redin Revista Facultad de Ingeniería

UNIVERSIDAD DE ANTIOQUIA 1803

Title: **Synthesis of (Ti/Si) mixed oxides for the removal of Cr(VI) in simulated effluents**

Authors: Gloria María Doria-Herrera, Nelson A. Ledesma, Juan A. Gutiérrez-Vélez, Hoover A. Valencia and Héctor Fabio Cortés-Hernández

DOI: **10.17533/udea.redin.20250674**

To appear in: *Revista Facultad de Ingeniería Universidad de Antioquia*

Received: October 24, 2024
Accepted: June 10, 2025
Available Online: June 10, 2025

Please cite this article as: G. M. Doria-Herrera, N. A. Ledesma, J. A. Gutiérrez-Vélez, H. A. Valencia and H. F. Cortés-Hernández. Synthesis of (Ti/Si) mixed oxides for the removal of Cr(VI) in simulated effluents, *Revista Facultad de Ingeniería Universidad de Antioquia*. [Online]. Available: https://www.doi.org/10.17533/udea.redin.20250674

Synthesis of (Ti/Si) mixed oxides for the removal of Cr(VI) in simulated effluents

Síntesis de óxidos mixtos (Ti/Si) CO para la remoción de Cr(VI) en efluentes simulados

Gloria María Doria-Herrera[1*], https://orcid.org/0000-0003-2148-8968 Nelson A. Ledesma[2] https://orcid.org/0009-0000-0314-4905 Juan A. Gutiérrez-Vélez[3] https://orcid.org/0009-0003-5166-9046 Hoover A. Valencia[4] https://orcid.org/0000-0001-9193-2089 and Héctor Fabio Cortés-Hernández[5] http://orcid.org/0000-0001-7242-0192

[1]Grupo de Investigación en Fisicoquímica Aplicada y Modelado Molecular GIFAMol, Universidad EAFIT. Medellín, Colombia
[2]Facultad de Ingeniería, Universidad EAFIT. Medellín, Colombia
[3]Laboratorio de Estupefacientes, Universidad de Antioquia. Medellín, Colombia
[4]Escuela de Química, Grupo de Investigación en Fisicoquímica Aplicada y Modelado Molecular GIFAMol, Universidad Tecnológica de Pereira. Pereira, Colombia
[5]Facultad de Ciencias, Departamento de Química, Grupo de Investigación en Fisicoquímica Aplicada y Modelado Molecular GIFAMol. Universidad del Tolima. Ibague, Colombia

*Corresponding author: Gloria María Doria-Herrera
E-mail: gmdoriah@eafit.edu.co

KEYWORDS
Waste treatment; composite material; metals; pollutants; experimental methods
Contaminación del agua; material compuesto; metales; contaminantes; métodos experimentales

ABSTRACT: The use of agroindustry residues as precursor materials in the absorption processes has taken a significant importance due to their great absorptive porous characteristics; however, the most critical drawback of the heavy metals is the difficulty of eliminating them, particularly, the Cr(VI), which is widely used in tannery but, at the same time, is considered a powerful cancerogenic and mutagenic agent. For this reason, it is crucial to seek strategies to eliminate, or form complexes for future immobilization, such heavy metals. This research proposes the synthesis of a mix of silica/titanium (Si/Ti) using the rice husk as the source of silica, and titanium tetrachloride as a precursor of titanium for the removal of the Cr(VI) in simulated effluents. TGA, IR-ATR analysis, SEM, powder diffraction and fluorescence were applied to verify the efficiency of the reaction and the adsorptive capacity. Three variables were considered significant in the adsorption process: pH; amount of dosage; and concentration of Cr(VI) contaminant, which were assessed independently for silica oxide, from which a removal rate of 53.4 %, pH 1, 1,5 g adsorbent/L and initial concentration of Cr(VI) 0.08 mg/L was obtained. For the mixed oxide from

---

a removal percentage of 97.2 % was obtained, with the best removal conditions at a pH of 1.5 g/L adsorbent dosage amount and Cr(VI) contaminant concentration of 0.08 mg /L.

RESUMEN: el uso de residuos de la agroindustria como materiales precursores en los procesos de absorción ha tomado una importancia significativa debido a que tienen grandes características de porosidad absorbente; sin embargo, el mayor inconveniente de los metales pesados es la dificultad que presentan para ser eliminados, en particular, el Cr(VI), que es ampliamente utilizado en curtiembres y considerado como un poderoso agente cancerígeno y mutagénico. Por ello, es importante la búsqueda de estrategias para su eliminación o acomplejar para la inmovilización. Esta investigación propone la síntesis de una mezcla sílice/titanio (Si/Ti) utilizando cascarilla de arroz como fuente de sílice y, como precursor del titanio, tetracloruro de titanio para la remoción del Cr(VI) en efluentes simulados. Para verificar la caracterización de la síntesis y comprobar las propiedades adsortivas se usó TGA, análisis IR-ATR, SEM, difracción de polvo y fluorescencia. Se identificaron tres variables significativas en el proceso de adsorción: pH; cantidad de dosificación; y concentración de Cr(VI) contaminante, y se aplicaron de forma independiente para el óxido de sílice, del cual se obtuvo una tasa de remoción del 53,4 %, pH 1, 1.5 g adsorbente/L y concentración inicial de Cr(VI) 0,08 mg/L. Para el óxido mixto se obtuvo un porcentaje de remoción del 97,2 %, con las mejores condiciones de remoción a un pH de 1,5 g/L de dosis de adsorbente y concentración de contaminante Cr(VI) de 0,08 mg/L.

1. Introduction

The search for new inexpensive and efficient materials for the treatment of effluents contaminated with heavy metals has been of great interest due to their environmental impact and the challenge that poses their difficult removal because of pH fluctuations (formation of microspecies) [1-2]. There are conventional methodologies in place, such as the electrochemical process, membrane filtration, and ionic interchange; however, those methods imply excessive operation cost, incomplete removal, sludge formation and generation of toxic by-products [3]. For this reason, the need to propose alternative treatment strategies that apply affordable, efficient, and environmentally friendly methodologies was identified. The adsorption processes are considered an option that meets these characteristics and that, in addition, takes advantage of agroindustry residues, which are otherwise commonly problematic due to their accumulation and difficult disposal, providing added value to these processes [4]. On the other hand, the binary composites, such as mixed transition metal oxides, present a very wide range of electronic properties, which makes them functional materials in various applications. Specifically for the case of this research, the silica and titanium oxides can be applied in photocatalysis[5] and heavy metal adsorption[6].

There are two species of rice seedlings that can be considered primary: *Oryza glaberrima* and *Oryza Sativa L.* The first species is grown almost exclusively in West Africa[7]; the second, constitutes the predominant species in terms of rice cultivation worldwide. It originates from Asia and, thanks to advances in genetic engineering, there are countless varieties of this species cultivated on the planet; the Miramono and Fedearroz 2000 Colombian varieties are prevalent in the rice-growing regions of the country[8].

This research proposes the synthesis of a mix of silica/Titanium Oxide (Si/Ti), using SiO_2 from rice husk and titanium chloride precursor, to evaluate its capacity as adsorbent in the removal of Cr(VI) from simulated wastewater. Subsequently, for the characterization of the synthetized composite, thermogravimetric analysis (TGA), infrared spectroscopy with attenuated reflectance (IR-ATR) analysis, scanning electron microscopy (SEM), powder diffraction, and fluorescence were applied to check the formation of the new composite. At last, for the quantification of the adsorption capacity, a simultaneous study of the effects of the several variables in the Cr(VI) adsorption process such as pH, dosage of the adsorbent was performed, and subsequently, the initial concentration of the pollutant was determined in order to establish the environmental conditions that yield the best percentages in the removal of Cr(VI)[9].

