Adsorptive removal of chromium (VI) from synthetic waters using magnetic lignocellulosic composites

Tanya Medina-Espinosa¹, Christopher Asimbaya¹, Salomé Galeas¹, Nelly M. Rosas-Laverde¹, Alexis Debut² and Víctor H. Guerrero¹,*

¹Department of Materials, Escuela Politécnica Nacional, Quito 170525, Ecuador
²Centro de Nanociencia y Nanotecnología, Universidad de las Fuerzas Armadas (ESPE), Sangolquí 171103, Ecuador

*Corresponding author: victor.guerrero@epn.edu.ec

Abstract. The removal of heavy metals from water is one of the major challenges that humanity must address to avoid negative potential impacts on the environment and human health. During the last few years, several adsorbents have been examined, in a search for highly efficient and cost-effective materials. In this work, we investigated the use of laurel, canelo and eucalyptus lignocellulosic sawdust residues (LRs) impregnated with magnetite nanoparticles (MNP), to remove $\text{Cr}^{6+}$ ions. Each LR was added to an aqueous solution in which MNP were being synthesized by coprecipitation. Two composite adsorbents were obtained, with LR:MNP ratios of 1:1 and 3:1. The materials obtained were characterized by X-ray diffraction, scanning and transmission electron microscopy, and infrared and Raman spectroscopy. The results obtained showed that the laurel composite was the best adsorbent, reaching a maximum removal efficiency and capacity of 99.8 % and 30.5 mg/g, respectively. The optimal contact time was 30 min and the process fitted the Langmuir isotherm model, showing small effects of the fraction of sawdust residues used to support the MNP. Further studies will be performed to optimize the composition of the composites aiming to reduce the amount of costly MNP used while ensuring a high removal performance.

1. Introduction
Wastewater from industries is one of the main sources of environmental pollution. Among water pollutants, heavy metals have gained great importance due to their persistence and toxicity [1]. The industries with this type of effluent include those that operate with metallic coatings, mining, automotive industry, tanneries, foundry operations, and alloy industries [2].

The chromate anion ($\text{CrO}_4^{2-}$) is very common in industrial wastewater, polluting and affecting human health. Hexavalent chromium, even at relatively low concentrations (from 0.10 mg/L), is a mutagen and a potential carcinogen [3]. That is why it is necessary to treat effluents, avoid contamination and reduce the risk generated by the presence of heavy metals. Several studies have been conducted on the removal of heavy metal ions such as $\text{Cr}^{6+}$. Activated carbon is widely used in adsorption, in addition to chemical precipitation, electrochemical reduction, ion exchange, biological methods, and electrocoagulation [4,5]. However, these methods have certain limitations in terms of efficiency, costs, and the generation of secondary products requiring subsequent treatment [6].

Adsorption is an alternative treatment for the removal of heavy metals using lignocellulosic residues such as sawdust, wood chips, fruit peels, etc. These residues are widely available, have a low cost, and
a relatively high specific surface area. The adsorptive removal is directly influenced by the amount of lignin present in the material [7,8]. The adsorption is promoted by reactions between the oxygens of the ionizable functional groups of lignin, and the metal ions in the solution [2]. Adsortion is directly related to the nature of the adsorbent material, and sometimes the kinetics of heavy metal adsorption is not optimal. In recent years there has been a great development of nanotechnology, which has helped to increase the adsorption efficiency of metal ions due to the increase in active sites [9]. One of the nanoparticles that has been most studied for this purpose is magnetite (Fe3O4) due to its magnetic properties that allows an easy recovery, and because it is a relatively simple and economically convenient method [10]. Additionally, this type of iron oxide nanoparticles can be obtained through a variety of environmentally friendly methods [11,12]. Magnetite nanoparticles (MNP) increase the performance of adsorbents by being incorporated into their surface. Among the adsorbents that have been studied together with MNP are sawdust, residues of tea, orange peels and almonds, and polymers such as chitosan. The applications of these composite materials are focused on the removal of colorants and heavy metals, especially zinc, chromium (VI), cobalt, lead, strontium and arsenic [13–15]. Using MNP modified with an anionic surfactant, zinc removals of 89.3% have been obtained from 20 mL solutions with initial concentration of 10 mg/L, in 5 min and with 10 mg of the adsorbent [16]. Orange peels impregnated with MNP remove up to 85% of cadmium after 40 min [17]. Removals of 95% of chromium (VI) have been obtained from 100 mL solutions with an initial concentration of 50 mg/L, in 100 min and with 0.5 g of MNP [18].

