Revista Ciencia en Desarrollo. Vol. 15 Num. 2. pp. 170 - 177
julio - diciembre 2024

https://doi.org/10.19053/01217488.v15.n2.2024.16183

Artículo de investigación

Chromium removal potential from tannery process by diatomaceous soil filtration.

Potencial de remoción de Cromo en procesos de curtiembre mediante filtración con suelos diatomáceos.

Edwin Anaya Jerez[1], Daniel Zuluaga Astudillo [2,5], July Carmona Álvarez[3], Juan Carlos Ruge Cárdenas [4], Eder Mosquera Quintero[5], Milagros Reyes Colmenares[5] y Diana Paola Reyes Murcia[6]

[1]Mag, Programa de Maestría en Ciencias Ambientales, Universidad de Ciencias Aplicadas y Ambientales U.D.C.A, Bogotá, Colombia.
[2]Mag, Programa de Doctorado en Ingeniería, Facultad de Ingeniería, Universidad Militar Nueva Granada.
[3]Mag, Programa de Ingeniería civil, Facultad de Ingeniería Ambiental y Civil, Universidad Antonio Nariño, Bogotá, Colombia.
[4]Ph. D., Programa de Ingeniería Civil. Universidad Militar Nueva Granada, Bogotá, Colombia.
[5]Ing, Programa de Especialización en Diseño y Construcción de Vías y Aeropistas, Escuela de Ingenieros Militares, Bogotá, Colombia.
[6]Ing, Sección de Investigación y Desarrollo, Laboratorio Concrelab, Bogotá, Colombia,

Recepción: : 4-jul-2023 **Aceptado:** 2-marzo-2024 **Publicado:** 23-julio-2024
Cómo citar: Anaya Jerez, E., Zuluaga Astudillo, D., Carmona Álvarez, J., Ruge Cárdenas, J. C., Mosquera Quintero, E., Reyes Colmenares, M., & Reyes Murcia, D. P. (2024). Potencial de remoción de Cromo en procesos de curtiembre mediante filtración con suelos diatomáceos. Ciencia en Desarrollo, 15(2). https://doi.org/10.19053/01217488.v15.n2.2024.16183

Resumen

El problema de la utilización de cromo en la industria del cuero para estabilizar la piel animal, está relacionado con los procesos de contaminación asociados, especialmente aquellos referentes con la descarga de aguas a nacimientos de ríos. Esto, debido a su alta toxicidad, sumado a las complicaciones de remoción de este metal pesado desde los líquidos. Debido a su gran área superficial y alta porosidad, los suelos de diatomeas pueden ser una buena alternativa como barrera filtrante en la captura de residuos de cromo. Esta investigación analizó y trató agua contaminada obtenida desde una fábrica curtiembre ubicada en la ciudad de Bogotá. Como material filtrante se utilizaron suelos diatomáceos de Estados Unidos y Colombia. El suelo norteamericano es de tipo multiespecie, mientras que el suelo colombiano se compone únicamente de la especie *Aulacoseira granulata*. El medio filtrante consiste en capas de tierra de diatomeas secas, de espesor variable, con y sin activación térmica, instaladas dentro de una cámara presurizada. Como conclusión, todas las probetas arrojaron porcentajes de eliminación de cromo. Los filtros de origen colombiano reportaron una mayor capacidad de remoción de Cr. Se redujo la acidez y la conductividad del agua, respecto de la muestra original.

Palabras Clave: capacidad de remoción de cromo, conductividad, industria curtiembre, pH, suelo diatomáceo.

Abstract

The problem of using chromium in the leather industry to stabilize animal skin is related to the associated contamination processes, especially those referred to as polluted water discharge to rivers. This situation, due to its high toxicity, added to the complications of removing this heavy metal from liquids. Diatomaceous soils can be a good alternative as a filtering barrier in capturing chromium residues due to their large surface area and high porosity. This investigation analyzed and treated contaminated water obtained from a tannery located in the city of Bogotá. Diatomaceous soils from the United States and Colombia were used as filter material. The north american soil is multispecies type, while the colombian soil is composed only of the *Aulacoseira granulata* specie. The filter medium consists of layers of dry diatomaceous earth, of variable thickness, with and without thermal activation, installed inside a pressurized chamber. In conclusion, all the samples showed chromium removal percentages. The filters of colombian origin reported a higher Cr removal capacity. The acidity and conductivity of the water were reduced compared to the original sample .

Keywords: chromium removal capacity, conductivity, diatomaceous soil, pH, tannery industry.

 E-ISSN: 2462-7658

1 Introduction

Processes like electroplating, ceramics and glass production, legal and illegal mining, and batteries manufacture are some of the industrial activities responsible for the dumping of heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg) in effluent water [1]. Tannery stages are recognized "as a primary source of pollution, due to the large volumes of wastewater" [2]. Water used for leather treatment mainly contains heavy metal ions such as mercury (Hg), arsenic (As), cadmium (Cd), lead (Pb) [3] and chromium (Cr) [4, 5, 6]. It is easy to demonstrate the permanence and accumulation of these metals in natural environments [7].

The lack of control over the discharge of contaminated water into the ecosystems threatens the organisms that live there [8] due to its high toxic level and the deficiency of the elimination of polluting residues [9]. Unfortunately, the national production of leather is not associated with modern technological processes [4], and highly polluting substances such as trivalent chromium salts continue to be used, which leads to a series of environmental problems that are difficult to treat [10]. The activities of the tanning process generate the highest proportion of Cr contamination in water residues.