2. Materials and methods

2.1. Sample collection of rice seedlings and rice husks from agroindustry residue

The rice seedlings and husks were obtained in two different regions of Colombia, specifically from Córdoba and Norte de Santander. These seedlings were taken for botanical identification at the University of Antioquia Herbarium (HUA), where information about the species and family of the specimens was obtained.

2.2. Preparation of rice husk samples

The rice husks from each of the regions were separately washed with distilled water to remove impurities, then dried at 100 °C in forced air oven for a period of 48 hours until moisture removal. The husks were later stored in sealed polyethylene bags for the next testing. Then, to collect the ashes from of the rice husk, 10 g of rice husk were calcined in a heating muffle at a temperature of 800 °C. At last, the calcined material was cooled for 2 hours and used for SiO_2 extraction[10].

2.3 Extraction of amorphous silica

For the extraction process, the rice husk ash (CCA) extracted in the above process was added to 100 mL of a 2.5 M aqueous NaOH solution at room temperature with constant stirring for 30 min, which was later heated at 120 °C for 20 minutes. The resulting slurry was filtered hot in a vacuum system. The ash residue retained on the paper was washed with hot distilled water to solubilize the sodium silicate. The filtration was later cooled and adjusted to pH 2 by adding 2.5 M H_2SO_4 to precipitate the silica. The precipitated solid was dried at 120 °C in a forced air oven for 15 hours, washed with distilled water to remove the impurities and, at last, dried again at 60 °C for 48 hours[11].

2.4 Synthesis of the mixed composite

For the synthesis of the composite, a concentration of 0.5 M $TiCl_4$ in 3 M HCl was prepared. The mixture was then transferred to a pre-weighed flat bottom balloon, and then SiO_2 (23.95 g) was added in a mass ratio proportion of 1:1 of SiO_2:$TiCl_4$. The mixture was refluxed with constant stirring at 300 rpm and 95 °C in oil bath for 2 hours.

2.5 Quantification of the Cr(VI) in the solution

For the quantification of Hexavalent Chromium, the colorimetric technique described in edition 22 of the standard methods for the analysis of potable and residual water, Method 3500-Cr B (Page 3-69 to 3-70) was used. Then, 10 minutes after preparing the reagent, absorbance was measured on the UVmini-1240 spectrophotometer at a wavelength of 540 nm.

2.6 Experimental design for the test

The following parameters were used in the adsorption process: Cr(VI) initial concentration; pH; and adsorbent dosage[12]. The selection criterion of low (-) and high (+) pH levels is associated to the preference of the polluting species at an acid pH[13]. To establish the adsorption process criteria, and with the help of statistical software **Statgraphics 19-X64**, an experimental design was developed using factorial design with three points to the center. Table 1 illustrates the minimum and maximum ranges of each of the parameters taken for the elaboration of the central composite design (DCC) for triplicate experiments.

Range	Initial Conc. (ppm)	pH	Dosage (g/L)
Minimum	0.08	1.00	0.30
Maximum	0.80	5.00	5.00

Table 1. Minimum and maximum ranges for the development of the DCC.

2.7. Characterization techniques

The rice ash, silica and mixed oxide compounds obtained were characterized by using X-ray fluorescence (FRX) techniques, with FRX X ARL 9800XP equipment, at Cementos Argos S.A. Santa Bárbara station; X-ray diffraction (XRD) with Bruker D8 Advance and TGA equipment, NETZSCH TG 209 F1, at the Interdisciplinary Institute of Sciences of Universidad del Quindío; Fourier Transform Infrared Spectroscopy (FTIR-ATR) with PerkinElmer Spectrum Two, in the Applied Chemistry Laboratory of Universidad Nacional de Colombia, Medellin; and SEM and X-ray Dispersive Energy Spectrometry Coupled to Scanning Electron Microscopy (EDS), with JSM-7100F Field Emission Scanning Electron Microscope, In The Laboratory Of Microscopy of ITM, Medellin, Colombia.

3. Results and discussion

3.1 Identification of rice seedlings

The rice seedlings used for this research originated from the Colombian regions of Córdoba and Norte de Santander, these samples were classified by the HUA. The results indicated that both specimens belong to the species *Oryza sativa L.* of the *Poaceae* family; the specimen from the Córdoba department corresponds to the variety of Creole rice known as Miramono and the specimen obtained from the rice-growing region of Norte de Santander belongs to the variety known as Fedearroz 2000. The results show that there is no significant difference in terms of species and family for both samples collected. The yield in the process of extracting silica from the CCA from Córdoba region was 81.35 %, while the variety from Norte de Santander was 78.82 %. The silica extraction showed losses of 12 and 15 % with respect to the amorphous SiO_2, which was 92.8 % in the CCA from Córdoba region and 95.8 % in the Norte de Santander variety.

3.2 Silica extraction from rice husk

In the extraction process, during the first 15 minutes, an almost brownish-yellowish coloration was observed, this has been described as the solubilization of the silica present in the ash by the formation of the Na_2SiO_3 suspension aggregate [14]. In the next stage, as the acidification process progressed, precipitated silica began to appear. Then, in the neutralization phase, the formation of a thick, white gel was observed, which was later dried[15].

After drying the gel, a white paste was obtained, which was washed, filtered, dried, and pulverized to obtain a fine powder as shown in Figure 1. The yield of the silica extraction in the CCA from the Córdoba region was 81.35 %, while in the extraction of CCA from the Norte de Santander region was 78.82 %, this means that, out of every 100 g of ash that were chemically treated with the previously described procedure, 81.35 g and 78.82 g were recovered, respectively. This indicates silica losses of 12 % and 15 % with respect to the amorphous silica content, which is 92.8 % in the CCA from the Córdoba region and 95.8 % in the CCA from the Norte de Santander region (this information will be expanded upon later in the elemental analysis of CCA). These losses of material are due to different factors: First, the silica in the gel phase (intermediate step in the extraction process) tended to remain adhered to the glass material; second, when filtering the material, the finer particles passed through the sieve; and finally, the silica powders were too fine and when handled they remained suspended in the air or adhered to other surfaces; these factors together made it difficult to recover the extracted material.

Figure 1. Products of the different steps of the amorphous silica extraction: (a) digestion of CCA in 2.5 M NaOH, (b) filtration of Na_2SO_3, (c) silica gel, (d) amorphous silica.

Later, the synthetized product became a very fine powder of white color, shown in Figure 2, its mass was measured at 20.45 g and the yield of the process was calculated at 60.02 % of the theoretical basis that was 34.07 g that would be generated from the 1:1 mass ratio of $TiCl_4$ and amorphous SiO_2 [16]. The results of the white appearance and the fineness of the mixed oxides are a characteristic trait of this type of composites [17].

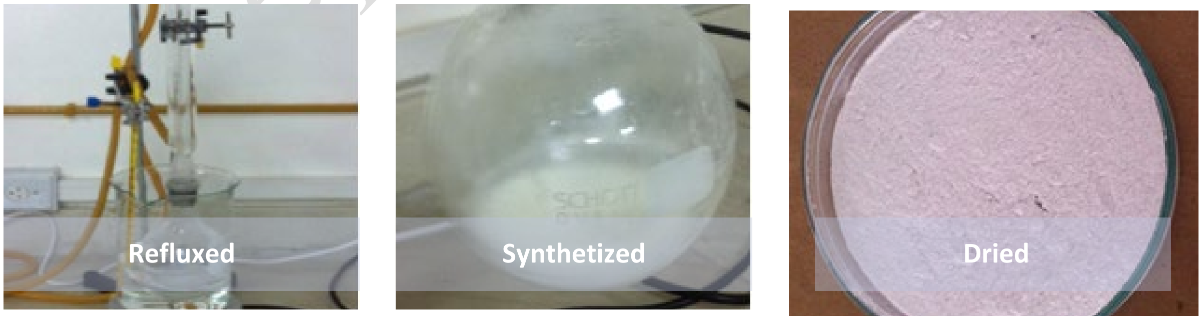


Figure 2. Reflux assembly for the synthesis of mixed oxides (TiO_2/SiO_2).

