

Reduction and Biosorption of Cr(VI) from Aqueous Solutions by Acid-Modified Guava Seeds: Kinetic and Equilibrium Studies

Marel Ortíz-Gutiérrez¹, Ruth Alfaro-Cuevas-Villanueva², Verónica Martínez-Miranda³, Orlando Hernández-Cristóbal⁴, Raúl Cortés-Martínez^{5*}

¹Master of Science Program in Environmental Engineering, Faculty of Biology, Michoacan University of Saint Nicholas of Hidalgo. C.U., C.P. 58060 Morelia, México

²Earth Sciences Research Institute, Michoacan University of Saint Nicholas of Hidalgo, Edif. U, C.U., C.P. 58060, Morelia, Michoacán, México

³Inter-American Institute of Water Technology and Sciences, Autonomous University of the State of Mexico. Carretera Toluca-Atzacomulco km 14.5, Unidad San Cayetano, C.P. 50200, Toluca, Estado de México, México

⁴National School of Higher Studies (ENES), Morelia Unit, National Autonomous University of Mexico. Antigua Carretera a Pátzcuaro 8701, col. Ex Hacienda San José de la Huerta, Morelia, México.

⁵Faculty of Chemistry Pharmacobiology, Michoacan University of Saint Nicholas of Hidalgo. Tzintzuntzan 173 Col. Matamoros, C.P. 58240, Morelia, Michoacán. México.

*Corresponding author: e-mail: raulcortesmtz@gmail.com

The use of guava seeds (GS) and acid-modified guava seeds (MGS) for the removal of Cr(VI) from aqueous solutions was investigated. Batch-type experiments were performed with Cr(VI) aqueous solutions and biosorbents to determine the kinetic and equilibrium sorption parameters. Results indicated that GS and MGS were capable of reducing and remove Cr(VI) from solutions, but the reduction was only observed at some experimental conditions. Infrared analysis showed that several functional groups were involved in the reduction, and biosorption of Cr(VI), particularly alcohol, phenolic, carboxylic, and methoxymethyl structures. The mechanisms of reduction and biosorption depended upon the type of biosorbent, pH, and temperature of the system. The pseudo-second-order kinetic model describes the kinetic sorption data, and the Langmuir-Freundlich (L-F) model describes the isotherm data in most cases. Significantly high total chromium biosorption capacities were obtained. Acid modification of guava seeds improves chromium biosorption performance.

Keywords: Guava seeds; chromium reduction; biosorption; isotherms.

Abbreviations

AAS	– Atomic absorption spectroscopy
EDS	– Energy Dispersive X-Ray Spectroscopy
FTIR	– Fourier Transform Infrared Spectroscopy
GS	– Guava seeds
GS-Cr	– Chromium-loaded guava seeds
L-F	– Langmuir-Freundlich model
MGS	– Acid-modified guava seeds
MGS-Cr	– Chromium-loaded acid-modified guava seeds
SEM	– Scanning Electron Microscopy
[GS, 25°C, pH2]	– Sorption system using guava seeds, at 25°C and pH 2
[GS, 25°C, pH6]	– Sorption system using guava seeds, at 25°C and pH 6
[GS, 45°C, pH2]	– Sorption system using guava seeds, at 45°C and pH 2
[GS, 45°C, pH6]	– Sorption system using guava seeds, at 45°C and pH 6
[MGS, 25°C, pH2]	– Sorption system using acid-modified guava seeds, at 25°C and pH 2
[MGS, 25°C, pH6]	– Sorption system using acid-modified guava seeds, at 25°C and pH 6
[MGS, 45°C, pH2]	– Sorption system using acid-modified guava seeds, at 45°C and pH 2
[MGS, 45°C, pH6]	– Sorption system using acid-modified guava seeds, at 45°C and pH 6

INTRODUCTION

The presence of heavy metals in wastewaters is of great concern because of their toxic and carcinogenic effects on human health and aquatic organisms¹. Wastewater discharges from different industries such as mining, electroplating, and tanneries, among others, are causing several water pollution problems worldwide. Some elements like zinc, iron, copper, cadmium, and chromium are frequently found in these types of waste streams². The problem with these pollutants is that they are not biodegradable, and they could accumulate in organisms at various trophic levels, causing disorders in the ecosystem and the food chain. Therefore, they can be considered as priority pollutants. These metals are dis-

charged through point and non-point sources into the aquatic ecosystems, and they can reach concentrations above maximum permissible levels³.

Valence states of chromium range from –2 to +6. The +3 and +6 oxidation states are the most commonly observed in chromium compounds, whereas +1, +4, and +5 states are rare⁴, but only Cr⁶⁺ and Cr³⁺ species have ecological importance due to their chemical properties, particularly in aquatic environments. Despite both chromium species could be harmful to organisms, Cr⁶⁺ represents a higher risk due to its toxic, carcinogenic and mutagenic properties when living organisms get in contact with this species, including humans. Different water discharges from several industries may have high

concentrations of Cr^{6+} ions, like those related to the production of dyes and pigments, galvanoplasty, mining, and leather factories, among others. Therefore, the elimination of chromium (VI) from these types of wastewaters is necessary before its discharge into the aquatic system⁴.

Conventional methods for the removal of metallic ions from wastewaters include redox reactions, chemical precipitation, reverse osmosis, ion exchange, and electrochemical techniques. Commonly, these methods show some disadvantages, such as low efficiencies in metallic ions removal (particularly when metals concentrations range of 10 to 100 mg/L), high reagent use, high-energy requirements, large amounts of sludge produced, or high costs of equipment^{5, 6}. Therefore, it is imperative to find consistent and straightforward techniques that could involve the use of local resources in the removal of metals from aqueous discharges at a low cost.

Among these techniques, biosorption could be considered as an alternative to conventional methods. Biosorption has proven its high performance for metallic ions removal from aquatic wastes. Also, this method can be considered as fast, selective, and precise since it has shown that in just a few minutes of treatment, high efficiencies in heavy metal removal can be reached⁷.

On the other hand, food waste is a severe issue worldwide, and reuse of these types of biomaterials is an important mitigation option. Since food waste is carbonaceous, it has different components in its matrix. As a result, it is probably suitable for preparing adsorbents⁸. In recent times; different low-cost biosorbents have been developed from several agro-wastes for Cr(VI) removal. The following materials have been reported for this purpose: treated waste newspaper⁴, groundnut shell⁹, date pits and olive stone¹⁰, soya cake¹¹, carrot waste¹², tea leaves dried biomass¹³, neem leaves and sawdust¹⁴, Fe-Modified peanut husk¹⁵, garlic stem and horse chestnut shell¹⁶, Oak (*Quercus robur*) acorn peel¹⁷, Teff straw¹⁸, and polyacrylic acid-grafted Macadamia nutshell powder¹⁹. For this reason, it is crucial to carry out research to develop new highly effective biosorbent materials in the treatment of industrial aqueous wastes, which allow their regeneration and reuse, as well as the recovery of metals²⁰.

The utilization of non-living biomass could be more convenient compared to the usage of viable cells as biosorbents since it is not necessary to add carbon and nitrogen sources for cell growth, besides that operating conditions and probable toxicity of metal ions towards living cells used as sorbents could also be a problem; in addition, biological constraints do not govern the processes, the retrieval of metallic ions from solutions is easy, and a totally reversible process can be achieved since non-living biomass can act as a cation exchanger. Nonetheless, the use of dead biomass can represent some disadvantages in adsorption processes, such as high sensitivity to sudden changes in pH of the solution, as well as rapid saturation of the biosorbent. In addition, the fact that living biomass can cause changes in the oxidation state of metal ions due to biological mechanisms may represent an advantage compared to the use of non-living biomass²¹. Despite this fact, it has been proven that also certain types of inactive biomass used

for chromium removal have been able to reduce the Cr^{6+} to Cr^{3+} ion in acidic aqueous solutions²². It has also been reported, especially at low pH values, that some of the Cr^{3+} ions generated by different reduction mechanisms can remain in the solution, concluding that the capacity of the biosorbent for chromium removal can be lower than its ability to reduce Cr^{6+} ²². Therefore, it is essential to find alternative materials that can simultaneously act as an excellent reducing agent and biosorbent.

It is well known that chromium reduction by lignocellulosic biosorbents takes place as chromate or dichromate ions in solution come into contact with electron donating functional groups present on the surface of the biosorbent, along with the participation of protons (H^+). It is crucial to identify electron donor groups on the surface of the biosorbent, such as amino and carboxyl, to understand reduction mechanisms in the system²³. Consequently, the protonation of functional groups could have a significant effect on the reduction of Cr^{6+} ions and consecutive biosorption of Cr^{3+} ions and acid modification of biosorbent material could help to enhance biosorption capacity for chromium.

Based on the above, guava seeds have great potential to be used as biosorbents for heavy metals in solution, especially Cr(VI). This fact can be explained since this biosorbent is non-living biomass of low cost and high availability, which means that it can be regenerated and reused in adsorption processes of effluents contaminated with this metal. Furthermore, this material is lignocellulosic, which provides properties suitable for reducing the oxidation state of Cr(VI) to Cr(III), thus reducing ion toxicity in aqueous solutions. Likewise, guava seeds have excellent mechanical and surface properties, which allow them to be chemically modified through an intense acid treatment to functionalize their external surface and thus increase the reduction of Cr(VI) in solution. Therefore, guava seeds were selected to determine their efficacy in reducing and removing Cr(VI) from aqueous solutions.

Therefore, this study aimed to evaluate chromium removal from aqueous solutions using acid-modified guava seeds as biosorbent by determining the fundamental kinetics and equilibrium biosorption parameters in batch systems with studying the effects of temperature and pH on the reduction and biosorption processes.