For the World Health Organization (WHO), the maximum concentration of heavy metals in water sources should be between 0.01 – 1 part per million (ppm); however, concentrations of up to 450 ppm have been reported in the effluents. Tanneries appear as one of the industries that contribute the most to the generation of this negative aspect. This situation is exposed in the study entitled "Effect of Activities on the physicochemical and microbiological characteristics of the Bogotá River throughout Villapinzón, Colombia" [10]. The document reports that in the tanneries dumping area, chromium (Cr) values were between 2 and 10 times above the concentrations that generate adverse effects on humans.

It is called tanning, the transformation of the skin of cattle or other animals in leather using tannins or chrome salts [11]. The tanning process consists of four main stages (Beamhouse, Tanyard, Post-tanning and Finishing) and 24 substages [12]. The unhairing substage contributes 70% of the organic load to the effluents, and its liquid residues contain alkali metals [13]. The most significant contamination occurs when Cr salts are applied to improve the resistance and protection of the leather [14]. In the "wet finishing stage", the leather characteristics of softness, color, and final shine are given. The last stage corresponds to the "dry finishing"; in this the leather's final appearance is imposed [15].

The wastewater from the unhairing process is characterized by its high sulfur content and is treated by oxidation with hydrogen peroxide [16]. In the tanning stages, pretreatment is carried out to remove solid elements. Primary treatment is applied to separate the organic materials by sedimentation, where flocculation and chemical coagulation techniques are implemented. A precipitating agent for Cr is selected for these purposes, such as MgO [17]. The precipitation time is slow, but the formation of crystals is large and facilitates decantation. Due to economic factors, some tanneries use Ca Hydroxide [11]. The sludge can be recycled through acidulation and dissolution processes [18]. Even a Cr-recycling process can be developed by applying sulfuric acid [11].

The wastewater from each stage is collected, treated separately, and mixed for joint treatment before being taken to the effluent [18]. In countries like Italy, the production processes have been modified by implementing organohalogenated substances (salts) as dyes that replace vinyl sulfates. It also performs salt-free curing and soaking processes and implements Cr Sulfate and rainwater recycling units for skin washing [19].

Bio adsorption studies are increasing, especially from materials of biological origin and biopolymers, such as Chitosan, which are previously subjected to physicochemical treatments to improve the adsorption capacity of heavy metals in wastewater. For industrial use [9], innovative experimental technologies for water purification have also been implemented using membrane-free inorganic nanoparticles (NPs) integrated with cellulose compounds. These nanocomposites achieve excellent efficiency in adsorbing pollutants such as As (V), As (III), Cu (II), Cr (VI) and organic molecules such as Rhodamine B and Methylene Blue, among others [20]. Materials with a large surface area, a porous structure, and surface polarity are alternative sources that can be implemented in heavy metal removal processes [1].

Diatomaceous earth or Diatomaceous soils come from the fossil remains of tiny planktonic algae called diatoms [21]; these are found in all types of water environments on earth [22] (oceanic, fluvial, lacustrine). All diatom species are composed of Silica [23]. When the algae die, the organic tissue decomposes, leaving its skeleton, which progressively deposits at the bottom of lakes and seas, forming a rock (diatomite) consisting mainly of Si, Al and traces of quartz, montmorillonite, and kaolinite [24]. Some properties of diatomites are their low density, high porosity, wide pore distribution range, the high void ratio [25], high adsorption capacity [26], and large specific surface area [27]. Various procedures have proposed removing heavy metals using diatomaceous soils, including ion exchange, electrostatic interaction, chelation, complexization, calcination, the adaptation of frustules with acid, and combination with tourmaline, among others [16].

The high porosity of diatoms (80 to 90% voids) makes it a material used in different industries as a filtration medium or as an absorbent in Oil spills. However, more research is necessary regarding its use as an adsorbent in wastewater treatment [1]. They have also been used for the removal of Nitrogen (N) and Phosphorus (P) [28]. Ref. [22] present a review of different types of chemical modifications of diatomaceous soils to adapt them and enhance their ability to remove heavy metals. Studies of diatomaceous soil modification through microemulsion processes and application of Mn Oxide are highlighted because of the increment of surface areas and the ability to remove Cr (III).

Ref. [16] carried out tests with an Iranian diatomite and reported a maximum Pb (II) adsorption capacity of 25 mg/g, proving that the adsorption of this metal depends on the ionic strength and pH. These tests were repeated up to five times, and the removal percentages remained between 88 and 86%; from this was concluded that the diatomite could be recycled and reused. Calcination at an optimal temperature is a modifying agent that helps increase the specific surface, the number of open pores, and the diatomite's hydroxyl groups, improving the cations' adsorption capacity. Similarly, ref. [2] applied an advanced technology to treat nanoparticles, loading nanopyroxene functionalized with Polyethyleneimine (PEI-PN) in a diatomite soil to eliminate the Cr (VI) ions present in a dichromate solution. Batch adsorption tests were carried out in a continuous process where three variables were handled, inlet flow (1 - 2 ml/min), concentrations(99% K Dichromate solution 100, 150, and 200 mg/l) and bed heights (7.5, 3.5, 2.5 cm).

The modified Diatomite was applied to treat samples of tannery wastewater. Compared with the non-modified one, the modified filter aid showed an outstanding performance and a higher removal efficiency. Ref. [16] evaluated the feasibility of using diatoms in their natural and modified state to treat secondary wastewater effluents. Fossils without treatment, at a dosage of 300 mg/l, showed positive results regarding removing organic materials and toxic metals, similar to that obtained with activated carbon. However, the performance is minimal when removing As, Phosphates, and Ammoniacal Nitrogen, even at 500 mg/l dosages. The modified diatomite's removal efficiency was higher (20% to 50%). With diatomite dosages of 150 mg/l, all regulatory limits for effluent discharge were acceptable. The treatment presented included crude diatoms with aluminum sulfate and lime, followed by ultrasonic mixing and calcination in a muffle at 450ºC for 2 hours.