3.3 Characterization of the TiO_2/SiO_2 composite

3.3.1 FRX analysis

The above results of a 92 % content of silica (Si) in the ashes from the Córdoba and Norte de Santander make a significant match in comparison to previous research, with between 85 % and 96 % [18]. Table 2 shows the elemental composition of the ashes, and the silica derived from the ashes of each region; the presence of potassium, calcium, and phosphorus oxides among others; as well as minerals commonly found in rice husks[18], [19]. These experiments presented a successful extraction of the silica from the ash of the rice husk. The FRX analysis showed that amorphous SiO_2 was obtained with a purity percentage of 97 %, the remaining 3 % was comprised of metal oxides derived from the husk ash; it should be noted that the concentrations of these oxides decreased significantly.

Composition (%)	**Source**				
	CCA-Cord	**CCA-Norte de S.**	**SiO_2-Cord.**	**SiO_2- Norte de S.**	**TiO_2/SiO_2**
Si	92.80	95.80	97.10	97.90	72.30
K	3.59	1.06	0.36	0.31	--
Ca	1.07	0.75	0.16	0.18	--
Hg	0.70	0.54	1.64	1.09	0.68
P	0.65	0.52	0.13	0	--
Ti	--	--	--	--	26.26
Others	1.19	1.32	0.61	0.52	0.42

Table 2. Elemental composition of CCA and mixed oxides TiO_2/SiO_2.

The elemental FRX analysis shows the presence of Mercury in the CCA and amorphous SiO_2. The presence of this heavy metal in the CCA and its amorphous SiO_2 can be attributed to the absorption of mercury by the roots of the rice seedlings from the surrounding medium or the flood or saturation water used in the irrigation of the crop [20][21]. The FRX analysis applied to the mixed oxides reveals that their elemental composition is of silica, at 72.30 %, followed by titanium, at 26.60 %, and, to a lesser extent, traces of mercury and other metallic elements in percentages of 0.70 and 0.42 respectively. The explanation for the presence of oxides is attributed to the natural source of the SiO_2, which is very similar to the results presented in the previous research [14], [21]. Finally, the results of this analysis regarding synthetized composite TiO_2/SiO_2 are consistent to previous research, with around 26 % using the precursor $TiCl_4$ [22].

3.3.2 XRD analysis

XRD diffractograms of the CCA of the Córdoba and Norte de Santander regions shown in the Figure 3 appeared in a band between (15°-30°) with a prominent peak that reaches its maximum in the mark of 22°, which is consistent with previous research, where it is mentioned as a characteristic of the ashes of the rice husk and is closely related to the amorphous silica [23]. On the other hand, the silica extracted from the ashes of both regions shows the same patterns in their respective diffractograms. Figure 3 shows the amorphous SiO_2 diffractograms of both regions[21-22].

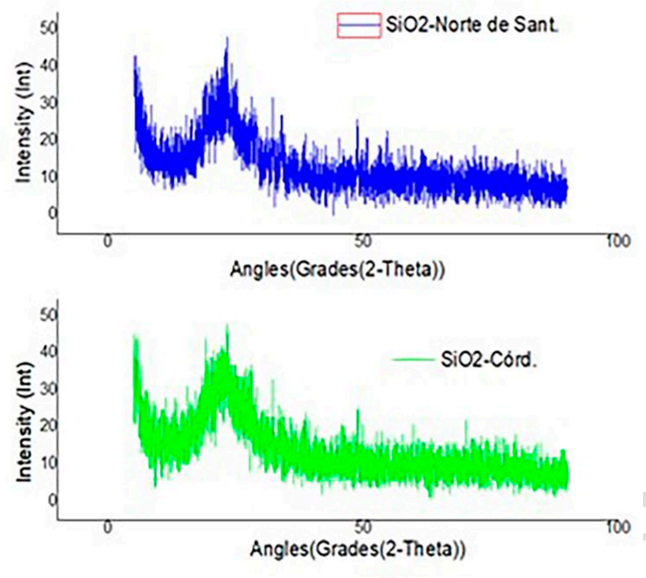


Figure 3. Diffractograms of the silica Córdoba Region and Norte de Santander Region.

Based on the diffractograms obtained from the rice husks and the silica from both regions in Figure 3, it can be affirmed that the ash obtained presents high contents of silica. In addition, both silica samples, present in the ashes and the extracted silica, exhibit characteristics typical of the amorphous silica, and additionally, the calcination at 800 °C did not cause significant variation in the morphology of the crystalline lattice of the silica extracted [24]24]. Furthermore, the diffractogram from the DRX analysis applied to the mixed oxides composite (Figure 4) shows a continuous band that is only interrupted at 27º by the formation of a peak in this band; this can be associated with amorphous SiO_2. Different peaks are present in the 36, 42, 54, and 70 degrees, which are characteristic of the anatase phase TiO_2 [16].

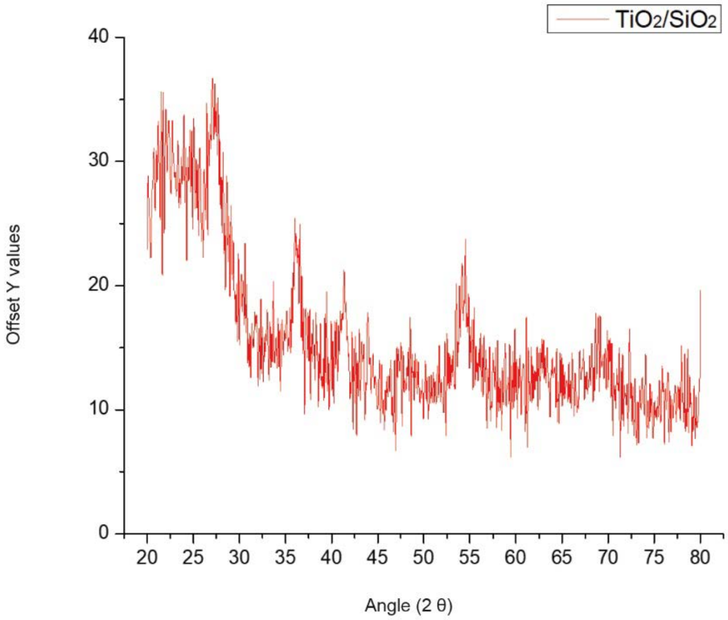
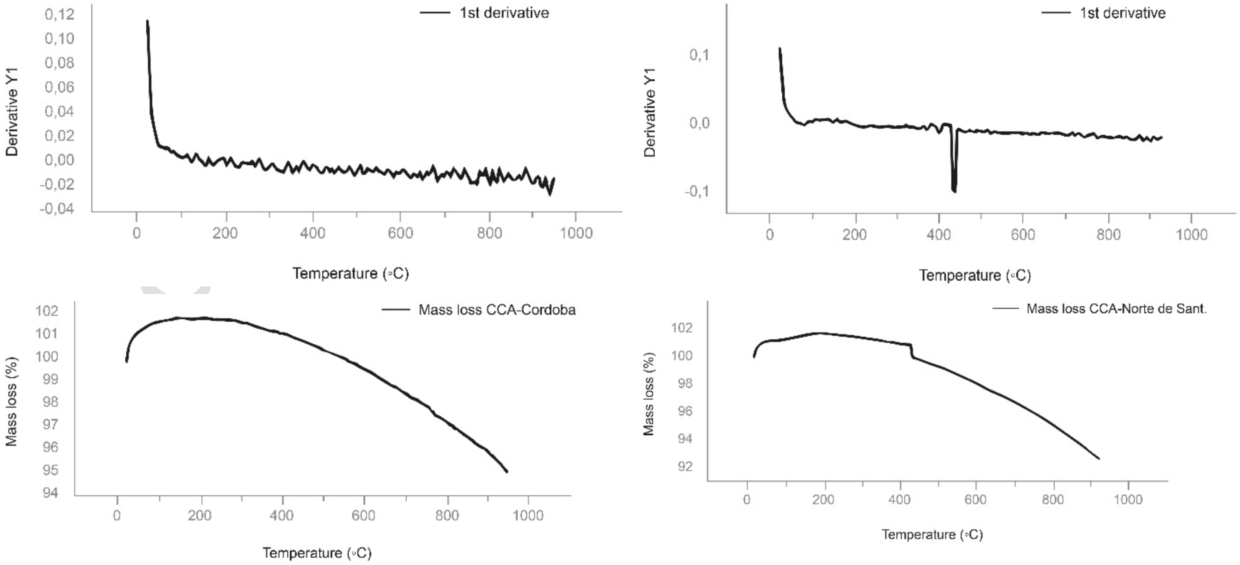