MATERIALS AND METHODS

Preparation and modification of biosorbent

To obtain the biosorbent used in this study, guava seeds from different industries were collected since they are considered a solid residue from agro-industrial activities. This solid residue is available in large quantities due to the vast production and use of the guava fruit in the region where it was collected. The seeds were used as a biosorbent because they have structural properties, such as their high content of lignin, cellulose, and protein, which could make them suitable for removing ionic pollutants from wastewaters. Guava seeds (GS) were obtained from a local food industry as a solid residue produced by its manufacturing process. The material was washed and rinsed several times with deionized water to remove fruit pulp traces and impurities. The

seeds were dried at room temperature, and then they were crushed and sieved to obtain the 1 mm size fraction for later use in the acid modification process and biosorption experiments.

For the acid modification of guava seeds (GS), a method proposed by Park et al.²⁴ was used: 5 g of GS were put in contact with 200 mL of H₂SO₄ 1M solution. The mixture was stirred at 200 rpm for 24 h. Later, the acid-modified guava seeds (MGS) were separated from the acid solution, and they were rinsed several times with deionized water. Finally, MGS was dried at 60°C for 24 h, and they were used for biosorption experiments without further modification.

Scanning Electron Microscopy (SEM)

SEM images of GS and MGS samples, as well as chromium-loaded acid-modified guava seeds (MGS-Cr), were obtained to determine their surface morphology and a semi-quantitative elemental composition. The samples were previously covered with copper to get these images, and then they were analyzed using a JSPM-5200 scanning electron microscope and a JEOL JSM-7600F FEG-SEM microanalysis detector.

Fourier Transform Infrared Spectroscopy (FTIR)

In order to understand and elucidate possible sorption and reduction mechanisms of chromium on GS, MGS, and MGS-Cr, Fourier Transform Infrared (FTIR, Bruker Tensor 27) analyses were performed to these samples. Measurements were recorded using KBr pellets with a wavelength ranging from 200 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹.

Kinetic experiments

Batch-type experiments with GS and MGS and aqueous solutions of hexavalent chromium were conducted to determine biosorption kinetics. For this purpose, 0.1 g of each biosorbents were put in centrifuge tubes with 10 mL of a 10 mg/L K₂Cr₂O₇ aqueous solution. The tubes were stirred at 120 rpm for different contact times ranging from 10 min to 48 h. Once the contact time was reached, the centrifuge tubes were removed from the stirrer, and the aqueous solution was decanted and filtered, storing the supernatant in different vials for later analysis of Cr(VI) by a standard colorimetric method in a visible spectrophotometer at 540 nm. The total concentration of Cr in the supernatant (i.e., the sum of the Cr⁶⁺ and Cr³⁺ ions present in the aqueous solution) was analyzed by atomic absorption spectroscopy (AAS)²⁵. The Cr³⁺ concentration was then estimated from the difference between the total Cr and Cr⁶⁺ concentrations^{1, 19}. These experiments were performed at two temperatures (25 and 45°C) and two distinct pH values (2 and 6) to ascertain the influence of these parameters over Cr(VI) sorption kinetics at these experimental conditions. These pH values were selected to determine the effects of the different chromium chemical species, as well as biosorbent's surface properties, on the reduction and biosorption processes. Temperature values were selected to demonstrate their effects on reducing kinetics and efficiency and infer if biosorption enhances when the temperature rises. Moreover, it is well known that chromium polluted wastewaters, particularly tannery

effluents, can present highly acidic conditions and low pH values (from 2.8 to 4.5, depending on the process stage) and high temperatures when they are discharged to the sewage or water bodies.

All biosorption experiments were performed thrice to determine its reproducibility, and the mean values were reported in all cases.

Effect of the biosorbent dosage

The influence of the biosorbent dosage on the equilibrium removal of Cr⁶⁺ ions was investigated by combining different GS and MGS masses, ranging from 0.01 to 0.2 g, together with 10 mL of a 10 mg/L K₂Cr₂O₇ solution in flasks. The flasks were shaken at two temperatures (25 and 45°C) at 120 rpm until sorption equilibrium was reached. Solutions were adjusted at two different pH values (2 and 6). The Cr(VI) and total chromium levels in the remaining solutions were determined by the AAS method, as mentioned above. Biosorption dosage tests were carried out in triplicate to assess reproducibility, and the mean values were reported.

Chromium biosorption isotherms

Biosorption batch-type tests were performed using GS and MGS samples and aqueous solutions of K₂Cr₂O₇ at concentrations from 10 to 300 mg/L. Temperatures of the tests were established at 25 and 45°C and two different pH values (2 and 6) were evaluated. These experimental conditions were set to assess the influence of these parameters on the maximum sorption capacities of natural and acid-modified guava seeds for chromium. Doses of GS and MGS samples were placed in centrifuge tubes with 10 mL of Cr(VI) aqueous solutions at different concentrations. The tubes were stirred in a reciprocal shaker until equilibrium time was reached. Once equilibrium was reached, the tubes were removed from the shaker, and the suspension was decanted and filtered. Then, the remaining solutions were kept at low temperature in vials for Cr(VI) and total chromium analysis by AAS. The experiments were also performed thrice, and the mean values were reported.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

SEM was used to analyze the surface morphology of GS, MGS, and MGS-Cr samples; it was utilized to detect the changes in the structure and surface properties of the samples because of the acid-modification and chromium adsorption processes. Results can be observed in Figures 1a and 1b for GS and MGS samples, respectively. It can be noticed that the sample has some particles adhered to its flat surface, and some wrinkled folds can also be observed. In the MGS sample (Fig. 1b), areas with single pleats, flat and creased parts contribute to more heterogeneous surface morphology. This type of surface conformation is significant since the surface area could increase as a result of the pores created in such flaws of the structure of the biosorbent. Besides, the deterioration of fibers due to chemical modification and heat treatment denotes cell degradation and color change²⁶. Moreover, the presence of particles adhered to the surface

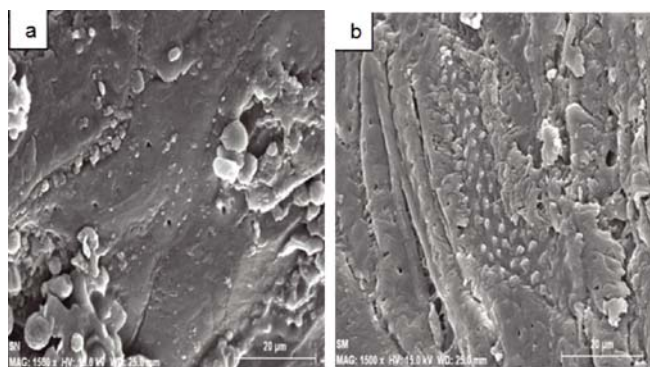


Figure 1. SEM images of different samples: a) GS observed at 1500x; b) MGS observed at 1500x

decreases after modification. Usually, acid-modification has been useful for cleaning and replacing the natural ions attached on the cell wall with H^+ and SO_4^{2-} species^{24, 27}. Semi-Quantitative elemental analysis by EDS was carried out on two specific areas of the MGS-Cr sample (Fig. 2a), where the plain and uniform surface was observed (point A), and also at the irregular part of the sample (point B). It can be noticed that despite the morphological properties of the surface in the material, a certain percentage of chromium adheres to GS-Cr and MGS-Cr as a result of the sorption process, showing a chromium amount of 1.3 g Cr/100 g GS-Cr and 2.2g Cr/100 g MGS-Cr, respectively. The presence of high or low concentrations of the different elements can be attributed to the heterogeneity of functional groups existent in the two specific areas that were analyzed. These facts imply that chromium can be adsorbed on GS and MGS sites, as shown in Figures 2a and 2b, respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra are shown in Figures 3 and 4, for the samples of adsorbents: GS, MGS, GS-Cr, and MGS-Cr. Samples of GS-Cr and MGS-Cr, collected from chromium biosorption tests at two different pH values (2 and 6), were used for these tests. In Figure 3, significant changes in the absorption peaks corresponding to the GS and GS-Cr samples are observed. Variations in these bands are related to $-CH$, $-CH_2$, $C=O$, $-NH$, and $-OH$ functional groups, also suggesting that oxygenated hydrocarbons associated functional groups predominate in these materials. It can be complicated to ascertain the existence of aromatic organic compounds in this type of biomaterials, as C-H stretching frequencies are often found, and superposition with O-H groups from alcohol

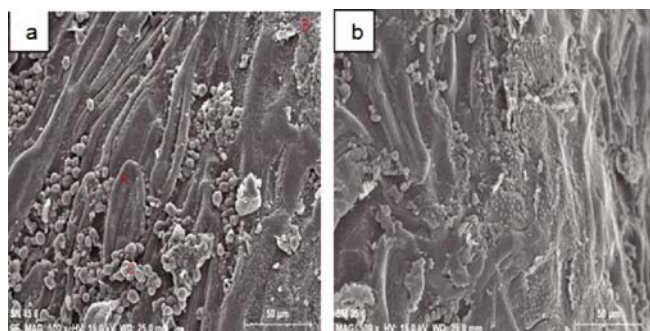


Figure 2. SEM images of different samples: a) GS-Cr observed at 500x; b) MGS-Cr observed at 500x