Around all the above, the present study analyzed the removal potential of chromium (III) present in wastewater coming from tanneries. For these purposes, variable thickness layers of diatomaceous soils of two origins were installed inside an air pressure chamber specially designed. The soils were thermally modified and acted as a filter medium for the contaminated liquid subjected to regulated downward flow pressure. The Colombian Ministry of Environment and Sustainable Development, through resolution 631-2015, established the parameters and maximum permissible values for the concentration of Cr in specific discharges on water bodies and public sewage systems. For manufacturing, tanning, and dressing of skins, the maximum value allowed for "Total Cr" is 1.50 mg/l. Data generated by the Colombian Institute of Hydrology, Meteorology and Environmental Studies IDEAM, through the report "State of the Environment and Renewable Natural Resources 2017 - 2018", show insufficient control points on water bodies to verifies the quality or concentration of polluting substances.

In the national territory, the primary pollutants from water sources come from urban areas and industrial activities such as mining, oil exploitation, and tanning. The pollutant load in tributaries is uncertain due to the disposal and treatment of solid waste, which according to [29], are close to 18,000 tons per day (ton/day).

In Colombia, multiple sources of exploitation of diatomaceous soils have been identified in Boyacá, Cundinamarca and Cauca [30] [31]. It allows projecting the potential use of diatomaceous soils for water treatment from leather production centers such as the municipality of Villa Pinzón (Cundinamarca) and the San Benito neighborhood in the City of Bogotá [12] [15].

The study entitled "Use of chromium eliminated in wastewater from tanneries (San Benito, Bogotá), through treatment with Sodium Sulfate" states that wastewater, without effective treatment, reaches concentrations of trivalent chromium between 2,000 to 8,000 mg/l [11]. The study called "quantification of the contamination of drinking water with hexavalent chromium and its relationship with tanneries, case study: San Benito", revealed the presence of hexavalent chromium (VI) in amounts greater than 50 (mg/l) in drinking water, this being the maximum limit stipulated by Colombian legislation following Resolution 2115 of 2007 [32].

Diatoms are unicellular, eukaryotic, and photosynthetic aquatic plants. They are algae with siliceous skeletons called frustules and grow in rich dissolved silica salty or freshwater [33]; their size ranges from 20 to 200 microns in length but can reach 2 millimeters [34].

Diatomite is a rock that comes from the fossil remains of aquatic plants and stands out for having an enormous absorption capacity; it is formed due to the compaction of diatom frustules. They are classified as pennate (bilateral symmetry) and centric (radial symmetry) [35]. When the algae die, the organic part disintegrates, but the frustule that gives it resistance and hardness properties is preserved; This accumulates in oceans or rivers, and over the centuries, the large deposits of fossilized algae known as diatomaceous soils are formed [36].

Diatoms have many chemical and physical-mechanical properties. They can be used as catalysts and supports. In the brewing industry, diatoms serve as filters; they can also improve the properties of soils. Frustules can be used as an admixture to concrete to improve its durability and compressive strength and reduce permeability; They can also be applied for enamels and medicines, among others [37]. Due to porosity and inert chemical capacity, diatom fossils have the property of retaining dissolved, suspended or colloidal particles and do not alter the characteristics of the filtered liquid [38]; can also retain microorganisms [35].

The Beamhouse and Tanyard stages are similar in all tanning companies; these are precisely where the most significant amount of chemical products are needed [39] (Table 1).

In Colombia, the tanning process generates 640 kg of solid waste for every 1,000 kg of salted skin. The total water consumption throughout the process is estimated to be between 15 and 40 m^3 ton^{-1} of fresh skin [40]. In the beamhouse stage, 80% of the Biological Oxygen Demand (BOD) is generated [39].

Table 1: Gravimetric load of chemical agents for the tanning process. Adapted from [39].

Stage	Chemical Load (kg/ton)
Beamhouse	149
Tanyard	187
Post-Tanning	55
Finishing	81

The main objective of the research is to determine the chromium removal potential from a chromium contaminated aqueous medium by applying pressure filtration, through diatomaceous soil strata of different origins, with thickness variation and thermal activation treatments.

2 Materials And Methods

For research development, variables and inputs were implemented. These are presented as solid and liquid phases. Procedures for filter and pressure chamber construction are also described.

Contaminated Liquid Source (Adsorbate)

This research used wastewater from industrial activities generated in a leather processing plant in the "San Benito" area in Bogotá (Colombia). The samples were taken from the tanks that house the water from the tanning stage (The phase when the Cr salts are added in order to produce resistance to biological decomposition) [41], being also the phase where the highest contaminant load of the water with Cr (III) is quantified [11]. Table 2 presents the characterization results of the samples.

Table 2: Initial characterization results from water sample.

Parameter	Unit	Quantity	Control Criteria
pH	pH	4.15	-
Hexavalent Chromium (VI)	mgCr6+/l	<0.04	-
Conductivity	µS/cm	112,900	-
Chemical Oxygen Demand (COD)	mg/02/l	2,326	maximum 1,800
Biological Oxygen Demand (BOD5)	mg/02/l	1,260	maximum 900
Total Suspended Solids (TSS)	mg/l	258.5	maximum 900
Sedimentary Solids (SSED)	ml/l	2.00	maximum 3.0
Fats and Oils	mg/l	<10.00	maximum 90
Chromium (Cr)	mg/l	686.00	maximum 1.5

Resolution No. 0631 (March 17th, 2015) establishes the parameters and maximum permissible limit values for discharge in surface water bodies, public sewage systems, and other provisions

Although the values of "Total Suspended Solids" and "Sedimentary Solids" are reported in the tanning stage (Table 2), it is worth clarifying that the most significant effects of solids are found in the preparatory stages in which the hair, fats, and tissues of different nature are removed. It is necessary to eliminate these phases so that the effects of Chromium concentrate on the leather surface. When taking the sample from the "tanning stage tanks", a homogeneous, bluish-green fluid, with no floating tissues, was recognized.

