

Physiochemical treatment of residual water from the cromatization process

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Abstract: The problem of environmental pollution brings with it issues that affect the development of all living beings, including plants, animals, and humans [1]. Water is one of the main natural resources affected by industrial activity, as many industrial processes depend on it for product manufacturing, or it is used as an essential auxiliary service in unit operations. Therefore, water treatment procedures must be established to help conserve its natural state and ensure its preservation for future generations [1]. Concern about environmental pollution has fostered research and development of sustainable technologies, as well as increasingly stringent regulations to ensure that industrial processes, through the use of clean technologies, reduce pollutant levels in effluents. Most companies generate wastewater with high concentrations of pollutants because treatment methods are economically unviable and have low effectiveness. In industry, chromium is used in: tanning processes, textile pigments, alloys, catalysts, anti-corrosion agents, batteries, fungicides, metal coatings, electroplating, etc. The objective of this study was to establish a methodology for reducing chromium VI to chromium III in wastewater, as well as its control to comply with the parameters established in Standard NOM-001-SEMARNAT-1996 [22]. The results obtained after treatment ranged from 0.059 to 0.99 mg/L of chromium III. It is concluded that treatment with sodium metabisulfite is a good option for chromium reduction. The key finding of this study is that the water can be reused for irrigating green areas.

Key words: waste water; Chromium VI; sodium metabisulfite

1 Introduction

Environmental pollution by heavy metals is primarily caused by anthropogenic activities, such as those carried out in the metallurgical, agricultural, and manufacturing industries, as well as by poor waste storage and disposal practices [19]. These industries release just over 5 million tons of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), vanadium (V), and zinc (Zn) into the environment each year [3]. These metals tend to persist indefinitely in the environment and eventually accumulate through the food chain, posing a serious threat to the health and well-being of living organisms [3]. Removing heavy metals from industrial wastewater is essential to reducing environmental pollution. Water pollution by heavy metals represents a significant environmental problem due to the toxic effects it has on human health. The main sources of water pollution by heavy metals come from industrial wastewater, such as that from metallizing, mining, tanneries, paint manufacturing, radiator production, smelting, and alloy industries, among others [1], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15]. The maximum permissible discharge for hexavalent chromium into receiving bodies of water must be less than 0.5 mg/L, according to the regulations establishing the

provisions for wastewater discharge, Executive Decree No. 21-2017 [2]. Chromium exists in more than one oxidation state, from Cr(0), the metallic form, to its hexavalent form, Cr(VI). Specifically, chromium in its +6 oxidation state is considered hazardous even in small concentrations, while Cr in the +3 oxidation state is essential for health under moderate conditions [4].

Hexavalent chromium can cause adverse short- and long-term effects, with the respiratory tract being the primary organ affected after exposure. Hexavalent chromium can cause lung cancer, irritation, or damage to the skin, eyes, nose, and throat. According to OSHA, the permissible exposure limit for hexavalent chromium per day is $5 \mu\text{g}/\text{m}^3$ [5], [1], [12]. Chronic inhalation exposure to hexavalent chromium in humans can cause septal perforation and ulceration, bronchitis, decreased lung function, pneumonia, asthma, and nasal itching. High levels of hexavalent chromium can also affect the liver, kidneys, gastrointestinal system, and immune system [6].

Currently, several companies still discharge wastewater without treatment. Hence the importance of this study as a contribution to the care of our environment.

Water pollution by Cr(VI) is due to untreated industrial effluents generated by the metallurgical industry, chrome plating, leather tanning, electroplating, wood preservation, the preparation of high-hardness, heat-resistant, anti-corrosive alloys, mining, and the production of cement, dyes, paints, and photographic materials [7], [8], [9]. Even when heavy metals are diluted and in undetectable quantities, their recalcitrant nature and persistence in water bodies cause their concentration to increase to toxic levels through processes such as biomagnification [8], [9], [10].