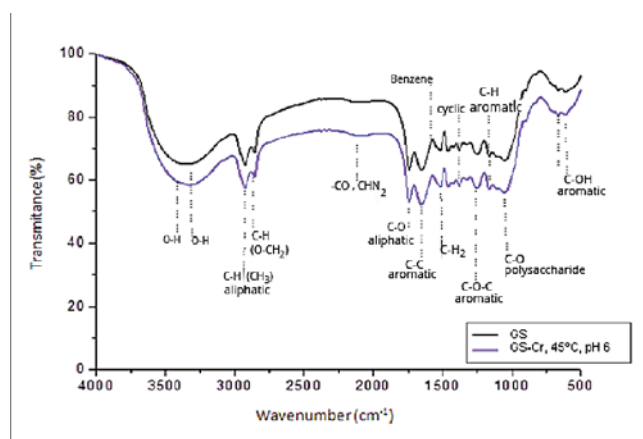


Figure 3. FTIR spectra of GS and GS-Cr samples

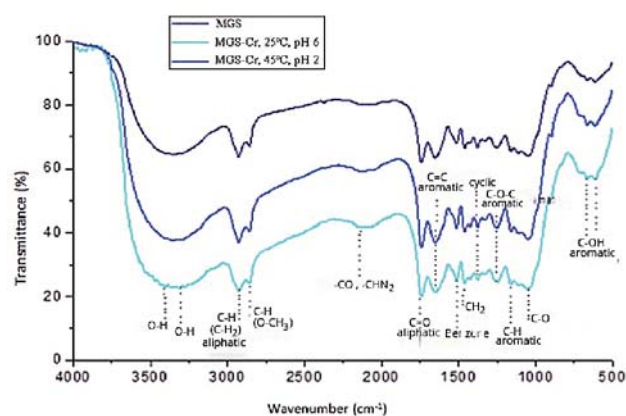


Figure 4. FTIR spectra of MGS and MGS-Cr samples at different temperatures and pH values

can occur since these are sections of critical functional groups²⁸. It is well known that guava seeds major structural components are cellulose, hemicellulose, lignin, and some extractive compounds (like lipids, proteins, etc.). As a result, the carboxylic acid, phenolic, hydroxyl, and carbonyl-related functional groups predominate in this biomaterial^{29, 30}. The bands observed from 2920 to 2924 cm^{-1} are associated with the vibration and stretching of the methyl bonds, as well as to the hydrophobic methoxy and methylene hydrophobic groups, contained in the hydrocarbons chain^{31, 32}.

Variations in peaks intensities in the GS and GS-Cr spectra (Fig. 3) indicate that the carboxylic, methoxymethyl ether, hydroxyl, and phenolic functional groups are implicated in chromium reduction and adsorption. This minor reduction in intensity could be attributed to ionic substitution, which produces analogous spectra in the two biosorbents³³. Bands observed at 3410, and 3380 cm^{-1} can be attributed to OH stretching³⁴. Depending on their position on glucose molecule, hydroxyl groups can develop two different forms of hydrogen bonds. One of these types is the one formed between two adjacent hydroxyl groups present in the glucose structure; this is called an intra-molecular link, which confers rigidity to cellulose structure. When a hydrogen atom connects two hydroxyl groups from different cellulose units, an inter-molecular bond takes place, and these types of interconnections are one of the reasons for supramolecular cellulose structures can be formed^{32, 35}. Besides, methyl (C-H), methoxy (O-CH₃) and aliphatic methylene (CH₂) stretch absorption bands were found at 2920 to 2850 cm^{-1} .

The band at 1615 cm^{-1} can be associated with the asymmetrical stretching of C=O in the carboxyl group, which can be found in hemicellulose or protein molecules in the GS structure. The peak at 1765 cm^{-1} is attributed to the C=O of an ester molecule that can be found in oils of GS material³⁴, and an aromatic ring vibration was observed, along with a C=C stretching at wavelengths near 1521 and 1606 cm^{-1} , respectively³⁶. Moreover, bands observed at 1360 to 1210 cm^{-1} corresponded to the O-H group from phenolic compounds, and the bands observed from 1247 to 1161 cm^{-1} corresponded to C-O-C groups and C-H from aromatic compounds, respectively.

An absorption band assigned to a functional group increase proportionately with the number of times this functional group exists within the molecule³⁷. The FTIR spectral analysis before and after chromium sorption on GS (Fig. 3) shows a substantial decrease in band intensities of specific functional groups after the biosorption of chromium; such as hydroxyl groups (aliphatic and cyclic), aldehyde groups (aliphatic and aromatic), carbonyl groups and methoxymethyl ether groups. This disparity indicates that such functional groups are involved in the removal of chromium by GS. Suksabye et al.³⁸ found that lignin participated in the Cr(VI) sorption mechanism; also proposing that carbonyl (C=O) and methoxy (O-CH₃) groups may be involved. They also suggested that coordinated covalent bonds with C=O and O-CH₃ groups are responsible for chromium reduction on the coir pith surface through electron donation from oxygen atoms to Cr(III) species.

Using MGS as biosorbent for chromium removal, a similar behavior on FTIR spectra was observed (Fig. 4) with a decrease in band intensities after chromium removal for the same functional groups involved when GS was used as biosorbent. It is important to mention that a higher decrease in band intensity was observed for the case of chromium removal with MGS at pH 6 and temperature 25°C than for the system, where MGS was used at pH 2 and 45°C . This behavior could be associated with a higher sorption capacity of the MGS at low temperature, as well as to chromium sorption mechanism related to Cr(VI) and Cr(III) chemical species present in aqueous solutions at these pH values.

Chemical characterization of GS was previously reported³⁹, and the main structural components of this biosorbent were: lignin (69.78%), hemicellulose (12.96%), cellulose (11.04%), and pectin (1.32%).

Kinetics Experiments

Figure 5 shows the adsorption data as a function of time for Cr(VI) and total chromium by GS at different temperatures. The curve of Cr(VI) removal at 25°C is defined by a relatively rapid removal at the early stages of the process (Fig. 5a). Biosorption of Cr(VI) on GS surface took place and then reduction occurred since biosorption happened first before electron transfer from donating groups occurred. An approximately 30 percent of Cr(VI) reduction from the aqueous solution was observed at 48 h of contact time, and almost 50 percent of Cr(VI) removal was reached at 120 h of contact time. Total chromium removal kinetics showed slow sorption on the first 48 h of contact time since the reduction process was taking place at this period, and sorption increased

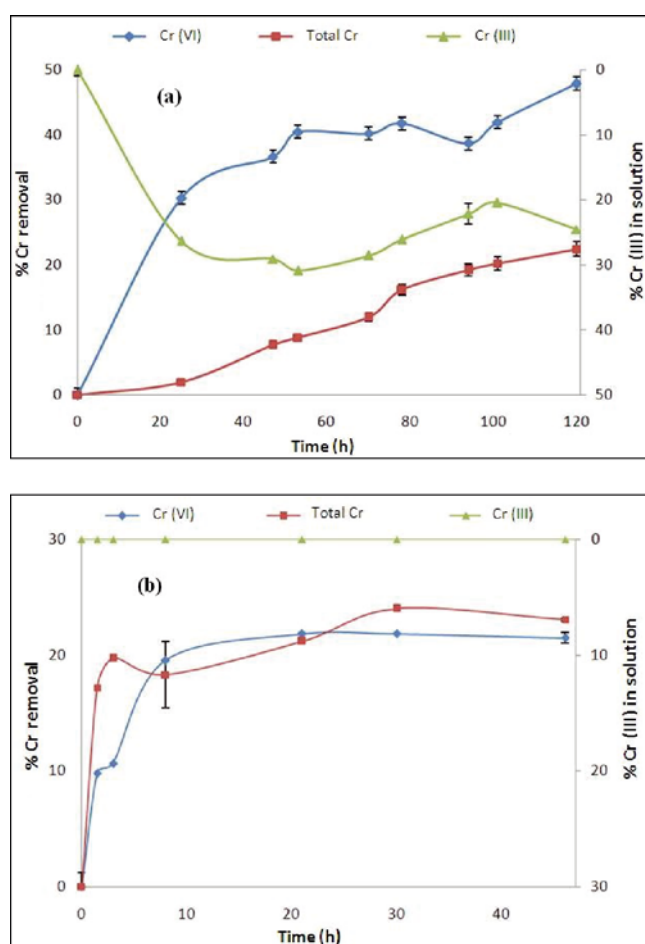


Figure 5. Cr(VI), Total Chromium and Cr(III) removal by GS as a function of time at different temperatures: a) 25°C , b) 45°C (pH = 6)

gradually until total chromium sorption equilibrium was reached approximately at 120 h. Total chromium removal started to rise gradually as Cr(III) was appearing on the solution; this fact suggests that Cr³⁺ was retained on the GS surface area since Cr(III) concentration started to decrease after 48 h of contact.

Figure 6 shows the chemical equilibrium diagram for chromium obtained using MEDUSA software⁴⁰. From this diagram, it can be noticed that both Cr(III) and Cr(VI) species can be present at different pH values as redox processes occur due to electron donor presence in solution. In this case, Cr(VI) reduction at pH 6 results in the formation of the Cr₂O₃ species; consequently, an increase in the Cr(III) concentration, as well as on

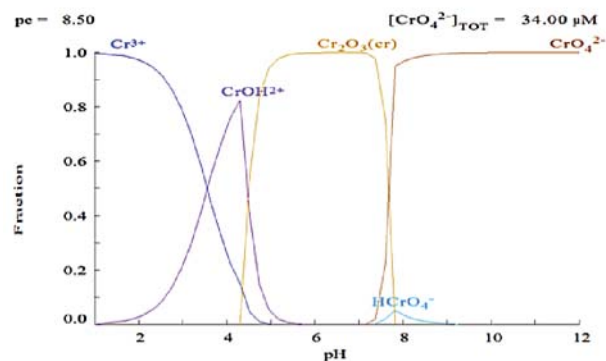


Figure 6. Equilibrium diagram of Cr(III) and Cr(VI) species in aqueous solution

the Cr(VI) removal, were observed (Fig. 5a). Cr_2O_3 appearance could be related to the bonding of Cr(III) to oxygen atoms on the surface of GS biosorbent; this is consistent with the fact that bands attributed to Cr-O bonding, with oxygen atoms from methoxy and carbonyl groups, were identified on GS-Cr FTIR spectra (Fig. 3). The formation of Cr_2O_3 species on the surface of lignocellulosic and pectic biosorbents has also been reported by Bellú et al.⁴¹.