Filter Layers Adsorbent

The filter elements implemented were Diatomaceous Soils of North American and Colombian origins. The first, exploited in the State of Utah, marketed under the brand " Diatomaceous Earth". The second, extracted from the Boyacá territory, was exploited and marketed by the company "Suplementos Agropuli SAS." The Scanning Electron Microscopy (SEM) tests identified the multispecies nature of the North American soil, with four types of diatom frustules. The monospecies condition of Colombian soil was recognized using the same technique.

The hydrometric tests determined that the two species' most considerable fraction of the particles are concentrated in the silt range. Colombian soil reports a clay content (<2 µm.) close to 18%, while North American soil registers a clay fraction of 2.5% (see figure 1). Specific Gravity (Gs) values for North American and Colombian soils are 2.66 and 2.69, respectively. Considering the antecedents, potential absorption, adsorption capacity (depending on the specific surface), and the superficial properties of the frustules (geometry, irregularities, and pores), a characterization of the different species was developed, particularly around its length, width, and height (see figures 2 and 3).

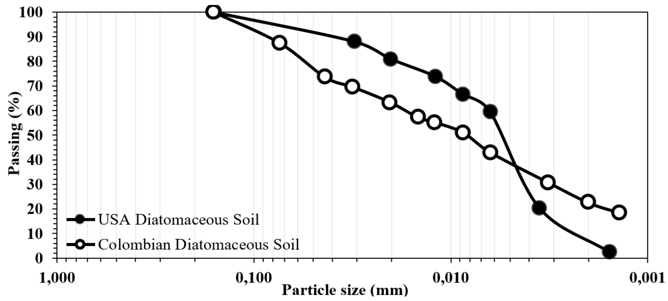

Figure 1: Particle Size Distribution_USA and Colombian samples

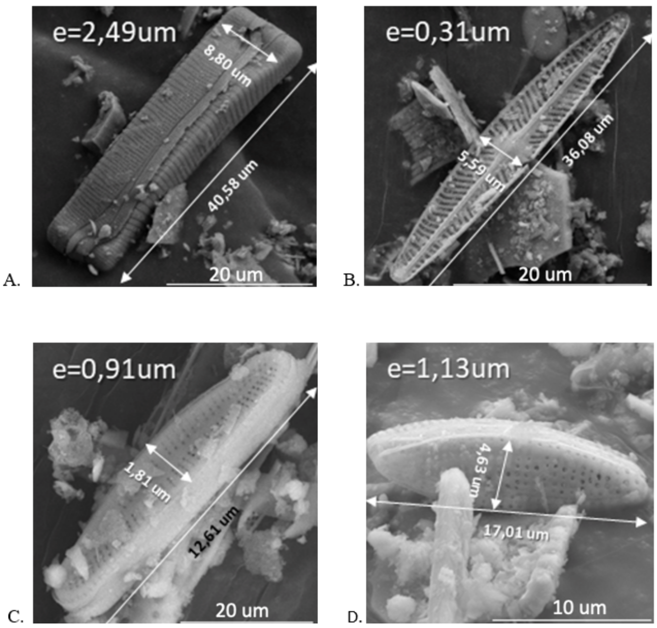

Figure 2: SEM Micrograph_ Identification of species Diatomaceous soil of North American origin. **A**. Oryzaformis holarctic **B.** Navicula cryptocephala **C.** Achnanthidium minutissimum **D.** Nitzschia soratensis

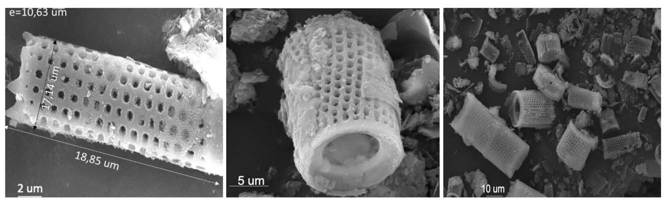

Figure 3: SEM Micrograph_Identification of species Diatomaceous soil of Colombian origin *Aulacoseira granulata*

From Table 3, it is recognized that the greatest lengths are found in some of the North American species (>40 µm.), while the greatest widths (17.14 µm.) and heights (10.63 µm.) were recorded in the Colombian frustules. At this point, it is essential to highlight the incidence of the shape of the fossil, which in the Colombian case turns out to be cylindrical and is associated with a more significant storage potential within its volume. At the same time, although North American species may be longer, they are not necessarily related to a greater accumulation space.

Table 3: Morphological characteristics for North American and Colombian frustules.

Origin	Specie	Average Geometric Characteristics (µm.)		
		Length	Width	height
USA	Orizaformis holarctica	40.58	8.806	2.494
	Navicula cryptocephala	36.084	5.593	0.31
	Achnanthidium minutissimum	12.613	1.818	0.911
	Nitzschia soratensis	17.018	4.63	1.132
Colombian	Aulocoseira granulata	18.851	17.147	10.635

The frustules of the different diatomaceous soils were characterized based on their pores through more than 1500 verifications. From this, the largest average pore size of the Colombian frustules was evident, whose value is 0.17 µm. The average value for the different North American species ranged between 0.004 and 0.02 µm.