Figure 4. Diffractogram of the mixed oxide composites.

3.3.3 TGA results

Initially, the loss of mass for the ash and the amorphous SiO_2 of the Córdoba Region is constant starting at 600 °C and, for the Norte de Santander pair, at 400 °C (Figure 5) with a total mass loss of 4 and 7 % (of mass) respectively. Based on the FRX elemental analysis, the negative change in mass is due to the loss of water adsorbed in its pores (approximately 2.23 % and 5.23 %). The shape of the curve indicates that the mass loss is gradual but constant, so it can be deduced that the water adsorbed physically into the pores of the material was removed first, and subsequently the loss of chemically bound water or hydroxyl groups begins[26].



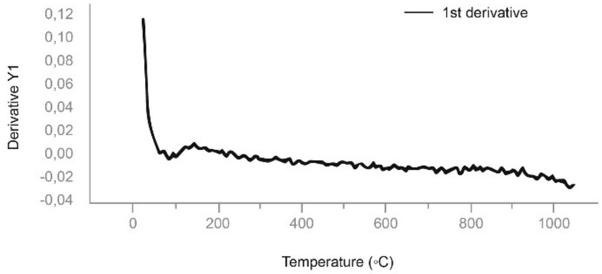
a. **b.**

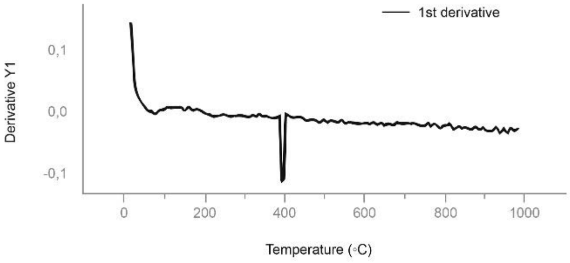
Figure 5. Thermogravimetric analysis (mass loss curve and first derivative) of CCA from the regions of **a.** Córdoba; and **b.** Norte de Santander.

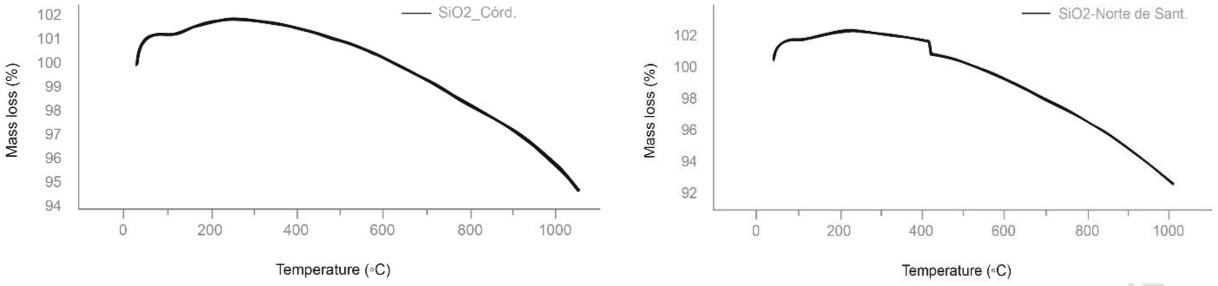
In the case of ash from the rice husks, the mineralization of organic-originated carbon may also include the conversion of these composites into carbon dioxide and water. In addition, phosphorus oxides, composed of both SiO_2 and ashes of the rice husk, have a low boiling point (360 °C), so it is deduced that the mass loss includes the volatilization of these oxides. Mercury (II) oxide decomposes at temperatures of 500 °C, so it is also inferred that part of the mass loss is induced by the decomposition of the mercury oxides. Amorphous silica begins to change its crystalline morphology when subjected to temperatures well above 800 °C [27]; consequently, the mass losses of that material presented at this temperature can occur by the reorganization of the crystalline network of the silica in its transition into quartz crystals or other structures of the crystalline silica [28].

Observing the first derivative of each curve, it can be deduced that the materials have high thermal stability and low reactivity, as well as characteristics of amorphous solids. This analysis shows that the ash and silica obtained are mostly amorphous silica with high chemical and thermal stability[29].

Figure 6 shows the first derivative of the mass loss of the SiO_2 from the Córdoba region, which is related to the thermogravimetric analysis of the other rice husk derivatives obtained for this research work. On the other hand, in the TGA analysis for the composite of mixed oxides, the shape of the thermogram curve reveals a rapid loss of mass of 10 % between 0 °C and 100 °C; it is inferred that this represents the loss of surface moisture (physically adsorbed), which is sustained by observing the first derivative of the mass loss curve. Henceforth, the loss of mass is less pronounced but constant, eventually losing 20 %. This mass loss is due to the elimination of chemically bound water and hydroxyl groups [26][30]. From the mark of 500 °C there is evidence of decomposition of the mercury oxides present in the material, as described in the FRX analysis. In perspective, the total mass loss is 30 %. By observing the first derivative, it is inferred that the composite has moderate thermal stability; however, mass losses induced by the reorganization of the crystalline structure of the composite are not ruled out[14].







a. **b.**

Figure 6. Thermogravimetric analysis (mass loss curve and first derivative) of silica from CCA **a.** Córdoba; **b.** Norte de Santander.

Figure 7 shows the mass loss curve, and the first derivative of the analysis applied to the composite TiO_2/SiO_2. The change is evident with respect to the other thermogravimetric analysis; for this reason, the synthesis product is checked.