For the case of Cr(VI) removal by GS at 45°C and pH 6, results are shown in Figure 5b where no formation of Cr(III) was observed; therefore, an anionic sorption mechanism is proposed in this case. Cr(VI) and total chromium adsorption curves are defined by a relatively rapid removal at the early stages of the process, approximately 10 h, until sorption equilibrium was reached at 30 h. It can also be observed that the chromium biosorption kinetics by GS is favored at high temperatures, suggesting an endothermic nature of the process for this system. Similar behavior was reported for Cr(VI) removal using *Ecklonia sp.* as biosorbent⁴². The fact that Cr(VI) reduction was inhibited at this temperature could be attributed to the loss of electron donating groups due to the physical deterioration of biosorbent because of the high temperatures of the solution⁴³.

Results for Cr(VI) and total chromium kinetics adsorption by MGS at different temperatures and pH 6 are shown in Figure 7. Sorption kinetics curves at 25°C are shown in Figure 7a. It was noticed that the sorption process increased relatively fast until equilibrium was

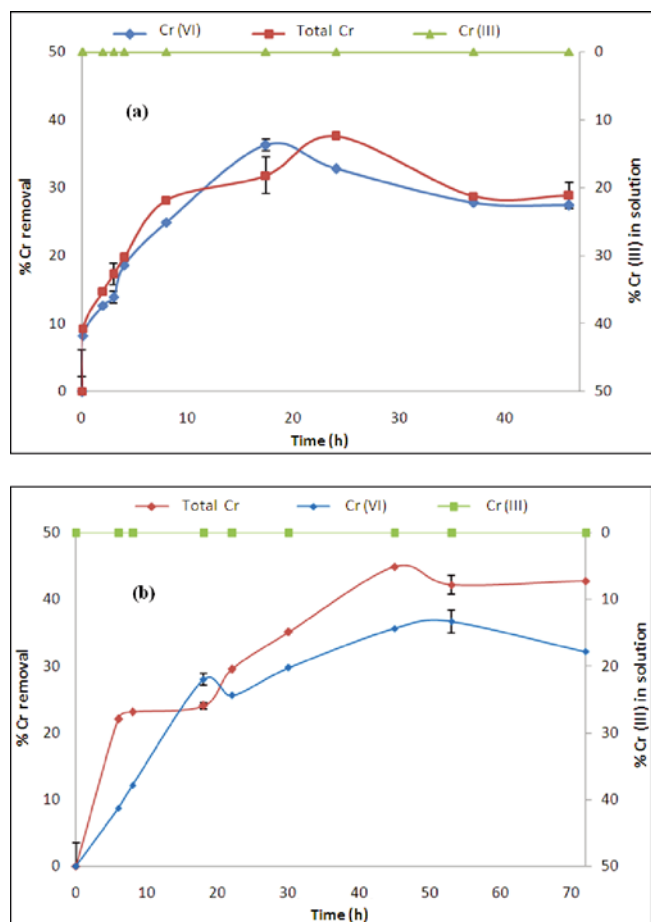


Figure 7. Cr(VI), Total Chromium and Cr(III) removal by MGS as a function of time at different temperatures: a) 25°C, b) 45°C (pH = 6)

reached at approximately 48 h of contact. No reduction of Cr(VI) occurred during the sorption process for MGS at 25°C. By comparing Cr sorption kinetics by using GS and MGS as biosorbents at the same temperature and pH 6, it can be established that acid modification of guava seeds significantly affects chromium sorption kinetics since equilibrium time decreased when MGS was used for Cr removal experiments. It was also noticed that the chemical reduction of Cr(VI) occurred when GS was used. Miretzky and Fernández-Cirelli⁴⁴, and Zheng et al.⁴⁵ mentioned that Cr(VI) reduced to Cr(III) by contact with electron-donating groups present in the biosorbent. FTIR analysis of GS revealed the existence of methoxyl, carbonyl, and phenolic groups, which were described as electron-donating groups⁴⁵. These groups were affected by acid modification and their presence on MGS surface decrease, as was observed on FTIR spectra (Fig. 4). This fact, together with chromium speciation in aqueous solution at pH 6, led to a different removal mechanism at these experimental conditions, where only biosorption of Cr(VI) species was observed at the two temperatures. Cr^{6+} to Cr^{3+} reduction depends on methoxyl, carbonyl groups, and phenolic groups, which are affected by acid modification and temperature. The mechanism begins with the reaction of the dichromate ion with water to generate the ion HCrO_4^- (Jones reagent, Cr(VI)) that in acidic medium generates chromium trioxide (CrO_3), which is capable of forming chromium esters with alcohol, carbonyl or phenol. These esters decompose for the elimination of Cr(VI) HCrO_3^- , which reacts with another species of Cr(VI), forming two species of Cr(V) that also oxidize alcohol or phenol and decompose in Cr(III).

Chromium sorption kinetics was also evaluated at pH 2 (at 25°C) with GS and MGS as biosorbents. The results of these experiments are shown in Figure 8, where Cr(VI) and total chromium sorption kinetics showed a relatively fast increase in the first 10 h of contact, reaching 100% of Cr(VI) removal using both materials. The fact that MGS shows Cr(VI) reduction indicates that the pH of the solution plays an essential role in the chromium removal mechanism by this type of material. It was observed that Cr(III) occurrence is faster in GS system (Fig. 8a) than for MGS (Fig. 8b), but a higher total chromium removal is achieved for MGS. Equilibrium time is reached faster for GS (48 h) than for MGS (92 h). It is known that H^+ ions participate in Cr(VI) reduction reaction; hence, at highly acidic conditions, these ions are present at high concentrations, and they could protonate surface functional groups on GS, and MGS, enhancing Cr(VI) reduction kinetics, particularly for MGS biosorbent. However, by comparing Cr(VI) reduction by GS and MGS, it can be observed that Cr(VI) reduction is negatively affected when guava seeds were acid-modified since Cr(III) concentrations in solutions become significant at approximately 15 h of contact time when Cr(VI) sorption has reached 40% removal (Fig. 8b). This fact indicates that there is a difference between Cr(VI) reduction mechanisms when GS and MGS are used as biosorbents since reduction begins almost immediately when GS present in solution (Fig. 8a). This fact suggests that Cr(III) ions were generated by electron transfer before Cr(VI) ions can be adsorbed.

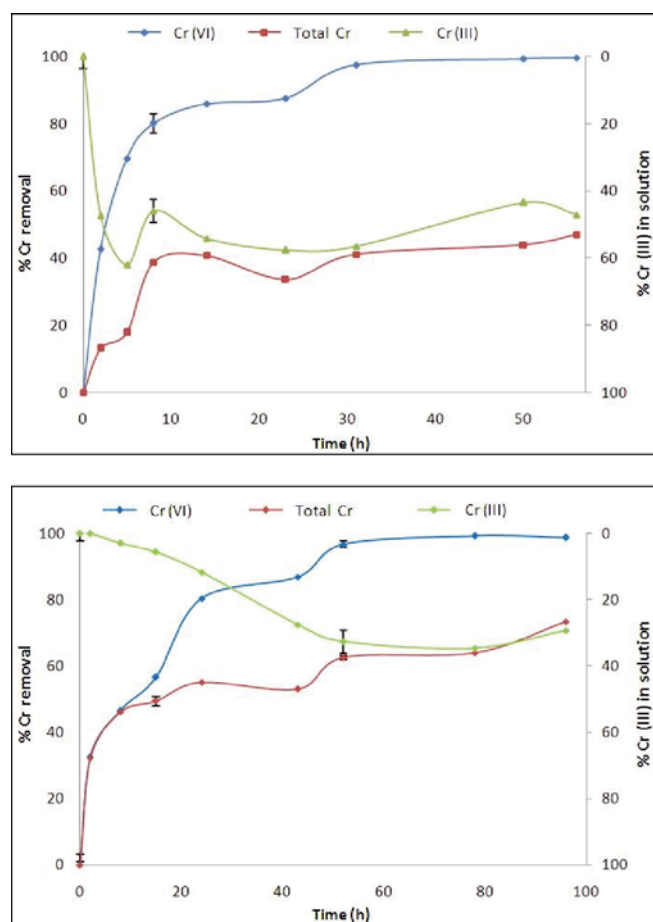


Figure 8. Cr(VI), Total Chromium and Cr(III) removal by: a) GS, and b) MGS as a function of time at 25°C and pH = 2

However, when MGS is present in solution (Fig. 8b), the reduction becomes significant after 16 h of contact time, indicating that Cr(VI) biosorption occurred on MGS before reduction. These results also indicate that Cr(VI) reduction, as well as Cr(III) biosorption, by GS and MGS are highly temperature and pH dependent.

Similar behavior is observed when kinetic sorption tests were performed at pH 2 and a temperature of 45°C, using GS and MGS as biosorbents (Fig. 9). It can be noticed that chromium reduction occurred relatively fast in both materials. For the case of Cr(VI) removal onto GS (Fig. 9a), a rapid reduction of Cr(VI) is observed until all of the Cr(VI) ions in solution, present as HCrO_4^- species, were reduced to Cr(III) at approximately 6 h of contact. Similar behavior was observed for the case of chromium reduction by MGS, but slightly fast reduction kinetics can be noticed, particularly at the first 4 h of contact (Fig. 9b). Kinetics of Cr(VI) reduction and Cr(III) biosorption onto GS and MGS, at these experimental conditions, were significantly faster than those carried out at lower temperatures and higher pH values. It is important to notice that total chromium removal begins as Cr(VI) occurs and total Cr kinetics is also faster than that obtained at lower temperatures, suggesting that both chromium species could be adsorbed on GS and MGS surface. This behavior also indicates that the sorption of Cr(VI) on biosorbent surface was not the control step to reduction under these experimental conditions. With these results, it can be established that the first step on Cr(VI) reduction mechanism is biosorption of HCrO_4^- species on highly protonated functional groups present on

GS and MGS surfaces, followed by reduction to Cr(III) ions by electron transfer of these groups.