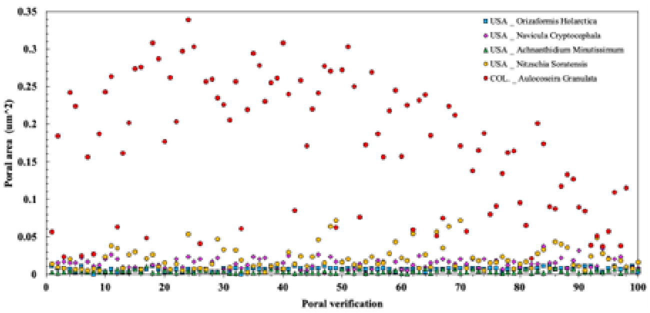

Figure 4: Poral Size USA and Colombian samples

It is essential to understand that different voids occur in diatom frustules. Initially, there are the pores associated with the silica shells. These are associated with diatoms processes to exchange substances with their environment. Then, there are the spaces related to the internal volume of the frustule, where the live diatom was contained. Finally, the spaces created by the irregular contact between particles (frustules) are recognized; these influence the soil mass's scale and not so much the individual absorption potential. However, all the pore spaces are a potential storage source of water or other substances.

Surface Modification

Thermal activation processes carried out surface modification. In both diatomaceous soil samples, the heat was induced through a microwave with 500 Watts power and during five minutes exposition. The sample size was limited to 300 grams to ensure homogeneity in the activation process. After a cooling period, the samples were packed in airtight bags and stored at 18°C - 20°C.

Filtration chamber and thicknesses of diatomaceous soil

A structure composed of two vertically aligned cylindrical acrylic tanks was designed for the filtration process. The cylinders have an internal diameter of 15 cm, 30 cm height, and a separation of 10 cm with a ball-type valve to avoid pressure loss, especially in the lower cylinder, where the filtering process takes place. The upper tank fulfils the functions of dosing and transitory storage of contaminated water. The entire system is supported by a metal structure that provides stability and verticality to the filtering process (figure 5).

The filter medium (with and without thermal activation) considered horizontal layers of dry diatomaceous soil installed at the bottom of the lower tank; it was compacted with a 110-gr load (20 cm free fall 10 repetitions). Thicknesses of 1, 3, 5, and 7 cm were applied. On top of the filter layers, a granular material was installed (3cm thickness) to act as an energy dissipator to prevent filter deformation due to the fall of water from the upper tank.

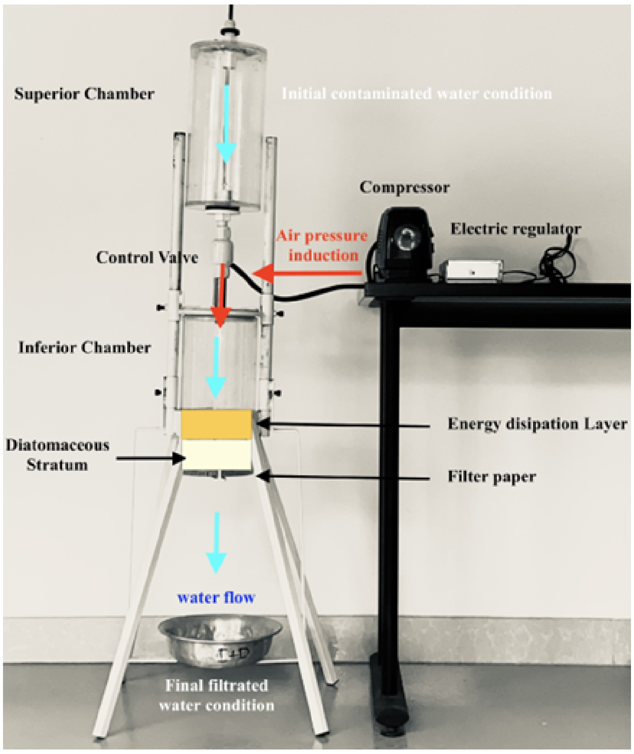

Figure 5: Pressurized filtration system structure.

The filtering process begins with the transit of the contaminated liquid from the upper chamber and subsequent fall on the dissipation layer. For the liquid to pass through the filtering layer (diatomaceous soil), it is necessary to boost the flow from the control valve. For these purposes, a 12V single-phase air compressor was implemented. As the pressure in the system increases, the water is expelled through the lower face of the lower cylinder, which has 2 mm diameter perforations throughout its area. A layer of Whatman No. 4 filter paper (diameter 150 mm) was installed between the filter layer and the base of the lower cylinder to avoid the loss of fine material. Once the fluid is expelled from the chamber, it is collected in a storage container, leaving the sample ready for laboratory tests. Each filtering process lasted approximately 15 minutes.

After the contaminated medium was filtered, the samples were stored in amber plastic containers, in volumes of approximately 1 liter, at 3.8°C. The laboratory analyses reported in this phase were pH, chromium concentration (Cr) mg/l, and Conductivity (µS/cm).

3 Results And Discussion

For all purposes (categorizing and results), a coding was adopted according to origin (USA or COL), activated state (ACT), not activated (NA) and layer thickness in cm (1, 3, 5 or 7). See Table 4

Table 4: Samples codification.

Origin	Activation state	Thickness (cm)	Code
USA	ACT	1	USA-ACT-1
	ACT	3	USA-ACT-3
	ACT	5	USA-ACT-5
	ACT	7	USA-ACT-7
	NA	1	USA-NA-1
	NA	3	USA-NA-3
	NA	5	USA-NA-5
	NA	7	USA-NA-7
COL	ACT	1	COL-ACT-1
	ACT	3	COL-ACT-3
	ACT	5	COL-ACT-5
	ACT	7	COL-ACT-7
	NA	1	COL-NA-1
	NA	3	COL-NA-3
	NA	5	COL-NA-5
	NA	7	COL-NA-7

ACT: thermal activation NA: no thermal activation

All samples showed a positive percentage of chromium (Cr) remotion. Below 2.5 cm of thickness, the removal percentage is higher in non-activated samples. The more significant potential for removal by the thermally activated Colombian sample is evident for greater thicknesses (> 2.5 cm). The highest Cr remotion for 1 cm thickness (28.19%) is associated with the USA non-activated condition. The highest Cr remotion for 7 cm thickness (52.54%) is associated with the COL-activated state (figure 6). The water samples treated by both soil types (COL or USA) reported an increment of pH for any activation condition and thickness, reducing the water acidity level comparatively to the original sample extracted from the tannery (pH 4.15). For all activation conditions, the filtered water's pH increment is observed as the thickness of the filter layer increases. The highest pH record (6.38) is associated with the COL-ACT-7 sample. The most negligible pH variation (4.26) is observed in the COL-NA-1 sample (figure 7).