The most common method for removing metals from industrial effluents is precipitation as hydroxides, using caustic soda (NaOH) or lime ($\text{Ca}(\text{OH})_2$) to achieve an alkaline pH. Ferrous and aluminum sulfates are often added as coagulants. However, Cr(VI) is soluble and does not precipitate at any pH value; moreover, these methods ultimately result in high costs due to the large amount of sludge generated, which has poor filtration properties and requires water neutralization after precipitation [4]-[16], [17], [18].

This research project presents the development of an experimental methodology outlining the steps for reducing chromium VI to chromium III in wastewater using sodium metabisulfite, as well as its control to comply with the parameters established in Mexican Standard NOM-001-SEMARNAT-1996 [22]. A coagulation-flocculation system was used for chromium adsorption. The coagulation-flocculation process is a useful method for separating very fine colloidal particles that exhibit high stability in water. Coagulation refers to the process of destabilizing and subsequently aggregating colloidal suspended particles present in water, to enhance the sedimentation or thickening stage in which these particles must be separated from the water [20], [21]. Destabilization is achieved by neutralizing their electrical charges, thus eliminating repulsive forces, canceling their zeta potential, and causing the colloids to aggregate due to mass action.

2 Methodology

2.1 The physicochemical treatment of the wastewater was carried out as follows:

(1) The sample was taken from the surface finishing baths of a metalworking company.

a) Neutralization: The water was neutralized with calcium hydroxide to adjust the pH of the water to a range of 7-8 units, thus allowing the coagulant product that is subsequently added to react efficiently.

b) Coagulation: This is a chemical technique whose objective is to destabilize colloidal particles (water contaminants). It turns out that most of the suspended particles in the wastewater are so small that their removal in the sedimentation tanks by gravity was not possible. Therefore, coagulation was carried out by adding aluminum sulfate (40 g/L) to destabilize the water contaminants and break the electrical forces that led to the formation of a chemical precipitate. At this stage, sodium metabisulfite was added to reduce chromium VI to Cr III, according to the sodium metabisulfite demand.

c) Flocculation: This is a slow mixing technique that induces the formation of agglomerates of destabilized particles, a product of the coagulation process in the previous stage. Generally, the formation of agglomerates (clumps of flocs) is increased by adding a polymeric product to the coagulated water mixture, which also contributes to an increase in the weight and sedimentation rate of the flocs formed. In this case, an acrylamide polymer was added.

d) Method for determining the sodium metabisulfite demand for the reduction of chromium VI to chromium III.

1) Pipette a 10 ml sample of wastewater, containing hexavalent chromium, into a 250 ml flask and dilute to 100 ml with distilled water.

2) Add 1 gram of potassium iodide (KI) crystals and stir until dissolved.

3) Add 15 ml of concentrated hydrochloric acid (HCl) to the flask.

4) Titrate with a 0.1N sodium thiosulfate solution, until the red-orange solution turns straw-colored.

5) Add 15 to 20 drops of starch indicator solution, the solution will turn dark purple, continue titrating slowly until the solution changes to light or pale green.

2.2 Calculations

(1) Calculation to determine the necessary amount of sodium metabisulfite.

a) ml of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) consumed $\times 1.45 = \text{lb Cr(VI)} / 1000 \text{ gal of water}$.

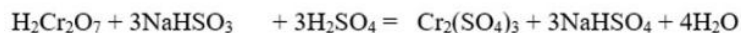
b) If the result is desired in mg/L, and 1 ml of sodium thiosulfate is consumed, the following conversion is performed:

Parts Per Million (p.p.m.) = $(1.45 \text{ lb})(1 \text{ gal})(0.454 \text{ kg})(1000 \text{ g})(1000 \text{ mg}) / (1000 \text{ gal})(3.785 \text{ L})(1 \text{ lb})(1 \text{ kg})(1 \text{ g}) = 173.92 \text{ mg/L}$.

c) The theoretical amount of sodium metabisulfite required to reduce chromium (VI) to chromium (III) is as follows:

To reduce 1 ppm of Cr (VI), 2.81 ppm of metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) are needed; in practice, it was taken as 3 ppm.

(2) The reduction reaction of Cr (VI) to Cr (III) is schematized as follows:



This reaction is instantaneous for pH values below 2.5.