In the above-mentioned investigations, the influence of the contact time and the amount of the composite material in the adsorption tests is mainly considered. However, the relative amounts of the MNP and the lignocellulosic sawdust residues (LR) used to obtain composite adsorbents has received relatively little attention. In this work, we studied the effect of the contact time and the fraction of the sawdust residues in composite adsorbents used for chromium (VI) removal, considering for this purpose two LR:MNP ratios, and three types of residues. Since the MNP are costly, compared to the LR, it would be beneficial to reduce the amount of magnetite required to obtain an efficient composite adsorbent.

2. Materials and methods
All the reagents used were analytical grade and the solutions were prepared using type 2 ultra-purified water. The reagents included ferric chloride hexahydrate (FeCl3·6H2O), ferrous chloride tetrahydrate (FeCl2·4H2O), and hydrochloric acid (HCl) from Panreac, and sodium hydroxide (NaOH) from Merck. Argon was used as an inert atmosphere for the synthesis of magnetite and the composite material. Potassium dichromate (K2Cr2O7) from Lobachemie was used for the removal tests. Three types of wood residues were used: Ecuadorian laurel (Cordia alliodora), canelo (Ocotea javitensis) and eucalyptus (Eucalyptus globulus), with a particle size between 74 and 150 µm. The residues were washed several times with ultra-purified water to remove impurities. Subsequently, each residue was dried at 80 °C for 12 h [13].

MNP were synthesized by the co-precipitation method, according to the chemical reaction:

$$\text{FeCl}_3+2\text{FeCl}_2+8\text{NaOH} \rightarrow 2\text{Fe}_3\text{O}_4+4\text{H}_2\text{O}+8\text{NaCl}$$ (1)

A 25 mL iron solution was prepared dissolving 8.649 g of FeCl3·6H2O, 3.181 g of FeCl2·4H2O, and 1 mL of 0.4 M HCl in distilled water; 250 mL of a 0.9 M NaOH solution was also prepared. Argon was bubbled into each solution for 15 min. The iron solution was added to the NaOH solution dropwise, and stirred at 1000 rpm for 45 min at 50 °C, with constant argon bubbling [19]. To obtain the composite adsorbent, each LR was added to the previous solution and the stirring was maintained for 45 min at 50 °C under argon atmosphere. The LR:MNP ratios used were 1:1 and 3:1. The resulting suspension was washed with distilled water until the pH of the solution was neutralized; the precipitate was magnetically separated and dried at 70 °C for 12 h. Finally, the composite obtained was disintegrated.

The lignin composition was determined according to ASTM D1106-96(2013). The functional groups in each LR and composite adsorbent were identified by a Perkin Elmer Spectrum 100/Spotlight 200 FTIR spectrometer [20]. Additionally, the magnetite and the composites were analyzed using Raman
spectroscopy (Horiba LabRAM HR Evolution) and X-ray diffraction (XRD) (Panalytical Empyrean). To determine the particle size of the magnetite, transmission electron microscopy (TEM) was performed with a FEI Tecnai G2 Spirit Twin microscope. The surface morphology of the composite materials was studied by scanning electron microscopy (SEM), using an Aspex PSEM Express equipment [13].

The conditions for the removal tests were established based on the work of previous authors. The amount of the composite adsorbent material used was 0.9 g, added to 100 mL of a 20 mg/L chromium (VI) solution, at pH 2.5 and 25 °C at 200 rpm. The removal using the MNP was studied under the same conditions. Each removal test was carried out considering different contact times, from 15 min to 160 min [18,21]. Filtered solutions of each test were analyzed using a HACH DR 1900 spectrophotometer according to the APHA 3500-Cr established method. Finally, adsorption isotherms were fitted for the chromium (VI) ion removal. The tests were carried out with 10, 20, 50, 100, 150 and 200 mg/L solutions. Freundlich and Langmuir models were used according to the corresponding linearized equations:

\[
\log q_e = \log K_F + (1/n) \log C_e \\
1/q_e = 1/q_{max} + 1/(K_L q_{max}) (1/C_e)
\]

where \(q_e\) is the ion adsorption capacity per unit mass of adsorbent (mg/g); \(C_e\) is the equilibrium concentration (mg/L); \(K_F\) and \(n\) are Freundlich isotherm constants that relate adsorption capacity and intensity, respectively; \(q_{max}\) is the maximum ion adsorption capacity as monolayer (mg/g); and \(K_L\) is a constant related to the adsorption energy for the Langmuir isotherm [7,10].