In general terms, the conductivity records are lower than the reports of the original water sample. For all activation conditions and soil type, a "u" type pattern is recognized, descent followed by ascent. The lower limit in the "NA" samples is observed when the thickness of the layers is 5 cm.

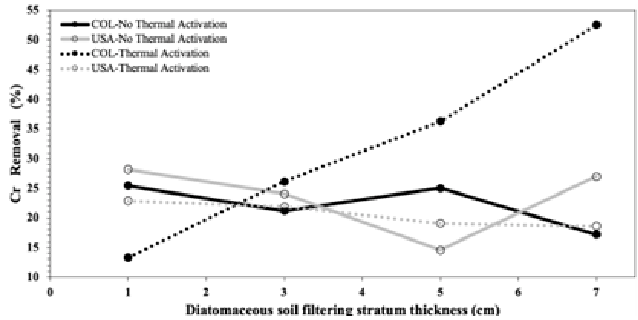

Figure 6: Chromium remotion as a function of soil thickness and activation conditions.

In the activated conditions, the lower value is at 3 cm. The average conductivity value in the "NA" conditions for both soils is lower than the average conditions of the activated samples (figure 8).

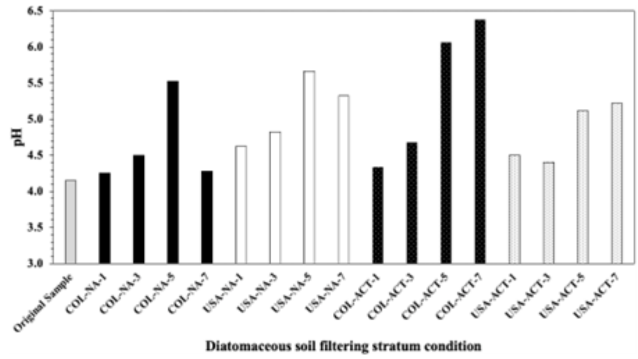

Figure 7: pH variation as a function of soil thickness and activation conditions COL: Colombian origin, USA: United States Origin NA: No Thermal Activation ACT: Thermal Activation, Soil Thickness (cm): 1, 3, 5, 7.

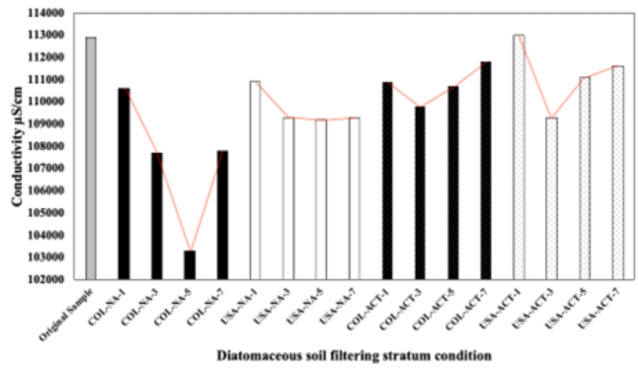

Figure 8: Conductivity variation as a function of soil thickness and activation conditions.

4 Conclusions

Applying diatomaceous soils as a filtering layer for chromium (Cr) remotion purposes resulted in positive for any activation condition or thickness. The most efficient effect (52.54%) was reported in Colombian soil, for 7 cm thickness, thermally activated state, when the microwave radiation time was 5 minutes and an adsorption temperature of 25°C was maintained.

The original tannery water samples (pH 4.15) treated by Colombian or North American diatomaceous layers derived in an increment of pH for any activation condition and thickness, reducing the water acidity level. In general, when tannery water is filtered, the conductivity records are lower than the reports of the original sample. The consolidation of results for all parameters and variables analyzed is presented in Table 5. A favorable context around the Colombian sample for 5 and 7 cm is observed in activated condition.

Sample Identification	Filter Thickness (cm)	pH	Conductivity (µS/cm)	Chromium record	Remotion (%)
Original Sample	-	4.15	112900	686	-
COL-NA-1	1	4.26	110600	511.6	25.42
COL-NA-3	3	4.50	107700	540.8	21.17
COL-NA-5	5	5.52	103300	514.6	24.99
COL-NA-7	7	4.28	107800	568.3	17.16
USA-NA-1	1	4.62	110900	492.6	28.19
USA-NA-3	3	4.82	109300	521	24.05
USA-NA-5	5	5.67	109200	586.1	14.56
USA-NA-7	7	5.32	109300	500.9	26.98
COL-ACT-1	1	4.34	110900	594.9	13.28
COL-ACT-3	3	4.68	109800	506.6	26.15
COL-ACT-5	5	6.07	110700	437.3	36.25
COL-ACT-7	7	6.38	111800	325.6	52.54
USA-ACT-1	1	4.50	113000	529.3	22.84
USA-ACT-3	3	4.40	109300	536	21.87
USA-ACT-5	5	5.11	111100	555.3	19.05
USA-ACT-7	7	5.22	111600	558.4	18.60

Due to the high interfacial area shown by diatom frustules, these form a negative ion substrate with an electrochemical imbalance that allows the attraction of certain types of cations, in this case, chromium. In addition to the physical filter function, there is an electrochemical explanation for the chromium removal phenomenon. It is interesting to highlight the largest pore area of the Colombian diatomaceous soil (see Figure 4), which is approximately five times higher than that reported by any of the North American species. This characteristic represents a greater "specific surface area" in contact with the contaminated fluid and a more significant remotion potential. From previous procedures and results can be proposed research lines around multiple filtering use for the same diatomaceous layer and the possibility of extracting the chromium that has been retained.