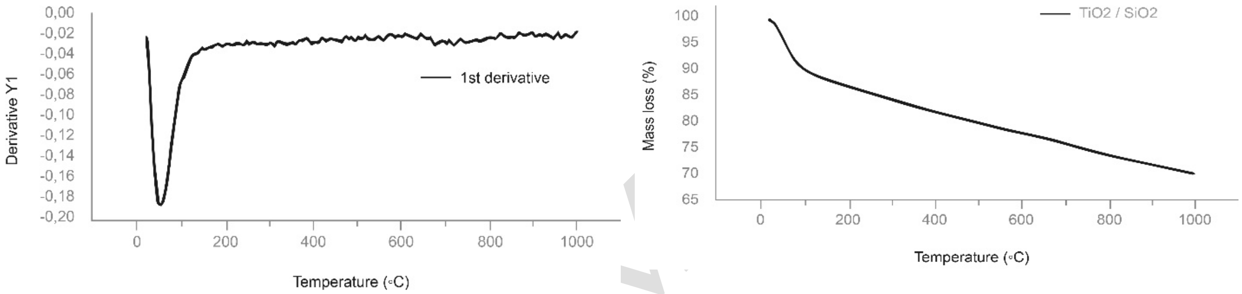


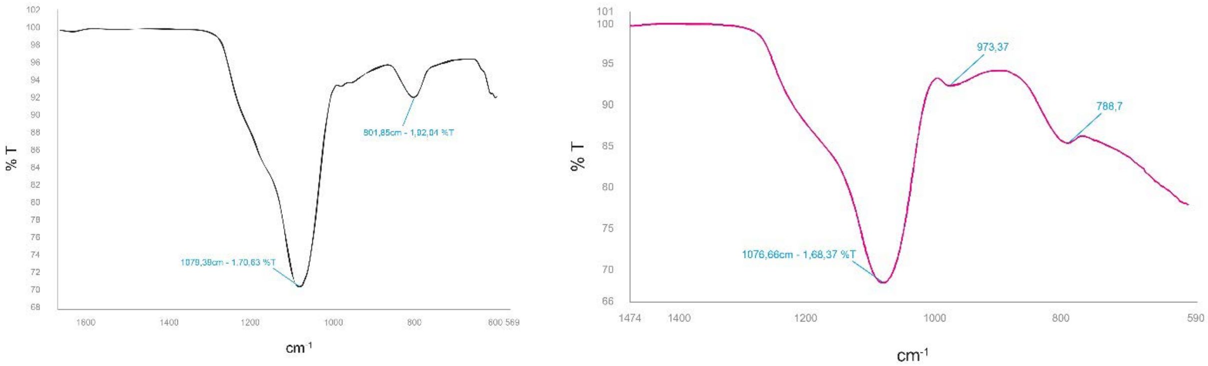
Figure 7. Thermogravimetric Analysis (mass loss curve and first derivative) composite TiO_2/SiO_2.

3.3.4 FTIR results

The amorphous SiO_2 of the Córdoba region sample was chosen for the synthesis of the mixed oxides TiO_2/SiO_2, since it did not exhibit morphological difference with the SiO_2 of Norte de Santander; consequently, the FTIR analysis was applied only to the silica from Córdoba, to evaluate the change in its morphology.

The SiO_2 spectrum (Figure 8a) shows three prominent peaks, one in the 1071 cm^{-1} region, which is characteristic of stretching movements of Si-O bonds; another in the 800 cm^{-1}, which is attributed to symmetrical or stretching movements of the Si-O-Si groups; and the latter in the 600 cm^{-1} band, which is assigned to the torsion movement in the O groups [31][32][33].

On the other hand, the spectrogram of the mixed oxides shows three peaks (Figure 8b), in 1078 cm^{-1}, 973 cm^{-1} and 788 cm^{-1}; the bands of 973 cm^{-1} and 788 cm^{-1} differ from those presented by amorphous silica. This difference is attributed to SiO_2 defects induced by the inclusion of Ti(IV) within the SiO_2 crystal structure. The first corresponds to vibrations in Ti-O-Si bonds; and the second, which is accompanied by a wide band, is related to stretching movements in the Ti-O-Ti bonds, characteristic of the anatase phase TiO_2[16].

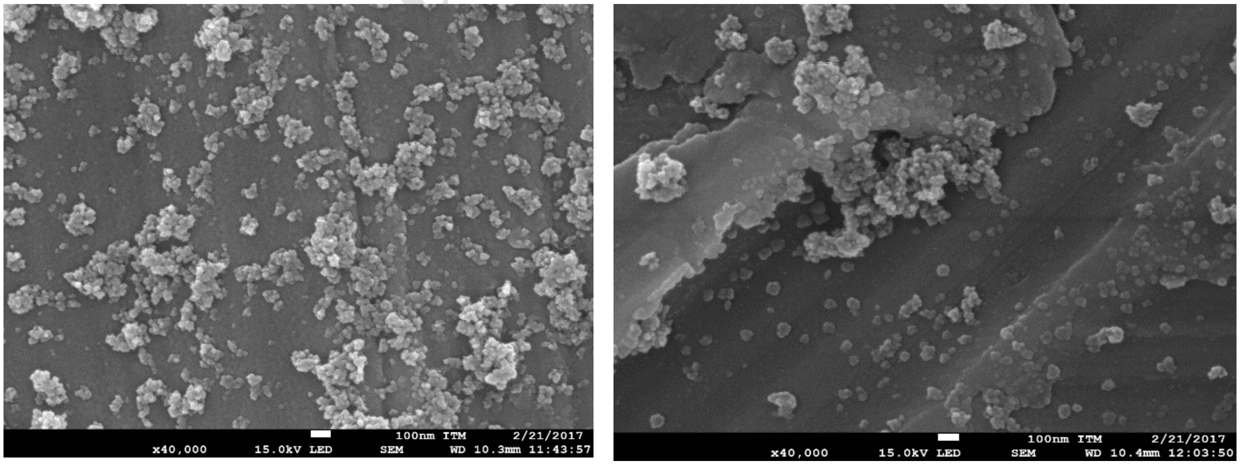


a. **b.**

Figure 8. FTIR spectroscopic analysis: **a.** Silica from Córdoba region. **b.** Mixed oxides TiO_2/SiO_2 synthetized.

3.3.5 SEM results

The SEM technique was applied to the amorphous SiO_2 extracted from the CCA from Córdoba and mixed TiO_2 /SiO_2 oxide, this technique seeks to analyze the changes in the morphology of the synthesis and the possible inclusion of the Ti(IV) ions inside its structure. In Figure 9a and Figure 9b, obtained by SEM at 40000X, it is observed that the SiO_2 surface has rough features and that there is presence of certain granular-shaped conglomerates in several sizes. When comparing the results with the micrography of the mixed oxide, it is evident that both materials present equal amorphicity, with very rough particles, which indicates high porosity. Titanium oxide and SiO_2 interacted so that the former adhered to the SiO_2 surface as a support.



a. **b.**

Figure 9. SEM of **a.** Córdoba silica and **b.** mixed oxides taken at 100 nm and magnification of 40000x.

The aforementioned interaction was evident when the elemental composition was analyzed by the EDS dispersive energy technique (Table 3), where it can be observed that the composition of the particles is clearly SiO_2; while, in the case of the mixed oxide, there is presence of titanium on silica, in contrast with the FTIR analysis. It is deduced that the TiO_2 is indeed supported on the SiO_2. Finally, in terms of percentages, it is expected that oxygen is present in a greater proportion due to the bonds it forms with titanium and silicon; thus, demonstrating that by using this semiquantitative tool (EDS) there is evidence that the inclusion of the particles occurred, forming Ti-O-Si bonds.

Elements (%)	**SiO_2 Weight (%)**	**TiO_2- SiO_2 Weight (%)**
O	62.94	68.01
Si	37.06	12.72
Ti	**----**	19.27
Total	**100.00**	**100.00**

Table 3. Percentage composition of the micrograph points of SiO_2 and TiO_2/SiO_2.

3.4 Experimental design results

For the experimental tests, a factorial analysis was carried out to establish the pH conditions, initial concentration and dosage of the adsorbent using the central composite design (CDC). The working ranges were shortlisted considering previous experiments and the reviewed literature. The selected values were between 0.08 ppm-0.80 ppm for the initial concentration of contaminant; a pH between 1.00-5.00; and adsorbent dosage of 0.30 g/L and 5.00 g/L. The software selected for the experimental design and analysis of results was **Statgraphics 19-X64**.