3 Results

After treatment, the chromium content in the wastewater was analyzed by atomic absorption using a Perkin Elmer atomic absorption spectrometer for three months. Tables 1, 2, and 3 show that the results are within the specification, as the standard establishes a maximum of 1.5 ppm of chromium in wastewater for agricultural irrigation (see Figures 1, 2, and 3).

Table 1. Chromium III content in wastewater in March 2021

Samples	Chromium Content (ppm)	pH	Observations
1	0.088	9.8	Within specification
2	0.36	9.5	Within specification
3	0.99	9.0	Within specification
4	0.14	8.96	Within specification
5	0.21	8.47	Within specification
6	0.13	8.43	Within specification
7	0.41	7.0	Within specification
8	0.22	6.98	Within specification
9	0.35	9.0	Within specification
10	0.15	7.2	Within specification

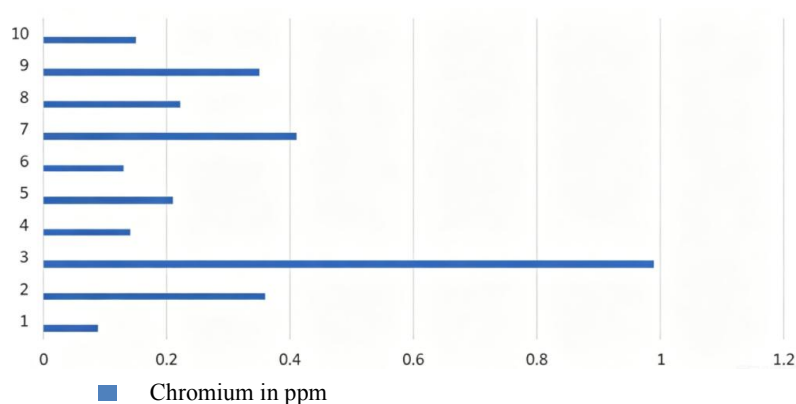


Figure 1. Chromium content in wastewater for the month of March.

Table 2. Chromium content in the month of April

Samples	Chromium Content (ppm)	pH	Observations
1	0.63	7.28	Within specification
2	0.21	9.3	Within specification
3	0.11	8.35	Within specification
4	0.25	8.13	Within specification
5	0.26	7.95	Within specification
6	0.26	8.25	Within specification
7	0.15	8.83	Within specification
8	0.46	7.67	Within specification
9	0.25	8.75	Within specification
10	0.20	8.5	Within specification

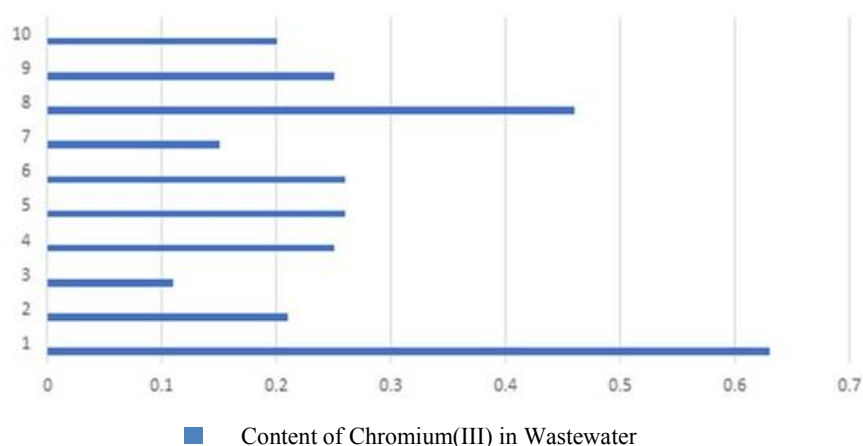


Figure 2. Chromium content in wastewater in the month of April.