The study of sorption kinetics allows determining the rate at which adsorbates are removed from the aqueous medium. It can be useful to know the diffusion steps that control the sorption process, and it is important to select the optimal operating conditions in the wastewater treatment design. Therefore, a non-linear regression analysis was used to fit total chromium sorption kinetic data to three empirical kinetic models to establish parameters of the biosorption systems under study, using the software Statistica v.7.0. The following empirical models were tested with kinetic data at different pH and temperature conditions:

The Lagergren equation, or pseudo first-order model is established by the following expression⁴⁶:

$$q_t = q_e(1 - e^{-k_L t}) \quad (1)$$

Where K_L is the Lagergren rate constant (min^{-1}); q_t is the quantity of adsorbed ion at any given time t (mg/g), and q_e is the quantity of adsorbed ion at equilibrium (mg/g).

The non-linear form of the pseudo-second-order equation, firstly proposed by Ho et al.⁴⁷, is:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (2)$$

Where K_2 is the pseudo-second-order rate constant ($\text{g}/\text{mg min}$); q_t is the quantity of adsorbed ion at any given time t (mg/g), and q_e is the quantity of adsorbed ion at equilibrium (mg/g).

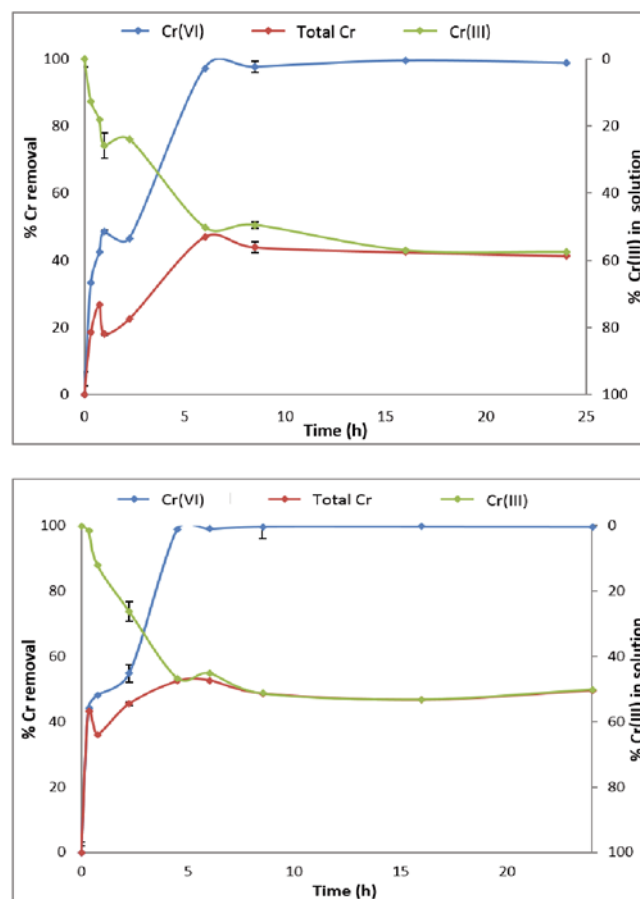


Figure 9. Cr(VI), Total Chromium, and Cr(III) removal as a function of time by a) GS and b) MGS, at 45°C and pH = 2

The following equation describes the Elovich model, which has been used to describe several adsorption systems that exhibit chemisorption removal mechanisms⁴⁸:

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (3)$$

Where q_t is the adsorbate concentration at any time, t , per weight of adsorbent, (mg/g); a is the initial adsorption rate (mg/g min), and b is the desorption rate Elovich constant, (g/mg).

Results showed that the model that best described total chromium kinetics onto GS and MGS is the pseudo-second-order model, in accordance with their correlation coefficients calculated from nonlinear regression analyses, followed by Lagergren equation. Elovich model did not fit well biosorption kinetics of all systems under study. Tables 1 and 2 show the parameters of the pseudo-second-order model, as well as correlation coefficients for total chromium biosorption on GS and MGS, respectively, at different experimental conditions.

Table 1. Pseudo-second-order model's parameters for total chromium biosorption onto GS

Biosorbent/ Parameters	GS			
	pH 2, 25°C	pH 2, 45°C	pH 6, 25°C	pH 6, 45°C
q_e (mg/g)	0.996	1.048	0.719	0.262
K_2 (g/mg · h)	0.391	0.764	0.086	0.879
R	0.997	0.984	0.989	0.932

Table 2. Pseudo-second-order model's parameters for total chromium biosorption onto MGS

Biosorbent/ Parameters	MGS			
	pH 2, 25°C	pH 2, 45°C	pH 6, 25°C	pH 6, 45°C
q_e (mg/g)	1.053	1.048	0.355	0.439
K_2 (g/mg · h)	0.112	1.146	0.944	0.131
R	0.963	0.959	0.954	0.975

Considering the pseudo-second-order rate constant (K_2) for the removal of total chromium, for the experiments where GS was used as biosorbent (Table 1), it was found that the system at 25°C and pH 6 [GS, 25°C, pH 6] presented the lowest value of this constant, producing an adverse effect on the equilibrium time of this system (94 h). Likewise, a slight increase in the rate constant was observed when the pH decreased, system [GS, 25°C, pH 2], while the interaction of the two factors, system [GS, 45°C, pH 2] caused a significant increase in the rate constant; both cases suggest a positive effect on the sorption kinetics; this was noticeable in shorter equilibrium times: 50 h for the system [GS, 25°C, pH 2] and 16 h for [GS, 45°C, pH 2] (Fig. 8a and 9a). The highest increase in the rate constant occurred in the system [MGS, 45°C, pH 6], which suggests that the increase in temperature positively and significantly affects the sorption kinetics of Cr(VI). Chen et al.⁴⁹ reported a similar behavior where the sorption rate increase was attributed to a lower barrier for the redox reaction at higher temperatures. However, when comparing the systems using MGS at

pH 6 (Table 2), a significant decrease in the sorption rate was observed at higher temperatures. These systems did not show chromium reduction, so that Cr(VI) sorption onto MGS was the predominant mechanism in these systems. Usually, an increase in temperature favors diffusion processes in a sorption system, when a porous adsorbent is used, improving sorption kinetics; therefore, we can assume that diffusion is not a governing step in adsorption kinetics on Cr(VI)-MGS systems.

Considering the system [MGS, 25°C, pH 6] as initial operating conditions, it was found that, for the kinetic experiments where MGS was used as biosorbent, when raising the temperature, system [MGS, 45°C, pH 6], and decrease the pH, system [MGS, 25°C, pH 2], a decrease in the biosorption rate constant was caused. The above indicates that these conditions do not have a positive effect on the sorption kinetics of Cr(VI), since they showed the most extended equilibrium times: 53 h for the system [MGS, 45°C, pH 6] (Fig. 7b) and 78 h for the system [MGS, 25°C, pH 2] (Fig. 8b), compared with 37 h for [MGS, 25°C, pH 6]. Finally, when two variables of the system (pH and temperature) were varied, i.e., the system [MGS, 45°C, pH 2], it seemed to positively affect the sorption rate since the constant for this system was the highest and the shortest equilibrium time was achieved (4.5 h).

Effect of adsorbent dosage

Batch tests were performed to determine the influence of the biosorbent dose on the reduction and biosorption of chromium with GS and MGS biosorbents, for the cases of the systems whose pH and temperature conditions significantly affected kinetic parameters. Figure 10 shows results from these experiments for the systems above-mentioned systems: [GS, 45°C, pH 6] (Fig. 10a), [MGS, 25°C, pH 6] (Fig. 10b), and [MGS, 45°C, pH 2] (Fig. 10c).

For the system [GS, 45°C, pH 6] (Fig. 10a), the increase in biomass dose increased the removal of Cr(VI) and total chromium until no significant variations in the removal were noticed at a dose of 0.07 g GS/10mL, while the reduction of Cr(VI) is not substantial. This behavior could be attributed to the low amount of electron donating functional groups when the amount of biosorbent is low. However, from the 0.09 g GS/10mL dose, there was a slight decrease in the removal of Cr(VI) and total chromium, as well as a considerable increase in the percentage of Cr(III) in solution; this could be associated with the increase in the amount of electron donor groups on the total surface of the biosorbent mass. Despite there is a higher Cr(VI) reduction, total chromium removal decreased; thus, it can be considered that chromium removal at these experimental conditions is not suitable at higher GS doses.

For the system [MGS, 25°C, pH 6], low biosorption of Cr(VI) and no reduction was observed at a low MGS dose (Fig. 10b), but in this case, a substantial reduction was noticed as MGS dose raised. Total chromium removal was significant, but at doses higher than 0.11 g/10mL a slight decrease occurred together with a higher reduction to Cr(III), indicating that higher doses of MGS do not improve total chromium removal. A different behavior was observed as the temperature of the MGS-Cr

