit; NCS: not	considered by the st	andard; A: riv	er for agricult	aral irrigation;

ACID MINE DRAINAGE TREATMENT USING EGGSHELL



Fig. 5. Mineralogical composition by X-ray diffraction of: (a) eggshell and precipitate formed in (b) treatment 1, (c) treatment 2, (d) treatment 3, (e) treatment 4, and (f) treatment 5.

In the case of Ca, the relative concentration decreased considerably, as shown in **figures 6** and **7a**, corresponding to ES and precipitates from T1, respectively. This behavior is expected because the Ca²⁺

ions were released from the CaCO₃ dissociation in an acidic aqueous medium. Furthermore, it is consistent with the increase in Ca²⁺ concentration in the treated AMD (**Table V**).

Elements			Concen	tration (%)		
	Egshell	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
Са	97	17	63	55	35	65
Al	0.7	35	12	16	25	11
Fe	< DL	29	9	12	17	10
Na	< DL	2	3	4	4	3
S	0.6	9	4	4	7	3
Zn	< DL	5	7	8	8	7

TABLE VI. EGGSHELL AND PRECIPITATE ELEMENTAL COMPOSITION.

DL. detection limit.



Fig. 6. Eggshell chemical composition determined by scanning electron microscopy with X-ray energy dispersion spectroscopy: (a) Ca, (b) Al, (c) Fe, (d) Na, (e) S, and (f) Zn.



Fig. 7. Chemical composition analysis of precipitate recovered from the treatment 1 determined by scanning electron microscopy with X-ray energy dispersion spectroscopy: (a) Ca, (b) Al, (c) Fe, (d) Na, (e) S, and (f) Zn.

CONCLUSION

The AMD neutralization treatment using ES was encouraging. The use of ES positively impacts the physical and chemical characteristics of the treated AMD and decreases the concentration of some PTHMM. In a relatively short time (3 h), using a concentration of 5 g of ES/L of AMD, it was possible to reach a final pH of 6.12 in T5, a value close to that established by NOM-127-SSA1-1994 (6.5-8.5). On the other hand, the treatment of AMD with ES (3 h) showed that this short time is enough for the treated AMD to achieve a pH value within the range established by NOM-001-SEMARNAT-1996. However, in a longer treatment time (264 h) using a concentration of 5 g of ES/L AMD, T5 improved the final pH value to 6.81, which falls within the range established by NOM-127-SSA1-1994. In terms of pH, the best treatment was T5. This means that a longer interaction time between ES and AMD favors a neutralizing effect on the latter. Additionally, it was observed that the ES-AMD interaction grants alkalinity to the treated AMD and that the maximum alkalinity (124 CaCO₃ mg/L) was observed in T5. Moreover, Eh in the treated AMD decreased ~50 % on average within 3 h in the five treatments. In addition, it was possible to remove up to 100 % of NO₃⁻ with the use of ES; however, the removal of SO₄²⁻ was not observed with these treatments.

On the other hand, it was determined that of the elements detected in raw AMD and considered by

the standards as PTHMM (Ba, Cd, Cr, Cu, Fe, Mn, Zn, Al, As, and Pb), Cd, Fe, Mn, Zn, Al, As, and Pb still exceeded the limits established by NOM-127-SSA1-1994 (SSA 2000) and NOM-001-SEMAR-NAT-1996 (SEMARNAT 1996) after the different treatments proposed in this work. This means that the quality of the treated AMD considering the PTHMM concentration is insufficient for this treated effluent to be discharged into a receiving body without representing an environmental risk. It is necessary to further decrease the concentrations of Cd, Zn, and As so that the AMD can be safely discharged into a receptor body (e.g., a river). Through the different treatments using ES, it was possible to decrease the concentration of all the PTHMM contemplated by the standards, including those that are already within the limits (Ba, Cr, and Cu). However, the best removal results could be observed in treatments T3 and T4. In the case of Fe and Al, their total removal (100%) form the AMD was achieved, while for Pb a removal of 55-82 % was achieved, enough to comply with the value established by the standard. The other PTHMM that exceeded the allowable concentration by the standard in the AMD (As, Cd, Mn, and Zn), it was possible to decrease the concentration; however, it was not enough to comply with the established maximum limits. The mineralogical composition of ES is calcite ~100 %; however, gypsum was formed (12-24%) after some treatments as part of the process.

ES is a domestic waste, and depending on its possible use for remediation, it can be valued as a useful material to prevent environmental deterioration through AMD treatment.