The ANOVA analysis reveals that the individual variables that influence the silica adsorption process are the pH and the initial concentration of Cr(VI), while the dosage of the adsorbent occupies fourth place in relevance in this process. For the adsorption tests with mixed oxides TiO_2/SiO_2, it was found that the influence exerted by the variables, expressed in decreasing order, is as follows: the dosage of the adsorbent; the pH; and the initial concentration of the contaminant. Figure 10 shows the Pareto diagrams, where it is evident the influence of the analyzed variables on the adsorption of Cr(VI) with both adsorbent materials.

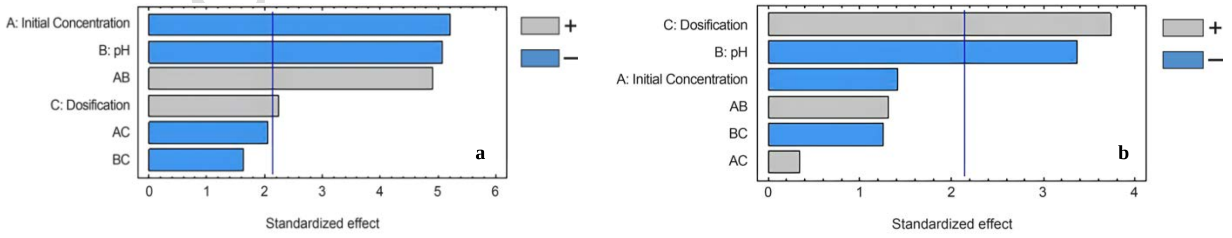


Figure 10. Pareto diagrams of the effect of experimental variables and their interactions on adsorption efficiency with **a.** silica and **b.** TiO_2/SiO_2 mixed oxides (A: Initial concentration of Cr (VI); B: pH; C: adsorbent dosage).

In the tests with silica, it is notable that the interactions between the variables, pH, and initial concentration of the contaminant, surpassed the dosage of the adsorbent in influence. Furthermore, the influence exerted by the interactions of adsorbent dosage versus initial concentration and dosage versus pH are barely noticeable. In the adsorption tests with mixed oxides, it was observed that the influence of pH vs initial concentration of Cr(VI) occupies fourth place in terms of importance, followed by the influence of the combinations of the pH/dosage and initial concentration/dosage variables.

Figure 11a and Figure 11b illustrate the effects of the individual variables. There, it is observed that the percentage of Cr(VI) removal with silica decreased as the concentration of the contaminant increased, reaching a minimum removal when reaching the maximum concentration evaluated in this work (0.80 ppm). On the contrary, in the adsorption with mixed oxides, the concentration of the contaminant is not a parameter that limits its effect as an adsorbent material in a considerable manner, since it is observed that the removal percentages were significant at high concentrations of the contaminant; however, it was also noted that as the concentration of Cr(VI) increased, the removal percentage decreased. It is also observed in the tests with both adsorbent materials that the more acidic the medium (low pH) is, the greater the yields in the removal process are. However, it is revealed that, with high amounts of silica, only slight increases in the removal percentages are achieved; while, with mixed oxides, the greater the amounts of the adsorbent, the better the results in the removal of Cr(VI).

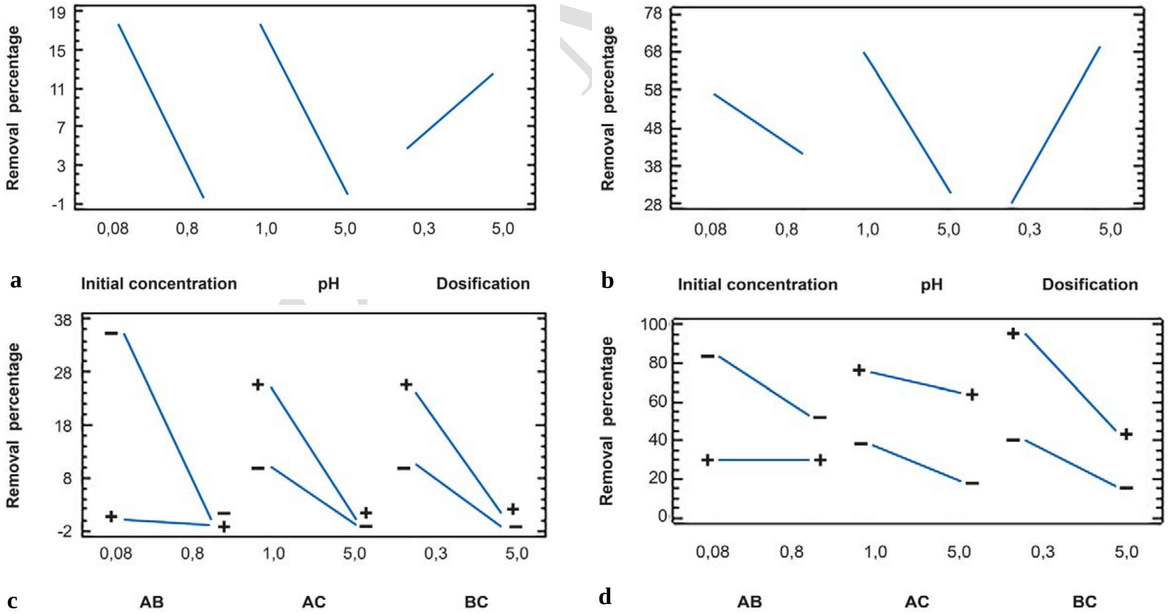
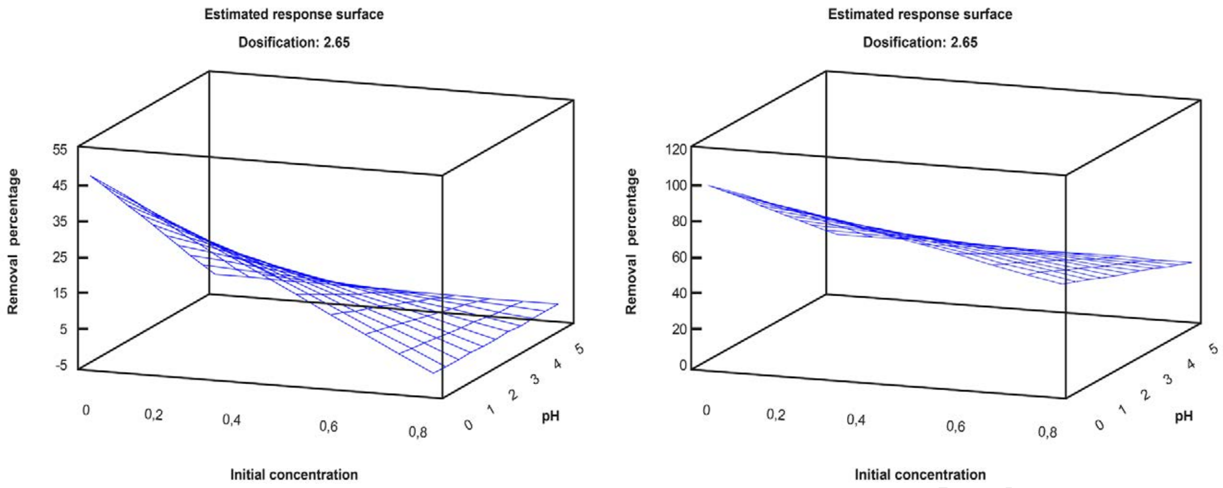


Figure 11. Influence of experimental variables on the adsorption process with silica and TiO_2/SiO_2 mixed oxides. **a.** Plot of main effects of individual variables of silica. b. Plot of main effects of individual variables of TiO_2/SiO_2 mixed oxides. c. Interaction graph between the variables of silica d. Interaction graph between the variables of TiO_2/SiO_2 mixed oxides. A: Initial concentration of Cr (VI), B: pH and C: Adsorbent dosage.