Ethical implications:

This study complied with national and international regulations. It does not require Ethics Committee.

Institutional Review Board Statement:

Not applicable.

Informed Consent Statement:

Not applicable.

Declaration of source of funds:

No external source. Authors own resources

Data Availability Statement:

Data sharing Not Applicable.

Conflicts of Interest:

The authors declare no conflicts of interest.

The authors confirm contribution to the paper as follows:

study conception and design: E A Anaya, D A Zuluaga data collection: E A Anaya, D A Zuluaga, E A Mosquera, M P Reyes, D P Reyes analysis and interpretation of results: E A Anaya, D A Zuluaga, J E Carmona, J C Ruge draft manuscript preparation: E A Anaya, D A Zuluaga, J E Carmona, J C Ruge All authors reviewed the results and approved the final version of the manuscript.

References

[1] M. A. M. Khraisheh, Y. S. Al-degs, and W. A. M. Mcminn, "Remediation of wastewater containing heavy metals using raw and modified diatomite," Chem. Eng. J., vol. 99, no. 2, pp. 177–184, 2004, doi: 10.1016/j.cej.2003.11.029.

[2] A. Hethnawi, W. Khderat, K. Hashlamoun, A. Kanan, and N. N. Nassar, "Enhancing Chromium (VI) removal from synthetic and real tannery effluents by using diatomite-embedded nanopyroxene," Chemosphere, vol. 252, 2020, doi: 10.1016/j.chemosphere.2020.126523.

[3] Y. Reyes, I. Vergara, T. Omar, D. Mercedes, and E. Gonzáles, "Contaminación por metales pesados: implicaciones en salud, amibieten y seguridad alimentaria" Indian J. Pediatr., vol. 24, no. 1, p. 14, 2016, doi: 10.1007/BF02796157.

[4] Á. Porras Chávez, "Descripción de la nocividad del Cromo proveniente de la industria curtiembre y de las Posibles Formas De Removerlo Description of Chrome Toxicity From the Tannery Industry and Possible Ways of Removing It," Rev. Ing. Univ. Medellín, vol. 9228, no. 17, pp. 41–50, 2010.

[5] L. F. Londoño Franco, P. T. Londoño Muñoz, and F. G. Muñoz Garcia, "Los Riesgos de los metales pesados en la salud humana y animal," Biotecnoloía en el Sect. Agropecu. y Agroindustrial, vol. 14, no. 2, p. 145, 2016, doi: 10.18684/bsaa(14)145-153.

[6] D. Boriskov, S. Efremova, N. Komarova, E. Tikhomirova, and A. Bodrov, "Applicability of the modified diatomite for treatment of wastewater containing heavy metals," E3S Web Conf., vol. 247, pp. 1–4, 2021, doi: 10.1051/e3sconf/202124701052.

[7] T. K. Marella, A. Saxena, and A. Tiwari, "Diatom mediated heavy metal remediation: a review," Bioresour. Technol., p. 123068, 2020, doi: 10.1016/j.biortech.2020.123068.

[8] M. Bilgin and Ş. Tulun, "Use of diatomite for the removal of lead ions from water: thermodynamics and kinetics," vol. 2818, 2015, doi: 10.1080/13102818.2015.1039059.

[9] C. Tejada, Á. Villabona, and L. Garcés, "Adsorción de metales pesados en aguas residuales usando materiales

de origen biológico," TecnoLógicas, vol. 18, no. 34, p. 109, 2015, doi: 10.22430/22565337.209.

[10] J. Díaz and C. Granada, "Efecto de las actividades antrópicas sobre las características fisicoquímicas y microbiológicas del río Bogotá a lo largo del municipio de Villapinzón, Colombia," Rev. la Fac. Med., vol. 66, no. 1, pp. 45–52, 2018, doi: 10.15446/revfacmed.v66n1.59728.

[11] N. Ortiz and J. Carmona, "Aprovechamiento De Cromo Eliminado En Aguas Residuales De Curtiembres (San Benito, Bogotá), Mediante Tratamiento Con Sulfato De Sodio," Luna Azul, no. 40, 2015, doi: 10.17151/luaz.2015.40.9.

[12] Alcaldía Mayor de Bogotá D.C., Guía de producción más limpia para el sector curtiembres de Bogotá Enfoque en vertimientos y residuos. 2018.

[13] M. A. Rincon Perez, "Los conflictos ambientales en Colombia," Los conflictos Ambient. en Colomb., 2017, doi: 10.2307/j.ctt1w76sz9.

[14] J. Ramirez, "Evaluación de la gestión integral de residuos sólidos en las curtiembres de san benito," Censo Curtiembre Salud Pública Hosp. Tunjuelito, vol. 28, no. 1, p. 18, 2014.

[15] Alcaldía Mayor de Bogota, Guia para la Gestión y Manejo Integral de Residuos Industria de Curtiembres y Tenerías. 2010.

[16] C. Zhao and W. Chen, "A review for tannery wastewater treatment: some thoughts under stricter discharge requirements," Environ. Sci. Pollut. Res., vol. 26, no. 25, pp. 26102–26111, 2019, doi: 10.1007/s11356-019-05699-6.