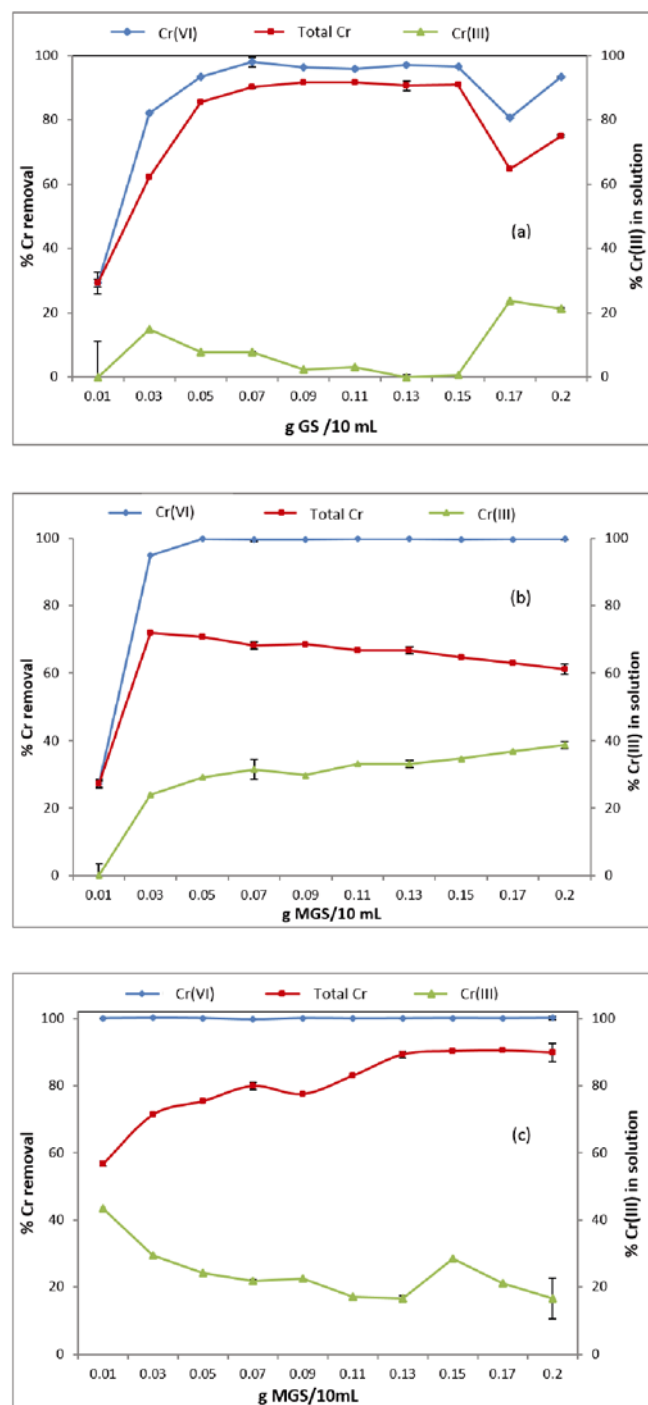


Figure 10. Effect of biosorbent dose on Cr(VI) reduction and biosorption at different experimental conditions: a) system [GS, 45°C, pH 6], b) system [MGS, 25°C, pH 6], and c) system [MGS, 45°C, pH 2]

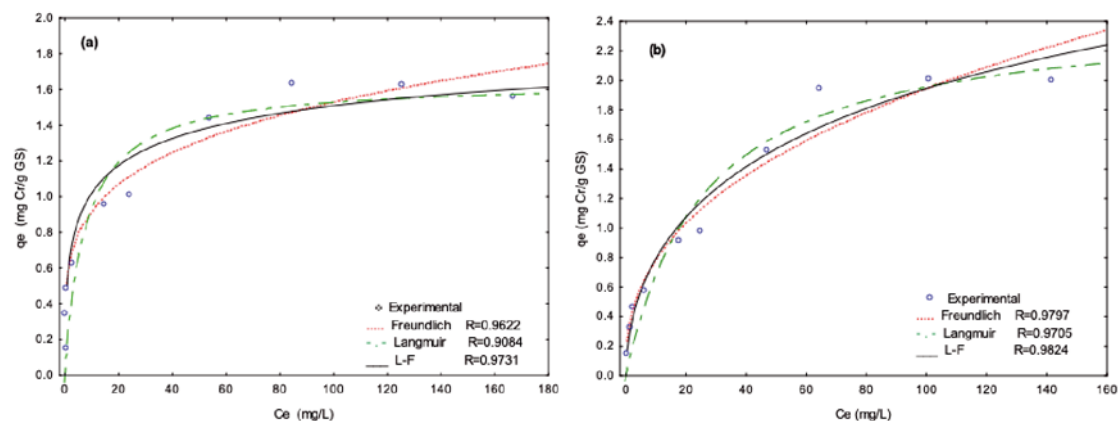


Figure 11. Biosorption isotherms on GS fitted to Freundlich, Langmuir and Langmuir-Freundlich (L-F) models for a) Cr(VI), and b) Total Cr. (pH 6, T = 45°C)

system increased at highly acidic conditions (Fig. 10c). In this system, reduction to Cr(III) was higher at low biosorbent doses, which agrees with the fast reduction and biosorption observed at the kinetic experiments at these experimental conditions. This fact corroborates the essential roles that high temperature and low pH play in Cr(VI) reduction and total chromium removal; however, it can be noticed that reduction decreases as MGS dose raises and total chromium removal was enhanced (Fig. 10c). The chromium reduction would be expected to be greater as the number of electron donor groups increases, but in this case, it was observed that at higher MGS doses the direct biosorption of Cr(VI) was promoted under these experimental conditions. This fact confirms that the mechanism of removal is the biosorption of chromate ions followed by its subsequent reduction to Cr(III).

Chromium biosorption isotherms

The biosorption isotherms were performed for the three systems that had a significant effect on chromium sorption kinetics: [GS, 45°C, pH 6], [MGS, 25°C, pH 6] and [MGS, 45°C, pH 2]. Total chromium and Cr(VI) were evaluated in these experiments. Biosorption raw data were fitted to three different isotherm models, through non-linear regression analyses, to establish each system's equilibrium parameters. Freundlich, Langmuir, and Langmuir-Freundlich (L-F) models were used to fit Cr(VI) and total chromium biosorption isotherms³². Figures 11, 12 and 13 show the results of these biosorption isotherm analyses for the systems evaluated at different experimental conditions. For the [GS, 45°C, pH 6] system (Fig. 11), a typical behavior was observed where sorption capacity increased rapidly at low chromium equilibrium concentrations due to high sorption sites availability, and then sorption capacity increased gradually as chromium concentrations started to increase. The biosorption capacity of Cr(VI) at these experimental conditions was 1.64 mg/g GS, and for total chromium, it was 2.01 mg/g GS. It is important to mention that in this case, there was no significant chemical reduction of Cr(VI); therefore, the metal was removed via the anionic adsorption mechanism. This behavior is consistent with that presented in the analysis of sorption kinetics. The L-F model best described isotherm data for both biosorbents. Similar behavior was observed for the system [MGS, 25°C, pH 6], but a significant reduction of Cr(VI)

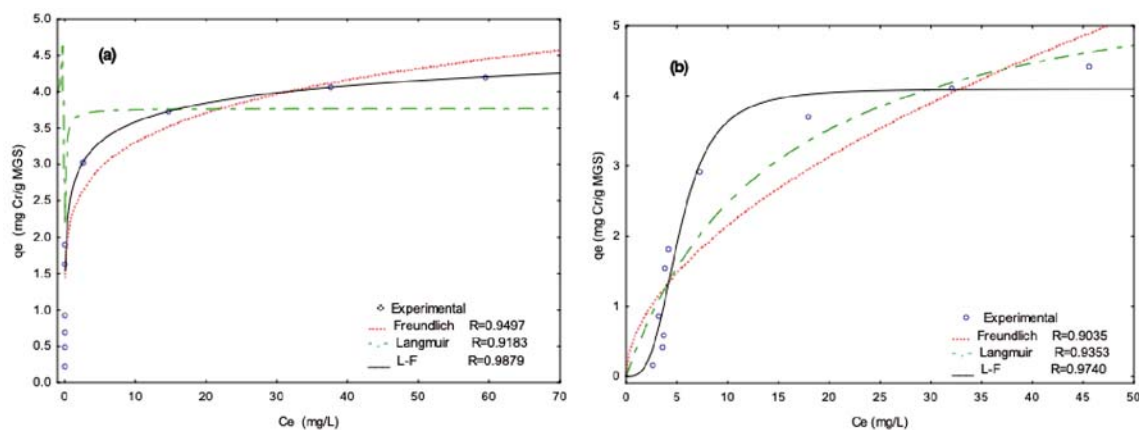


Figure 12. Biosorption isotherms on MGS fitted to Freundlich, Langmuir and Langmuir-Freundlich (L-F) models for a) Cr(VI), and b) Total Cr. (pH 6, T = 25°C)

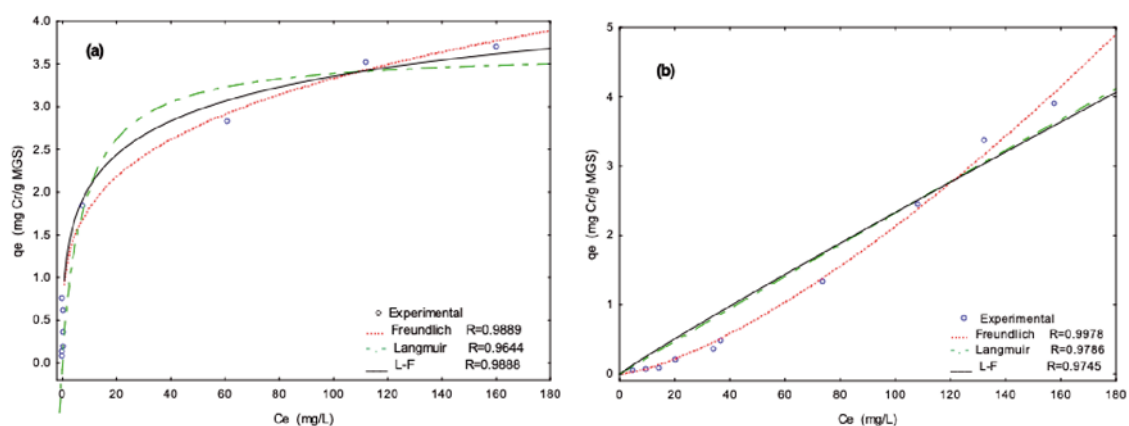


Figure 13. Biosorption isotherms on MGS fitted to Freundlich, Langmuir and Langmuir-Freundlich (L-F) models for a) Cr(VI), and b) Total Cr. (pH 2, T = 45°C)

occurred, and sorption capacities for Cr(VI) and total chromium were 4.19 mg/g MGS and 4.42 mg/g MGS, respectively (Fig. 12).