Figure 11c and Figure 11d show the interactions between the variables and the combinations between variables under study and their effect on the adsorption process with each of the adsorbent materials. It is observed that, in the adsorption tests with SiO_2 , the lower the pH and the lower the initial concentration of the contaminant, the better results are obtained in the removal of Cr(VI); therefore, the removal percentages are higher at a lower initial concentration of the contaminant and a greater amount of the adsorbent and, finally, at a lower pH and a greater amount of the adsorbent, the better results in the adsorption process are obtained. Consequently, in the adsorption tests with mixed oxides, it is observed, on the one hand, that the highest removal percentages occur at low concentrations of Cr(VI) and low pH, and on the other hand, that the performance increases as the concentration of the contaminant and the amount of the adsorbent material increases. Finally, the adsorption process is more efficient when the pH is low and the amount of adsorbent increases. Then, the response surface shown in Figure 12 indicates that the optimal conditions of the medium for the removal of the Cr(VI) contaminant with both adsorbent materials were at pH 1, with low concentrations of the contaminant and high dosages of the adsorbent. Furthermore, high concentrations of hexavalent chromium, a less acidic pH, and low amounts of adsorbent are the least favorable adsorption medium for the removal of Cr(VI) in both adsorption processes (with silica and mixed oxides).

Taking all the above into account, it is concluded that the medium that favors the adsorption of Cr(VI) with silica is at an acidic pH with low concentrations of Cr(VI), with better results obtained if high quantities of the adsorbent material are applied. For the adsorption tests with mixed oxides, it is concluded that the dosage of the adsorbent had a strong effect on the removal percentages of Cr(VI), since it is observed that the greater the amount of adsorbent, the higher the removal percentages of the contaminant. Furthermore, pH was proven to be a very important variable in the adsorption process with mixed oxides; it exerts less influence on the removal, which means that the material adsorbs the Cr(VI) contaminant in a wider pH range. Finally, the influence of the initial concentration of the contaminant is not very significant, since high removal percentages were obtained at both low and high concentrations of Cr(VI). Taking all into consideration, it can be concluded that the mixed oxide composite is a better adsorbent material than silica and that it can operate significantly better at high concentrations of the contaminant with broader pH ranges (between 1 and 3). It is worth noting that prior research shows that the adsorption processes of hexavalent chromium benefited from an acidic pH.



a. **b.**

Figure 12. Response surface of Cr(VI) adsorption tests with **a.** silica and **b.** TiO_2/SiO_2 mixed oxides.

4. Conclusions

The CCA of both regions, Córdoba and Norte de Santander, contain percentages of silica greater than 92 %, since high concentrations of amorphous silica were satisfactorily obtained and calcination at 800 °C did not cause significant variation in the morphology of the crystalline lattice obtained from the silica. The TiO_2/SiO_2 mixed oxide was synthesized with an elemental composition of predominantly silicon oxides (72.3 %) and titanium (26.6 %) using titanium tetrachloride $TiCl_4$ and silica (SiO_2) extracted from the rice husks as precursors. The FTIR spectra of the mixed oxide in the 973 cm^{-1} and 788 cm^{-1} regions differ from those presented by the amorphous silica. This change is attributed to SiO_2 defects induced by the inclusion of Ti(VI) within the crystalline structure of silica. Futhermore, the most favorable factors in the adsorption process with silica are the pH and the initial concentration of Cr(VI), while the dosage of the adsorbent occupies the fourth place in relevance in this process. The experimental parameters, where the highest percentages of removal were obtained, were: Cr(VI) initial concentration of 0.08 ppm, pH 1, and adsorbent dosage of 5 g/L, meaning low concentrations of the contaminant, acid pH and high adsorbent contents; therefore, high concentrations of hexavalent chromium, less acidic pH and low amounts of the adsorbent were the less favorable adsorption medium for removal of the contaminant.

5. Declaration of competing interest

We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

6. Acknowledgment

To the scholarship from the Ministry of Science and Technology for financial support through call 647 of 2015. To UNAD for its support for the development of Research and the UTP for the financial Support in the project "Evaluación de la potencial aplicación de perovskitas de titanio para la degradación de cafeína y nicotina presentes en las aguas finales de la planta de tratamiento de la Universidad Tecnológica de Pereira".

6. Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

7. Author contributions

Gloria M. Doria-Herrera: Was the researcher in charge of developing the methodology related to the analysis of hexavalent chromium in water and advisor of the experimental design. N. A. Ledesma and J. A. Gutiérrez-Vélez: Were the student researchers who executed the experiments developed in this research. H. F. Cortés-Hernández: Was the advisor on the extraction and synthesis methodology of the composites obtained. Finally, H. A. Valencia: Was the advisor in all the characterization of the compounds obtained.

8. Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

References

[1] R. Chakraborty, A. Asthana, A. K. Singh, B. Jain, and A. B. H. Susan, "Adsorption of heavy metal ions by various low-cost adsorbents: a review," *Int J Environ Anal Chem*, vol. 102, no. 2, pp. 342–379, 2022, doi: 10.1080/03067319.2020.1722811.

[2] W. Liu *et al.*, "Insight into pH dependent Cr(VI) removal with magnetic Fe3S4," *Chemical Engineering Journal*, vol. 359, no. Vi, pp. 564–571, 2019, doi: 10.1016/j.cej.2018.11.192.

[3] H. Karimi-Maleh *et al.*, "Recent advances in removal techniques of Cr(VI) toxic ion from aqueous solution: A comprehensive review," *J Mol Liq*, vol. 329, no. VI, p. 115062, May 2021, doi: 10.1016/j.molliq.2020.115062.

[4] A. K. Priya *et al.*, "Investigation of mechanism of heavy metals (Cr6+, Pb2+& Zn2+) adsorption from aqueous medium using rice husk ash: Kinetic and thermodynamic approach," *Chemosphere*, vol. 286, Jan. 2022, doi: 10.1016/j.chemosphere.2021.131796.

[5] D. Giuranno *et al.*, "Interface design in lightweight sic/tisi2 composites fabricated by reactive infiltration process: Interaction phenomena between liquid si-rich si-ti alloys and glassy carbon," *Materials*, vol. 14, no. 13, 2021, doi: 10.3390/ma14133746.

[6] Y. Wang, Z. Xing, Z. Li, X. Wu, G. Wang, and W. Zhou, "Facile synthesis of high-thermostably ordered mesoporous TiO2/SiO2 nanocomposites: An effective bifunctional candidate for removing arsenic contaminations," *J Colloid Interface Sci*, vol. 485, pp. 32–38, 2017, doi: 10.1016/j.jcis.2016.09.022.

[7] V. Degiovanni, L. Berrio, and R. Charry, "Origen , taxonomía , anatomía y morfología de la planta de arroz (Oryza sativa L .)," *Producción eco-eficiente del arroz en América Latina*, pp. 35–59, 2017, [Online]. Available: https://cgspace.cgiar.org/bitstream/handle/10568/82462/origen-ff4737f6.pdf?sequence=1

[8] V. Degiovanni Beltramo, J. Gómez, and J. Sierra, "Análisis de crecimiento y etapas de desarrollo de tres variedades de arroz (Oryza sativa L.) en Montería, Córdoba," *Temas Agrarios*, vol. 9, no. 1, pp. 21–29, 2004, doi: 10.21897/rta.v9i1.620.