Table 3. Chromium Content in Wastewater in May 2021

Samples	Chromium Content (ppm)	pH	Observations
1	0.20	8.6	Within specification
2	0.059	9.63	Within specification
3	0.24	7.57	Within specification
4	0.24	8.12	Within specification
5	0.68	7.64	Within specification
6	0.15	7.10	Within specification
7	0.11	10.78	Within specification
8	0.22	7.5	Within specification
9	0.19	8.42	Within specification
10	0.20	8.41	Within specification

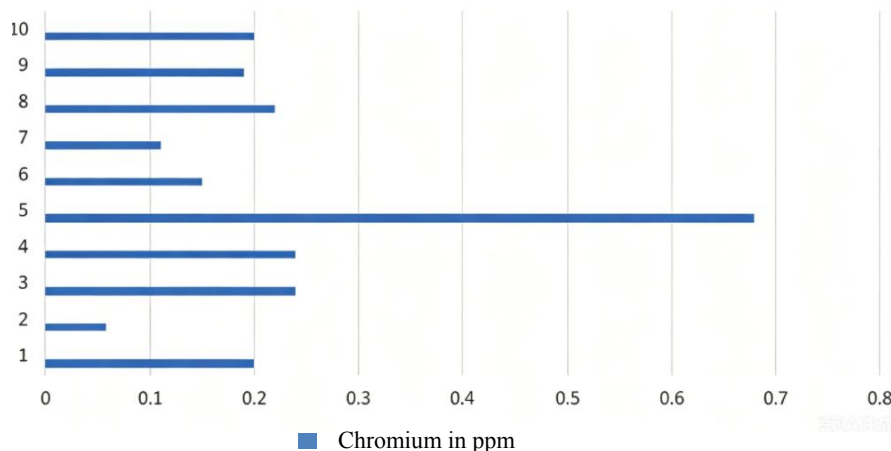


Figure 3. Chromium content in wastewater in the month of May.

As can be seen in Figure 1, the chromium III content in the treated wastewater during the month of March ranged from 0.088 to 0.99 ppm.

In April, the chromium III content in treated wastewater ranged from 0.11 to 0.66 ppm.

In May, the chromium III content of treated wastewater ranged from 0.059 to 0.68 ppm.

The results obtained after treatment were within specification.

It should be noted that before water treatment, the chromium was in oxidation state VI. And all the chromium VI values were out of specification (greater than 1.5 ppm).

The importance of this study lies in the company's contribution to sustainable development, since the decision was made not to continue discharging untreated water, but instead, as a socially responsible company, to treat wastewater before discharging it.

4 Conclusion

The quality of the treated water was improved, as the chromium levels in the three months of study remained within the specification of the parameter established as maximum (1.5 mg/L), since without treatment all the samples analyzed were out of specification.

As can be seen, it is of paramount importance to treat wastewater for its subsequent use, since it can be used in toilets, or used as irrigation water in the green areas of companies where there are surface treatment processes with chromium.

It is recommended to continue treating wastewater, as well as continuing to check the chromium content after chromium reduction to avoid disposing of off-specification water, since chromium VI is a highly toxic element that can cause health problems such as cancer, among others.

The importance of this study lay in the reduction of Chromium VI to Chromium III, since at the company where the study was conducted, water was discharged into the sewer system without treatment, as was the case with other companies in the industrial sector, thus polluting the environment. Furthermore, the chromium was being discarded in its oxidation state VI.

This study lays the foundation for subsequent studies to improve water treatment as the beginning of a continuous improvement of the surface finishing process.

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Conflicts of interest

The author declares no conflicts of interest regarding the publication of this paper.