For the [MGS, 45°C, pH 2] system, a different behavior was noticed since a non-favorable form of adsorption isotherm was observed at low solute concentrations, for total chromium removal (Fig. 13b); however, a favorable adsorption behavior appeared as chromium concentration increased. This fact indicates that the mechanism of Cr(VI) reduction followed by Cr(III) adsorption affects adsorption equilibrium significantly at low Cr concentrations when using MGS as adsorbent at these experimental conditions. Freundlich model was the best to describe total chromium isotherm data. This model implies heterogeneity of adsorption and predicts an increase in the concentrations of adsorbed solute as its concentration increases in the solution⁵⁰; therefore, as Cr(VI) reduction occurs, Cr(III) concentration increases, and adsorption of this ion occurs on the surface of MGS. At higher Cr(VI) concentrations, reduction to Cr(III) is favored; hence, adsorption of this ion is enhanced.

Table 3 shows the maximum biosorption capacities of various biosorbents⁵¹⁻⁵⁴, including GS and MGS. In general, the biosorption capacities of modified biosorbents were higher than that of the unmodified adsorbents, particularly for GS and MGS. Compared to other biosorbents, GS and MGS showed similar biosorption capacities, except for untreated biomass of palm branches. However, the listed biosorbents (Table 3) do not report the reduction of hexavalent chromium, and this

is an excellent advantage for GS and MGS biosorbents since the Cr(III) species is less toxic than Cr(VI).

This study aimed to evaluate the removal of chromium removal using acid-modified guava seeds (MGS), determine basic biosorption parameters in batch systems, and the effects of temperature and pH on the reduction and biosorption processes. The efficiency of MGS to reduce Cr(VI) and remove it from aqueous solutions has been proven in batch systems at different experimental con-

Table 3. Comparison of maximum biosorption capacities of different materials for Cr(VI) removal

Biosorbent	Biosorption capacity (mg/g)	Conditions	Reference
Green alga (<i>C. glomerata</i>)	3.77	pH 2, 45°C	51
Palm branches	25	pH 2, 25°C	52
Orange peels	7.14	pH 2, 34°C	53
Untreated banana stalk	6.8	25°C	54
Untreated corn cob	18.7	25°C	54
Untreated sunflower waste	12.2	25°C	54
Acid-modified banana stalk	7.4	25°C	54
Acid-modified corn cob	23.6	25°C	54
Acid modified sunflower waste	12.2	25°C	54
GS	2.01	pH 6, 45°C	This study
MGS	4.42	pH 6, 25°C	This study

ditions. The relatively fast kinetics of the reduction-biosorption systems indicate that these systems can remove chromium from tannery and electroplating wastewaters in a continuous system since the batch systems proved to be efficient at different pH, temperature and concentration conditions. However, some other parameters that can affect the reduction of Cr(VI) and biosorption of chromium (like the presence of other anions, for instance) must be evaluated first to determine their influence on Cr removal in batch systems. Moreover, dynamic behavior in a continuous mode (fixed bed or fluidized bed systems) of this biosorbent to remove Cr must also be assessed first to establish its performance, leading to scaling up the system if it is suitable.

CONCLUSIONS

Acid-modified guava seeds (MGS) can reduce and remove Cr(VI) from aqueous solutions. It has been proven that the acid modification of biosorbent enhances Cr(VI) removal. There is a high dependence on Cr(VI) reduction to pH and temperature and is independent of the type of biosorbent used (GS or MGS). A chemisorption process was responsible for chromium removal from aqueous solutions, involving different functional groups on the surface of biosorbent. Cr(VI) removal was relatively fast, depending on the systems' pH and temperature. MGS has a significant chromium biosorption capacity compared to conventional and unconventional adsorbents, with the advantage of Cr(VI) reduction to a less toxic chromium species. MGS has a great potential to be used as an adsorbent in the treatment of chromium polluted real effluents.

ACKNOWLEDGMENTS

The authors are grateful for the technical assistance of B. Villalobos-Castañeda and to the financial support provided by Coordinación de la Investigación Científica-UMSNH (grant CIC-UMSNH-2019).

LITERATURE CITED

1. Prabhakaran, S.K., Vijayaraghavan, K. & Balasubramanian, R. (2009). Removal of Cr (VI) ions by spent tea and coffee dusts: reduction to Cr (III) and biosorption. *Ind. Eng. Chem. Res.* 48(4), 2113–2117. DOI: 10.1021/ie801380h.
2. Mathialagan, T. & Viraraghavan, T. (2003). Adsorption of cadmium from aqueous solutions by vermiculite. *Sep. Sci. Technol.*, 38(1), 57–76. DOI: 10.1081/SS-120016698.
3. Navarro, A.E., Ramos, K.P., Agapito, R. & Cuizano, N.A. (2006). Propiedades ácido-básicas de *Lentinus edodes* y cinética de biosorción de Cadmio (II). *Rev. Lat. Rec Nat.*, 2(2), 47–54. (In spanish) Retrieved January 20, 2020 from <https://www.itson.mx/publicaciones/rlnr/Documents/v2-n2-1-propiedades-%C3%A1cido-b%C3%A1sicas-de-lentinus-edodes.pdf>.
4. Dehghani, M.H., Sanaei, D., Ali, I. & Bhatnagar, A. (2016). Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: kinetic modeling and isotherm studies. *J. Mol. Liq.* 215, 671–679. DOI: 10.1016/j.jhazmat.2007.07.033.
5. Abdel Hameed, M.S. (2006). Continuous removal and recovery of lead by alginate beads, free and alginate-immobilized *Chlorella vulgaris*. *Afr. J. Biotech.* 5(19). DOI: 10.5897/AJB2006.000-5070.

6. Mehta, S.K. & Gaur, J.P. (2005). Use of algae for removing heavy metal ions from wastewater: progress and prospects. *Crit. Rev. Biotech.* 25(3), 113–152. DOI: 10.1080/07388550500248571.
7. Crist, R.H., Oberholser, K., McGarrity, J., Crist, D.R., Johnson, J.K. & Brittsan, J.M. (1992). Interaction of metals and protons with algae. 3. Marine algae, with emphasis on lead and aluminum. *Env. Sci. Technol.* 26(3), 496–502. DOI: 10.1021/es00027a007.
8. Fan, X.D., & Zhang, X.K. (2015). Adsorption of heavy metals by adsorbents from food waste residue. *J. Residuals Sci. Technol.* 12, 155–158. DOI:10.12783/issn.1544-8053/12/s1/22.
9. Bayuo, J., Pelig-Ba, K.B. & Abukari, M.A. (2019). Adsorptive removal of chromium (VI) from aqueous solution unto groundnut shell. *Appl. Water Sci.* 9(4), 107. DOI: 10.1007/s13201-019-0987-8.
10. Mangwandi, C., Kurniawan, T.A. & Albadarin, A.B. (2020). Comparative biosorption of chromium (VI) using chemically modified date pits (CM-DP) and olive stone (CM-OS): Kinetics, isotherms and influence of co-existing ions. *Chem. Eng. Res. Des.* 156, 251–262. DOI: 10.1016/j.cherd.2020.01.034
11. Daneshvar, N., Salari, D. & Aber, S. (2002). Chromium adsorption and Cr (VI) reduction to trivalent chromium in aqueous solutions by soya cake. *J. Hazard. Mat.* 94(1), 49–61. DOI: 10.1016/S0304-3894(02)00054-7.
12. Jawad, A. & Karim, S.K.A. (2020). Cr (VI) ions removal from aqueous solutions using carrot residues as an adsorbent. *Science Letters*, 13(2), 30–36. DOI: 10.24191/sl.v13i2.7871.
13. Das, S.H., Saha, J., Saha, A., Rao, A.K., Chakraborty, B. & Dey, S. (2019). Adsorption study of chromium (VI) by dried biomass of tea leaves. *J. Indian Chem. Soc.* 96(4), 447–454. Retrieved June 15, 2020 from http://www.indianchemicalsociety.com/portal/uploads/journal/2019_04_6_Extended_1556592447.pdf.
14. Aggarwal, R. & Arora, G. (2020). Assessment of biosorbents for chromium removal from aqueous media. *Materials Today: Proceedings*. In press. DOI: 10.1016/j.matpr.2020.04.837.
15. Olguin, M.T., Lopez-González, H. & Serrano-Gómez, J. (2013). Hexavalent chromium removal from aqueous solutions by Fe-modified peanut husk. *Water Air Soil Pollut.* 224(9), 1654. DOI: 10.1007/s11270-013-1654-6.
16. Parlayici, Ş. & Pehlivan, E. (2015). Natural biosorbents (garlic stem and horse chesnut shell) for removal of chromium (VI) from aqueous solutions. *Environ. Monit. Assess.* 187(12), 763. DOI: 10.1007/s10661-015-4984-6.
17. Kuppusamy, S., Thavamani, P., Megharaj, M., Venkateswarlu, K., Lee, Y.B. & Naidu, R. (2016). Oak (*Quercus robur*) acorn peel as a low-cost adsorbent for hexavalent chromium removal from aquatic ecosystems and industrial effluents. *Water Air Soil Pollut.* 227(2), 62. DOI: 10.1007/s11270-016-2760-z.
18. Wassie, A.B., & Srivastava, V.C. (2016). Teff straw characterization and utilization for chromium removal from wastewater: Kinetics, isotherm and thermodynamic modelling. *J. Env. Chem. Eng.* 4(1), 1117–1125. DOI: 10.1016/j.jece.2016.01.019.
19. Ntuli, T.D. & Pakade, V.E. (2020). Hexavalent chromium removal by polyacrylic acid-grafted *Macadamia* nutshell powder through adsorption–reduction mechanism: adsorption isotherms, kinetics and thermodynamics. *Chem. Eng. Commun.* 207(3), 279–294. DOI: 10.1080/00986445.2019.1581619.
20. Alfaro-Cuevas-Villanueva, R., Hidalgo-Vázquez, A.R., Cortés Penagos, C.D.J., & Cortés-Martínez, R. (2014). Thermodynamic, kinetic, and equilibrium parameters for the removal of lead and cadmium from aqueous solutions with calcium alginate beads. *Sci. World J.* 2014, DOI: 10.1155/2014/647512.
21. Pinzón-Bedoya, M.L. & Vera Villamizar, L.E. (2009). Kinetic modeling biosorption of Cr (III) using orange shell. *Dyna.* 76(160), 95–106. (In spanish) Retrieved february 20, 2020 from http://www.scielo.org.co/scielo.php?pid=S0012-73532009000400009&script=sci_arttext&tlng=en.
22. Netzahuatl-Muñoz, A.R., del Carmen Cristiani-Urbina, M. & Cristiani-Urbina, E. (2015). Chromium biosorption from

Cr (VI) aqueous solutions by Cupressus lusitanica bark: kinetics, equilibrium and thermodynamic studies. *PLoS One*, 10(9). DOI: 10.1371/journal.pone.0137086

23. Cao, W., Wang, Z., Ao, H. & Yuan, B. (2018). Removal of Cr (VI) by corn stalk based anion exchanger: the extent and rate of Cr (VI) reduction as side reaction. *Colloids Surf. A Physicochem. Eng. Asp.* 539, 424–432. DOI: 10.1016/j.col-surf.2017.12.049.