[17] G. Salas Colotta, "Reuso de cromo en el tratamiento de efluentes de una curtiembre," vol. 8, pp. 61–67, 2005.

[18] S. Xiang, J. Deng, Y. Zhao, and K. Cheng, "Improvements and application of flocculation technology in leather wastewater treatment," 2016.

[19] S. Martinez Buitrago and J. Romero Coca, "Revisión del estado actual de la industria de las curtiembres en sus procesos y productos: un análisis de su competitividad," Rev. Fac. Ciencias Económicas, vol. 26, no. 1, pp. 113–124, 2017, doi: 10.18359/rfce.2357.

[20] J. Yu, A. C. Wang, M. Zhang, and Z. Lin, "Water treatment via non-membrane inorganic nanoparticles/cellulose composites," Mater. Today, vol. 50, no. xx, pp. 329–357, 2021, doi: 10.1016/j.mattod.2021.03.024.

[21] H. He, Y. Luo, Z. Luo, and C. Yu, "Diatomite-Based Material as an Adsorbent or Photocatalyst for Water Treatment," Prog. Chem., vol. 31, no. 4, pp. 561–570, 2019, doi: 10.7536/PC180919.

[22] A. F. Danil et al., "Machine Translated by Google Diario de materiales peligrosos diatomita y diatomita modificada para la extracción de metales pesados del agua," vol. 242, pp. 14–31, 2012.

[23] H. Li, Q. Xie, N. Chen, H. Xu, and L. Ma, "Research progress of adsorption on heavy metals from aqueous solutions by modified diatomite," 2015.

[24] A. Vargas, "La tierra moler o 'diatomita' como sistema de remoción de sustancias químicas en el laboratorio.," Rev. Cienc. y Tecnol., vol. 25, no. 1, pp. 83–96, 2009.

[25] P. Moslehi and P. Nahid, "Heavy metal removal from water and wastewater using raw and modified diatomite," Int. J. Eng. Trans. B Appl., vol. 20, no. 2, pp. 141–146, 2007.

[26] H. Li, Q. Xie, N. Chen, H. Xu, and L. Ma, "Research progress of adsorption on heavy metals from aqueous solutions by modified diatomite," Key Eng. Mater., vol. 697, pp. 766–770, 2016, doi: 10.4028/www.scientific.net/KEM.697.766.

[27] Y. Zhao, G. Tian, X. Duan, X. Liang, J. Meng, and J. Liang, "Environmental applications of diatomite minerals in removing heavy metals from water," Ind. Eng. Chem. Res., vol. 58, no. 27, pp. 11638–11652, 2019, doi: 10.1021/acs.iecr.9b01941.

[28] A. Ozkan and H. Berberoglu, "Physico-chemical surface properties of microalgae," Colloids Surfaces B Biointerfaces, vol. 112, pp. 287–293, 2013, doi: 10.1016/j.colsurfb.2013.08.001.

[29] L. Artuz, M. Martínez, and M. Claudia, "Las industrias curtiembres y sus incidencia en la Contaminación de Río Bogotá," 2011.

[30] Agropulí, "Tierra de Diatomeas - Agropullí - Ltda Silicio Asimilable: dioxido de silicio (SiO2)amorfo. Enmienda de uso Agrícola," no. 9865, 2015.

[31] Y. Montoya, S. Sala, A. Vouilloud, N. Aguirre, and Y. Plata, "Lista de las diatomeas de ambientes continentales de Colombia," List. las diatomeas Ambient. Cont. Colomb., vol. 14, no. 2, pp. 13–78, 2013, doi: 10.21068/bc.v14i2.282.

[32] J. Reyes, "Cuantificación de la Contaminación del Agua Potable con Cromo Hexavalente y su Relación con las Curtiembres. Caso de Estudio: San Benito, Bogotá.," pp. 1–57, 2013.

[33] S. Manosalva and W. Naranjo, Diatomitas geología, caracterización y potencial uso industrial (Boyacá, COlombia). 2009.

[34] U. College London and M. Olney, "Microfossil Image Rocevery and circulation for learning and education," Micropalaeontology Unit, 2002. https://www.ucl.ac.uk/GeolSci/micropal/diatom.html(accessedNov.15,2021).

[35] P. Caballero and D. Zuni, "Elaboración de filtros de diatomita activada con adición de quitosano para la descontaminación de las aguas del Rio Chili a nivel de laboratorio," Universidad Nacional de San Agustín de Arequipa, 2017.

[36] Rojas Karen, "Remoción de arsénico (V) y cromo (VI) presente en lechos acuáticos mediante el uso de tierra de diatomeas recubierta con sales de hierro, arequipa," Universidad Católica de Santa María, 2016.

[37] A. S. Avramenko, M. V. Cherepanova, V. S. Pushkar', and S. B. Yarusova, "Diatom characteristics of the Far East siliceous organogenic deposits," Russ. Geol. Geophys., vol. 56, no. 6, pp. 947–958, 2015, doi: 10.1016/j.rgg.2015.05.010.

[38] S. Manosalva and W. Naranjo, Diatomitas. Geología, Caracterización y Potencial Uso Industrial, 1st ed. Sogamoso, Boyacá: UPTC Publicaciones, 2009.

[39] R. Méndez, "producción limpia en la industria de curtiembre," 2007.

[40] A. Alzate and O. Tobón, "Manual Ambiental Sectoria Proyecto Gestion Ambiental en la Industrial de Curteimbre en Colombia," Cent. Nac. Prod. más Limpia, pp. 28–42, 2004.

[41] J. Rivera Corredor, "El Residuo Líquido De Las Curtiembres Estudio De Caso: Cuenca Alta Del Río Bogotá the Liquid Remainder of the Tanneries Case Study: High River Basin of the Bogota River," vol. 16, no. 2, pp. 14–28, 2006.