ACKNOWLEDGMENTS

Mariana Martínez Castrejón, Jonathan Ramirez Nava, and Rocío Lley García Mesino received a graduate scholarship from CONACyT, Mexico, registration numbers, 733907, 744493,, and 772080, respectively. Also, the authors are gratefully for the technical support provided by MSc. Mauro Esteban García Salas and MSc. Analine Berenice Vázquez Bahéna. Finally, the authors recognize the input and suggestions of the anonymous reviewers of the Journal, which allowed to improve the manuscript significantly.

ABBREVIATIONS

AMD	Acid mine drainage
CaCO3	Calcium carbonate

Cl ⁻ Chloride anion
DL Detection limit
EhRedox potential
EsEggshell
FeS ₂ Iron sulfide (pyrite)
ICP-AES Inductively coupled plasma-atomic
emission spectroscopy
NO ₃ ⁻ Nitrate anion
PTHMM Potentially toxic heavy metals and metal-
loids
SEM-EDS . Scanning Electron Microscopy with
Energy Dispersive X-ray Spectroscopy
SGM Servicio Geológico Mexicano
SO_4^{2-} Sulfate anion
T_X 'Duplicate of each treatment
WHO World Health Organization
XRD X-ray diffraction
X _f X final concentration
X _i X initial concentration

Greek characters

- Removal efficiency η
- η_{NO_3} -....Nitrates removal efficiency
- η_{SO_42} -....Sulfates removal efficiency
- η_{PTMM}.....Potentially toxic metals and metalloids
- removal efficiency
- σ Electrical conductivity

REFERENCES

- Abinandan S., Subashchandrabose S.R., Venkateswarlu K. and Meghraj M. (2017). Microalgae-bacteria biofilms: A sustainable synergistic approach in remediation of acid mine drainage. Applied Microbiology and Biotechnology 102, 1131-1144. https://doi.org/10.1007/ s00253-017-8693-7
- Akcil A. and Koldas S. (2006). Acid mine drainage (AMD): Causes, treatment and case studies. Journal of Cleaner Production 14, 1139-1145. https://doi. org/10.1016/j.jclepro.2004.09.006
- Amuda O.S., Giwa A.A. and Bello I.A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. Biochemical Engineering Journal 36, 174-181. https://doi.org/10.1016/j. bej.2007.02.013
- ASTM (1999). Standard test methods for chloride ion in water test, designation: D 512-89 (method B-Silver Nitrate Titration). An American National Standard, Philadelphia, USA, 7 pp.
- Bai B., Wu Y. and Grigg R.B. (2009). Adsorption and desorption kinetics and equilibrium of calcium

lignosulfonate on dolomite porous media. The Journal of Physical Chemistry C 113, 13772-13779. https://doi. org/10.1021/jp9028326

- Carreto-Morales E.Y., López-Díaz J.A., Martínez-Castrejón M., Talavera-Mendoza O., Almazán-Núñez R.C. and Hernández-Flores G. (2021).
 Sewage sludge from Taxco de Alarcón wastewater treatment plant as substrate to cultivate *Panicum maximum*. Revista Mexicana de Ciencias Geológicas 38 (3), 164-177. https://doi.org/10.22201/cgeo.20072902e.2021.3.1617
- CEPAL (2006). Espacios iberoamericanos. Comisión Económica para América Latina y El Caribe. Santiago de Chile, Chile, 165 pp.
- Chapman P.M., Wang F., Janssen C.R., Goulet R.R. and Kamunde C.N. (2003). Conducting ecological risk assessments of inorganic metals and metalloids: Current status. Human and Ecological Risk Assessment: An International Journal 9, 641-697. https://doi. org/10.1080/713610004
- Cho B. S. (1994). A study on heavy metal adsorption using shrimp shell. M.Sc. thesis. Chosun University, Korea.
- Dipak R., Greenlaw P.N. and Shane B.S. (1993). Adsorption of heavy metals by green algae and ground rice hulls. Journal of Environmental Science and Health, Part A 28, 37-50. https://doi. org/10.1080/10934529309375861
- Esmaeili A., Mobini M. and Eslami H. (2019). Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies. Applied Water Science 9, 1-6. https://doi.org/10.1007/ s13201-019-0977-x
- Espinosa-Rodríguez M.A., Arteaga Balderas E.A., Zambrano Cárdenas R.M. and González Torres L. (2010). Cinética de oxidación de la pirita, subproducto ácido del drenaje de la mina La Guitarra. Ingenierías 13, 63-69.
- Fernández M. and Arias J. (2000). La cáscara del huevo: un modelo de biomineralización. Monografías de Medicina Veterinaria 20 (2).
- Ferral-Pérez H. and Galicia García M. (2020). Bioprecipitation of calcium carbonate by *Bacillus subtilis* and its potential to self-healing in cementbased materials. Journal of Applied Research and Technology 18, 245-258. https://doi.org/10.22201/ icat.24486736e.2020.18.5.1280
- Jiménez-Rodríguez A.M., Durán-Barrantes M.M., Borja R., Sánchez E., Colmenarejo M.F. and Raposo F. (2009). Heavy metals removal from acid mine drainage water using biogenic hydrogen sulphide and effluent from anaerobic treatment: Effect of pH. Journal of Hazardous Materials 9, 759-765. https://doi.org/10.1016/j. jhazmat.2008.10.053