24. Park, D., Yun, Y.S. & Park, J.M. (2005). Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. *Chemosphere*. 60(10), 1356–1364. DOI: 10.1016/j.chemosphere.2005.02.020.

25. da Rocha Ferreira, G.L., Vendruscolo, F., & Antoniosi Filho, N.R. (2019). Biosorption of hexavalent chromium by *Pleurotus ostreatus*. *Heliyon*, 5(3), e01450. DOI: 10.1016/j.heliyon.2019.e01450.

26. Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., & Pichette, A. (2012). Study of the degradation behavior of heat-treated jack pine (*Pinus banksiana*) under artificial sunlight irradiation. *Polym. Degrad. Stabil.* 97(7), 1197–1214. DOI: 10.1016/j.polymdegradstab.2012.03.022

27. Yun, Y.S. (2004). Characterization of functional groups of protonated Sargassum polycystum biomass capable of binding protons and metal ions. *J. Microbiol. Biotechn.* 14(1), 29–34. Retrieved march 20, 2020 from <http://www.jmb.or.kr/journal/download.php?Filedir=../submission/Journal/014/&num=1822>.

28. Ghani, W.A.W.A.K., Mohd, A., da Silva, G., Bachmann, R.T., Taufiq-Yap, Y.H., Rashid, U., & Ala'a, H. (2013). Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: chemical and physical characterization. *Ind. Crop. Prod.* 44, 18–24. DOI: 10.1016/j.indcrop.2012.10.017.

29. Wahab, M.A., Jellali, S. & Jedidi, N. (2010). Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling. *Bioresour. Technol.* 101(14), 5070–5075. DOI: 10.1016/j.biortech.2010.01.121.

30. Tandy, S., Healey, J.R., Nason, M.A., Williamson, J.C., Jones, D.L. & Thain, S.C. (2010). FT-IR as an alternative method for measuring chemical properties during composting. *Bioresour. Technol.* 101(14), 5431–5436. DOI: 10.1016/j.biortech.2010.02.033.

31. Vázquez-Guerrero, A., Alfaro-Cuevas-Villanueva, R., Rutiaga-Quinones, J.G. & Cortés-Martínez, R. (2016). Fluoride removal by aluminum-modified pine sawdust: effect of competitive ions. *Ecol. Eng.* 94, 365–379. DOI: 10.1016/j.ecoleng.2016.05.070.

32. Ayoob, S., Gupta, A.K., Bhakat, P.B., & Bhat, V.T. (2008). Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. *Chem. Eng. J.* 140(1–3), 6–14. DOI: 10.1016/j.cej.2007.08.029.

33. Marín, Rangel, V.M., Cortés, Martínez, R., Cuevas Villanueva, R.A., Garnica, Romo, M.G. & Martínez, Flores, H.E. (2012). As (V) biosorption in an aqueous solution using chemically treated lemon (*Citrus aurantifolia* swingle) residues. *J. Food Sci.* 77(1), T10-T14. DOI: 10.1111/j.1750-3841.2011.02466.x

34. Hon, D.N. & Shiraishi, N. (2000). *Wood Cellulosic Chemistry* New York, USA: CRC press.

35. Fiol, N., Escudero, C. & Villaescusa, I. (2008). Chromium sorption and Cr (VI) reduction to Cr (III) by grape stalks and yohimbe bark. *Bioresour. Technol.* 99(11), 5030–5036. DOI: 10.1016/j.biortech.2007.09.007.

36. Peng, H., Salmén, L., Stevanic, J. S., & Lu, J. (2019). Structural organization of the cell wall polymers in compression wood as revealed by FTIR microspectroscopy. *Planta.* 250(1), 163–171. DOI: 10.1007/s00425-019-03158-7

37. Coates, J. (2000). Chapter in *Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), New Jersey, USA: John Wiley & Sons.

38. Suksabye, P., Thiravetyan, P., Nakbanpote, W. & Chayabutra, S. (2007). Chromium removal from electroplating wastewater by coir pith. *J. Hazard. Mat.* 141(3), 637–644. DOI: 10.1016/j.jhazmat.2006.07.018.

39. Sánchez-Sánchez, H.A., Cortés-Martínez, R. & Alfaro-Cuevas-Villanueva, R. (2013). Fluoride removal from aqueous solutions by mechanically modified guava seeds. *Int. J. Sci.: Basic Appl. Res.* 11, 159–172. Retrieved June 20, 2020 from <https://gssrr.org/index.php/JournalOfBasicAndApplied/article/view/1326/1204>.

40. Puigdomenech, Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA) (version 18), Inorganic Chemistry Department, Royal Institute of Technology, Stockholm, Sweden 2010. Retrieved December 19, 2019 from <https://www.kth.se/che/medusa/downloads-1.386254>.

41. Bellú, S., Sala, L., González, J., García, S., Frascaroli, M., Blanes, P., García, J., Sales-Peregrin, J., Atria, A., Ferrion, J., Harada, M., Cong, C. & Niwa, Y. (2010). Thermodynamic and dynamic of chromium biosorption by pectic and lignocellulosic biowastes. *J. Wat Res. Prot.* 2(10), 888. DOI: 10.4236/jwarp.2010.210106.

42. Park, D., Yun, Y. S. & Park, J. M. (2005). Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. *Chemosphere*. 60(10), 1356–1364. DOI: 10.1016/j.chemosphere.2005.02.020

43. Park, D., Yun, Y.S. & Park, J.M. (2010). The past, present, and future trends of biosorption. *Biotechnol. Bioproc. E.* 15(1), 86–102. DOI: 10.1007/s12257-009-0199-4.

44. Miretzky, P. & Cirelli, A.F. (2010). Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. *J. Hazard. Mat.* 180(1–3), 1–19. DOI: 10.1016/j.jhazmat.2010.04.060.

45. Zheng, Y.M., Liu, T., Jiang, J., Yang, L., Fan, Y., Wee, A.T. & Chen, J.P. (2011). Characterization of hexavalent chromium interaction with Sargassum by X-ray absorption fine structure spectroscopy, X-ray photoelectron spectroscopy, and quantum chemistry calculation. *J. Colloid Interf. Sci.* 356(2), 74–748. DOI: 10.1016/j.jcis.2010.12.070.

46. Lagrergen, S. (1898). Zur Theorie Der Sogenannten Adsorption Gelöster Stoffe Kungliga Svenska Vetenskapsakademien. *Handlingar*, 24(4), 1–39. DOI: 10.1007/BF01501332

47. Ho, Y.S., McKay, G., Wase, D.A.J. & Forster, C.F. (2000). Study of the sorption of divalent metal ions on to peat. *Adsorpt. Sci. Technol.* 18(7), 639–650. DOI: 10.1260/0263617001493693

48. Low, M.J.D. (1960). Kinetics of chemisorption of gases on solids. *Chem. Rev.* 60(3), 267–312. DOI: 10.1021/cr60205a003.

49. Chen, H., Dou, J. & Xu, H. (2017). Removal of Cr (VI) ions by sewage sludge compost biomass from aqueous solutions: reduction to Cr (III) and biosorption. *Appl. Surf. Sci.* 425, 728–735. DOI: 10.1016/j.apsusc.2017.07.053.

50. Araújo, C.S., Almeida, I.L., Rezende, H.C., Marcionilio, S.M., León, J.J. & de Matos, T.N. (2018). Elucidation of mechanism involved in adsorption of Pb (II) onto lobeira fruit (*Solanum lycocarpum*) using Langmuir, Freundlich and Temkin isotherms. *Microchem. J.* 137, 348–354. DOI: 10.1016/j.microc.2017.11.009.

51. Al-Homaidan, A.A., Al-Qahtani, H.S., Al-Ghanayem, A.A., Ameen, F. & Ibraheem, I.B. (2018). Potential use of green algae as a biosorbent for hexavalent chromium removal from aqueous solutions. *Saudi J. Biol. Sci.* 25(8), 1733–1738. DOI: 10.1016/j.sjbs.2018.07.011.

52. Shouman, M.A., Fathy, N.A., Khedr, S.A., & Attia, A.A. (2013). Comparative biosorption studies of hexavalent chromium ion onto raw and modified palm branches. *Adv. Phys. Chem.* Vol. 2013. DOI: 10.1155/2013/159712.

53. Khalifa, E.B., Rzig, B., Chakroun, R., Nouagui, H. & Hamrouni, B. (2019). Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent. *Chemometr. Intell. Lab.* 189, 18–26. DOI: 10.1016/j.chemolab.2019.03.014.

54. Mahmood-ul-Hassan, M., Suthor, V., Rafique, E. & Yasin, M. (2015). Removal of Cd, Cr, and Pb from aqueous solution by unmodified and modified agricultural wastes. *Environ. Monit. Assess.* 187(2), 19. DOI: 10.1007/s10661-014-4258-8.