[9] H. Memedi *et al.*, "Removal of Cr(VI) From Water Resources by Using Different Raw Inorganic Sorbents," *Quality of Life (Banja Luka) - APEIRON*, vol. 14, no. 3–4, 2017, doi: 10.7251/qol1603077m.

[10] H. B. Yener and S. S. Helvacı, "Effect of synthesis temperature on the structural properties and photocatalytic activity of TiO 2 / SiO 2 composites synthesized using rice husk ash as a SiO 2 source," vol. 140, pp. 84–93, 2015, doi: 10.1016/j.seppur.2014.11.013.

[11] P. U. Nzereogu, A. D. Omah, F. I. Ezema, E. I. Iwuoha, and A. C. Nwanya, "Silica extraction from rice husk: Comprehensive review and applications," *Hybrid Advances*, vol. 4, p. 100111, Dec. 2023, doi: 10.1016/j.hybadv.2023.100111.

[12] Y. Wang, C. Peng, E. Padilla-Ortega, A. Robledo-Cabrera, and A. López-Valdivieso, "Cr(VI) adsorption on activated carbon: Mechanisms, modeling and limitations in water treatment," *J Environ Chem Eng*, vol. 8, no. 4, 2020, doi: 10.1016/j.jece.2020.104031.

[13] T. Zang *et al.*, "Removal of Cr(VI) by modified and immobilized Auricularia auricula spent substrate in a fixed-bed column," *Ecol Eng*, vol. 99, pp. 358–365, 2017, doi: 10.1016/j.ecoleng.2016.11.070.

[14] H. B. Yener and Ş. S. Helvaci, "Effect of synthesis temperature on the structural properties and photocatalytic activity of TiO2/SiO2 composites synthesized using rice husk ash as a SiO2 source," *Sep Purif Technol*, vol. 140, pp. 84–93, 2015, doi: 10.1016/j.seppur.2014.11.013.

[15] T. Rasheed, M. Adeel, F. Nabeel, M. Bilal, and H. M. N. Iqbal, "TiO2/SiO2 decorated carbon nanostructured materials as a multifunctional platform for emerging pollutants removal," *Science of the Total Environment*, vol. 688, pp. 299–311, 2019, doi: 10.1016/j.scitotenv.2019.06.200.

[16] R. Nandanwar, P. Ingh, F. F. Syed, and F. Z. Haque, "Preparation of TiO2/SiO2 nanocomposite with non-ionic surfactants via sol-gel process and their photocatalytic study," *Oriental Journal of Chemistry*, vol. 30, no. 4, pp. 1577–1584, 2014, doi: 10.13005/ojc/300417.

[17] N. Farhana Jaafar, N. Farhana Jaafar, M. Khairuddean, and N. Nordin, "A Review on Recent Progression of Modifications on Titania Morphology and its Photocatalytic Performance," *Acta Chim Slov*, vol. 67, no. 2, pp. 361–374, 2020, doi: 10.17344/acsi.2019.5161.

[18] T. Serrano, M. Borrachero, J. Monzó, and J. Paya, "Morteros aligerados con cascarilla de arroz: Diseño de mezclas y evaluación de propiedades," pp. 128–136, 2012.

[19] A. T. O. Ramírez, M. R. Tovar, and O. Silva-Marrufo, "Rice husk reuse as a sustainable energy alternative in Tolima, Colombia," *Sci Rep*, vol. 14, no. 1, Dec. 2024, doi: 10.1038/s41598-024-60115-5.

[20] M. Argumedo, A. Consuegra, J. Marrugo, and J. Vidal, "Exposición a mercurio en habitantes del municipio de San Marcos (Departamento de Sucre) debida a la ingesta de arroz (Oryza sativa) contaminado," *Revista salud pública*, vol. 15, no. 6, pp. 903–915, 2013.

[21] C. M. R. Almeida, M. E. Ghica, and L. Durães, "An overview on alumina-silica-based aerogels," *Adv Colloid Interface Sci*, vol. 282, p. 102189, 2020, doi: 10.1016/j.cis.2020.102189.

[22] L. Galeano, J. A. Navío, G. M. Restrepo, and J. M. Marín, "Preparación de Sistemas Óxido de Titanio/Óxido de Silicio (TiO2/SiO2) mediante el Método Solvotérmico para Aplicaciones en Fotocatálisis," *Informacion Tecnologica*, vol. 24, no. 5, pp. 81–92, 2013, doi: 10.4067/S0718-07642013000500010.

[23] C. G. Rocha, D. A. M. Zaia, R. V. D. S. Alfaya, and A. A. D. S. Alfaya, "Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents," *J Hazard Mater*, vol. 166, no. 1, pp. 383–388, 2009, doi: 10.1016/j.jhazmat.2008.11.074.

[24] R. A. Bakar, R. Yahya, and S. N. Gan, "Production of High Purity Amorphous Silica from Rice Husk," *Procedia Chem*, vol. 19, pp. 189–195, 2016, doi: 10.1016/j.proche.2016.03.092.

[25] R. M. Mohamed, I. A. Mkhalid, and M. A. Barakat, "Rice husk ash as a renewable source for the production of zeolite NaY and its characterization," *Arabian Journal of Chemistry*, vol. 8, no. 1, pp. 48–53, 2015, doi: 10.1016/j.arabjc.2012.12.013.

[26] E. Pabón, S. Borja, O. Javier, and A. Ramirez, "Síntesis Y Caracterización De Óxidos Mixtos De Sílice-Titania Preparados Por Método Sol-Gel Prepared By Sol – Gel Method and Hydrothermal Treatment," *Revista EIA*, vol. 10, no. 19, pp. 123–132, 2013.

[27] S. Steven, E. Restiawaty, and Y. Bindar, "Routes for energy and bio-silica production from rice husk: A comprehensive review and emerging prospect," *Renewable and Sustainable Energy Reviews*, vol. 149, no. May 2020, p. 111329, 2021, doi: 10.1016/j.rser.2021.111329.

[28] L. P. Quiñones, M. L. Pérez, Y. M. Rodríguez, U. Tecnológica, D. La Habana, and J. Antonio, "Availability of SIO2 from the controled burning of Mayabeque," *Revista Ciencia y Construcción*, vol. II, no. 1, pp. 3–13, 2021.

[29] C. M. R. Almeida, M. E. Ghica, and L. Durães, “An overview on alumina-silica-based aerogels,” *Adv Colloid Interface Sci*, vol. 282, p. 102189, 2020, doi: 10.1016/j.cis.2020.102189.

[30] H. G. Palhares, B. S. Gonçalves, L. M. C. Silva, E. H. M. Nunes, and M. Houmard, “Clarifying the roles of hydrothermal treatment and silica addition to synthesize TiO2-based nanocomposites with high photocatalytic performance,” *J Solgel Sci Technol*, vol. 95, no. 1, pp. 119–135, 2020, doi: 10.1007/s10971-020-05265-4.

[31] S. a. Abo-El-Enein, M. a. Eissa, a. a. Diafullah, M. a. Rizk, and F. M. Mohamed, “Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash,” *J Hazard Mater*, vol. 172, no. 2–3, pp. 574–579, 2009, doi: 10.1016/j.jhazmat.2009.07.036.

[32] Y. Ding and D. Su, “Purifying Native In-Situ Mastoid SiO 2 from Rice Husk,”. *Energy Procedia*, vol. 16, pp. 1269–1274, 2012, doi: 10.1016/j.egypro.2012.01.203.

[33] F. M. Mohamed, K. A. Alfalous, and M. El Gamal, “Utilization of Poly Inorganic Coagulants Impregnated with Activated Silica Derived from Rice Husk Ash in Treatment of Grey Water,” *Water, Energy, Food and Environment*, vol. 1, no. 2, pp. 13–23, 2020, doi: 10.18576/wefej/010202.