- Kalyoncu-Ergüler G. (2015). Investigation the applicability of eggshell for the treatment of a contaminated mining site. Minerals Engineering 76, 10-19. https:// doi.org/10.1016/j.mineng.2015.02.002
- Kinoshita K., Okamoto S., Shimogiri T., Kawabe K., Nishida T., Kakizawa, R., Yamamoto Y. and Maeda, Y. (2002). Gene constitution of egg white proteins of native chicken in Asian Countries. Asian-Australasian Journal of Animal Sciences 15, 157-165. https://doi. org/10.5713/ajas.2002.157
- Krauskopf K.B. and Bird D.K. (2003). Introduction to geochemistry. 3rd ed. McGraw-Hill, New York, USA, 348 pp.
- Lee M. Y., Hong K. J., Kajiuchi T. and Yang, J. W. (2004). Determination of the efficiency and removal mechanism of cobalt by crab shell particles. Journal of Chemical Technology and Biotechnology 79, 1388-1394. https://doi.org/10.1002/jctb.1139
- Lesnierowski G. and Stangierski J. (2018). What's new in chicken egg research and technology for human health promotion? A review. Trends in Food Science and Technology 71, 46-51. https://doi.org/10.1016/j. tifs.2017.10.022
- Li Y.-L., Wang J., Yue Z.-B., Tao W., Yang H.-B., Zhou Y.-F. and Chen T.-H. (2017). Simultaneous chemical oxygen demand removal, methane production and heavy metal precipitation in the biological treatment of landfill leachate using acid mine drainage as sulfate resource. Journal of Bioscience and Bioengineering 124, 71-75. http://dx.doi.org/10.1016/j.jbiosc.2017.02.009
- Lottermoser B.G. (2010). Mine wastes: Characterization, treatment and environmental impacts. 3rd ed. Springer, New York. USA, 304 pp. https://doi.org/10.1007/978-3-642-12419-8
- Macías F., Pérez-López R., Caraballo M.A., Cánovas C.R. and Nieto J.M. (2017). Management strategies and valorization for waste sludge from active treatment of extremely metal-polluted acid mine drainage: A contribution for sustainable mining. Journal of Cleaner Production 141, 1057-1066. https://doi.org/10.1016/j. jclepro.2016.09.181
- Méndez-Ortiz B.A., Carrillo-Chávez A., Monroy-Fernández M.G. and Levresse G. (2012). Influencia del pH y la alcalinidad en la adsorción de As y metales pesados por oxihidróxidos de Fe en jales mineros de tipo skarn de Pb-Zn-Ag. Revista Mexicana de Ciencias Geológicas 29 (3), 639-648.
- Meschkea K., Herdegena V., Aubelb T., Janneckb T. and Repkea J.-U. (2015). Treatment of opencast lignite mining induced acid mine drainage (AMD) using a rotating microfiltration system. Journal of Environmental Chemical Engineering 3, 2848-2856. https:// doi.org/10.1016/j.jece.2015.10.013