References

- [1] M. N. A. Al-Azzawi, S. M. Shartooh, S. Al-Hiyaly, "The Removal of Zinc, Chromium and Nickel from Industrial Waste-Water Using Banana Peels", *Iraqi Journal of Science*, pp. 72-81, 2013.
- [2] Asamblea Nacional, "Decreto Ejecutivo N°. 21-2017", en *La Gaceta, Diario Oficial*, p. 48, 2017.
- [3] B. Volesky, Z. R. Holant, "Biosorption of Heavy Metals", *Biotechnol. Prog.*, no. 11, pp. 235-250, 1995.
- [4] J. Guertin, *Toxicity and Health Effects of Chromium (All Oxidation States)*. Chromium (VI) Handbook, pp. 215-234, 2004.
- [5] OSHA, *Hexavalent Chromium*, Washington, 2009.
- [6] EPA, *Chromium Compounds*, 2000, <https://www.epa.gov/sites/production/files/2016-09/documents/chromium-compounds.pdf>
- [7] M. Aguilar, et al., "Remoción de plomo de soluciones acuosas por titanato de potasio dopado con sílice", *Rev. Int. Contam. Ambient*, vol.25, no. 3, pp.125-132, 2009.
- [8] B. Atkinson, F. Bux, H. Kasan, *Considerations for Application of Biosorption Technology to Remediate Metal-Contaminated Industrial Effluents*, Water SA, pp. 129-135, 1998.
- [9] S. Kamsonlian, S. Suresh, C. Majumder, S. Chand, "Characterization of Banana and Orange Peels: Biosorption Mechanism", *International Journal of Science Technology & Management*, pp. 1-7, 2011.
- [10] Z. Abbasi, M. Alikarami, E. Nezhad, F. Moradi, V. Moradi, "Adsorptive Removal of Co^{2+} and Ni^{2+} by Peels of Banana from Aqueous Solution", *Universal Journal of Chemistry*, 90-95, 2003.
- [11] APHA, AWWA, WEF. "Standard Methods for the Examination of Water and Wastewater", En *3500-Cr B. Colorimetric Method* (pp. 69-70). Washington: American Public Health Association, 2012.
- [12] A. Ashraf, S., Khalid, M. Fazal, "Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent", *Elsevier*, pp. 1-10, 2016.
- [13] B. Meroufel, O. Benali, M. Benyahia, "Adsorptive removal of anionic dye from aqueous solutions by Algeriankaolin: Characteristics, isotherm, kinetic and thermodynamic studies", *J. Mater. Environ. Sci.*, pp. 482-491, 2013.
- [14] P. Deshmukh, G. Khadse, V. Shinde, P. Labhasetwar, "Cadmium Removal from Aqueous Solutions Using Dried Banana Peels as An Adsorbent: Kinetics and Equilibrium Modeling", *Journal of Bioremediation & Biodegradation*, no. 8, pp. 395, 2017.
- [15] M. Díaz, R. Contreras, M. Guardiola, C. Mayo del Río, "Kinetic study of absorption of chromium (VI) using Canary Bananas Peels in contaminated water", *International Journal of Innovation and Scientific Research*, pp. 139-145, 2017.
- [16] M. Kumar, C. Majumder, "Bio-adsorptive Removal of Cr (VI) from Stimulated Tannery Waste Water using Different Adsorbents and Compare with GAC" *Krishi Sanskriti*, pp. 73-86, 2014.
- [17] M. Romero-Sevilla, S. Sánchez-Cuadra, M. Benavente Silva, "Aplicación de Quitosano modificado en el tratamiento de aguas residuales de tenerías", *Nexo Revista Científica*, pp. 104-119, 2018.
- [18] J. Memon, S. Memon, M. Bhanger, M. Khuhawar, "Banana Peel: A Green and Economical Sorbent for Cr(III) Removal", *Pak. J. Anal. Environ. Chem.*, pp. 20-25, 2009.

- [19] M. Rege, J. Petersen, D. Johnstone, C. Turik, D. Yonge, W. Apel, "Bacterial reduction of hexavalent chromium by *Enterobacter cloacae* strain HO1 grown on sucrose", *Biotechnology Letters*, vol. 19, no. 7, pp. 691-694, 1997.
- [20] F. Rosales-Ayala, D. Rovira-Quezada, R. Campos-Rodríguez, "Calidad de las aguas residuales de tipo especial en la ciudad La Libertad, El Salvador", *Tecnología en Marcha*, vol. 32, no. 3, pp. 135-145, Jul.-Sep., 2019. doi: <https://doi.org/10.18845/tm.v32i3.4504>
- [21] L. Torres, J. Cárdenas, M. Moctezuma, V. Martínez, I. Acosta, "Remoción de cromo hexavante por la cáscara de plátano (*Musa cavendishii*)", *Química Hoy, Chemistry Sciences*, pp. 29-32, 2012.
- [22] SEMARNAT, NOM-001-SEMARNAT-1996, 1996.