- Muliwa A. M., Leswifi T. Y. and Onyango M. S. (2018). Performance evaluation of eggshell waste material for remediation of acid mine drainage from coal dump leachate. Minerals Engineering 122, 241-250. https:// doi.org/10.1016/j.mineng.2018.04.009
- Nugteren H.W., Janssen-Jurkovícová M. and Scarlett B. (2002). Removal of heavy metals from fly ash and the impact on its quality. Journal of Chemical Technology & Biotechnology 77, 389-395. https://doi.org/10.1002/ jctb.600
- Oliveira D.A., Benelli P. and Amante E.R. (2013). A literature review on adding value to solid residues: eggs shells. Journal of Cleaner Production 46, 42-47. https:// doi.org/10.1016/j.jclepro.2012.09.045
- Park H.J., Jeong S.W., Yang J.K., Kim B.G. and Lee S.M. (2007). Removal of heavy metals using waste eggshell. Journal of Environmental Sciences 12, 1437-1441. https://doi.org/10.1016/S1001-0742(07)60234-4
- Pozo G., Pongy S., Keller J., Ledezma P. and Freguia S. (2017). A novel bioelectrochemical system for chemical-free permanent treatment of acid mine drainage. Water Research 126, 411-420. https://doi. org/10.1016/j.watres.2017.09.058
- Sánchez-Montoya G., Talavera-Mendoza O., Hernández-Flores G., Díaz-Villaseñor E., Ramírez-Guzmán A.H. and Galarza-Brito Z. (2019). Potentially toxic elements determination and chemical-microbiological analysis of potable water in Taxco de Alarcón, Guerrero. Revista Mexicana de Ciencias Geológicas 36, 147-158. https://doi.org/10.22201/ cgeo.20072902e.2019.2.927
- SE (2001). Norma Oficial Mexicana NMX-AA-036-SC-FI-2001. Análisis de agua-Determinación de acidez y alcalinidad en agua naturales, residuales y residuales tratadas. Secretaría de Economía. Diario Oficial de la Federación, August 1.
- SEMARNAT (1996). Norma Oficial Mexicana NOM-001-SEMARNAT-1996. Límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales. Secretaría de Medio Ambiente, Recursos Naturales y Pesca. Diario Oficial de la Federación, April 23.
- SGM (2019). Anuario estadístico de la minería mexicana, 2018. Servicio Geológico Mexicano. Pachuca, Hidalgo, Mexico, 544 pp.

- Smith M.W. and Skema V.M. (2001). Evaluating the potential for acid mine drainage remediation through remining in the Tangascootack Creek watershed, Clinton County, Pennsylvania. Minerals Engineering 53 (2), 28-35.
- SSA (2000). Modificación a la Norma Oficial Mexicana NOM-127-SSA1-1994. Salud ambiental. Agua para uso y consumo humano-Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización. Secretaría de Salud. Diario Oficial de la Federación, June 20.
- UNA (2018). Compendio de indicadores económicos del sector avícola. Unión Nacional de Avicultores [Online]. https://una.org.mx/compendio-de-indicadoreseconomicos-2018/ 15/01/2019
- Valdés-Figueroa J. (2009). La cáscara del huevo: ¿Desecho o valor agregado para la salud humana y la producción avícola? Una experiencia cubana. Revista Cubana de Alimentación y Nutrición 19, 84-102.
- Vélez-Pérez L.S., Ramírez-Nava J., Hernández-Flores G., Talavera-Mendoza O., Escamilla-Alvarado C., Poggi-Varaldo H.M., Solorza-Feria O. and López-Díaz J.A. (2020). Industrial acid mine drainage and municipal wastewater co-treatment by dual-chamber microbial fuel cells. International Journal of Hydrogen Energy 45 (26), 13757-13766. https://doi.org/10.1016/j. ijhydene.2019.12.037
- WHO (2011). Guidelines for drinking-water quality. 4th ed. incorporating the 1st addendum. World Health Organization, Geneva, Switzerland, 631 pp.
- Yilmaza T., Yucela A., Cakmaka Y., Uyanika S., Yurtsevera A. and Ucarb D. (2019). Treatment of acidic mine drainage in up-flow sulfidogenic reactor: metal recovery and the pH neutralization. Journal of Water Process Engineering 32, 100916. https://doi.org/10.1016/j. jwpe.2019.100916
- Yu B., Zhang Y., Shukla A., Shukla S.S. and Dorris K.L. (2000). The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper. Journal of Hazardous Materials 80, 33-42. https://doi. org/10.1016/S0304-3894(00)00278-8
- Zhang T., Tu Z., Lu G., Duan X., Yi X., Guo C. and Dang Z. (2017). Removal of heavy metals from acid mine drainage using chicken eggshells in column mode. Journal of Environmental Management 188, 1-8. https://doi. org/10.1016/j.jenvman.2016.11.076