3. Results and discussion

3.1. Materials characterization

The amount of lignin (dry basis) was 31.84 % in laurel, 28.28 % in canelo and 18.28 % in eucalyptus. According to Lee and Rowell (2004), the material with the greatest lignin content, has a greater number of phenolic groups and therefore a greater capacity to remove metal ions [20]. Therefore, laurel was expected to adsorb higher amounts of chromium (VI), compared to the other two residues.

As illustrated in figure 1, TEM showed that the average diameter of the MNP synthesized was 11.3 nm. This figure also shows the SEM micrographs of the composites obtained with 1:1 and 3:1 canelo:MNP ratios, where the surface of the lignocellulosic residue coated with the magnetite nanoparticles is observed. Magnetite agglomerates with different shapes and sizes are formed due to magnetic attraction. In the composite with a 3:1 ratio, a smaller amount of nanoparticles is observed coating the canelo fibers. Similar results were observed for the laurel and eucalyptus composites.

XRD patterns of the synthesized magnetite and the composite materials in a 1:1 ratio are shown in Figure 2.a. Magnetite exhibits characteristic peaks at indices 220, 311, 400, 422, 511, and 440 between 30° and 63°. These results correspond to the cubic spinel crystal structure of magnetite [22]. Every composite obtained, with the three LR and the two LR:MNP ratios studied, showed the magnetite peaks mentioned. This allowed us to verify the presence of the nanoparticles on the adsorbent surface. Figure 2.b shows the Raman spectrum obtained during the characterization of the MNP. The most representative peak is found around 670 cm\(^{-1}\). The appearance of the band around 350 - 385 cm\(^{-1}\) in the magnetite spectrum may be due to the bond between the OH- groups and the Fe\(^{3+}\) ions. Furthermore, by having nanoparticulated material, the width of the lines of the Raman spectra can be broadened [23].

Figure 3 shows the FTIR spectra of the lignocellulosic canelo residue, and the composites with 1:1 and 3:1 LR:MNP ratios, where the characteristic peak of lignin is in the band around 1500 cm\(^{-1}\), which corresponds to the vibration of the aromatic skeleton of the benzene ring. The stretching of the OH bonds of the phenol and alcohol groups is showed in the bands around 3300 cm\(^{-1}\) [13,24,25]. The presence of magnetite nanoparticles on the lignocellulosic residues is evidenced in the spectra in the band around 600 cm\(^{-1}\), which corresponds to the vibrational stretching of the Fe-O bond [13,24,25].
Figure 1. TEM images of the MNP and SEM images of the composites of canelo impregnated with MNP in (a) 1:1, and (b) 3:1 ratios.

Figure 2. (a) X-ray diffraction patterns of the MNP and the composites with a 1:1 LR to MNP ratio. (b) Raman spectra of the MNP synthesized.

Figure 3. FTIR spectra for (a) canelo, eucalyptus and laurel residues, and (b) composites with 1:1 and 3:1 canelo residue:magnetite nanoparticle ratios.

3.2. Effect of the adsorbent dose
Figure 4 shows that the chromium (VI) removal efficiencies using the composite adsorbents with 1:1 and 3:1 LR:MNP ratios are practically the same. This illustrates the direct influence of magnetite nanoparticles on the adsorption of heavy metal ions, which lies in the presence of Fe and O atoms that, by adsorbing OH- radicals from the solution, increase the OH- groups on the magnetite surface. The interactions between these groups and the metal ions improve the removal performance [26]. Table 1 summarizes the results obtained in the adsorption tests with each composite material.
Table 1. Chromium (VI) adsorptive removal efficiency using magnetic lignocellulosic composites and a 30 min contact time.

| LR : MNP ratio | Laurel - MNP | Canelo - MNP | Eucalyptus - MNP |
|----------------|-------------|-------------|-----------------|
| 1:1            | 99.78 %     | 99.60 %     | 98.77 %         |
| 3:1            | 99.64 %     | 99.59 %     | 98.42 %         |

3.3. Effect of the contact time

Figure 4 shows a steep slope for the first 30 min during the removal of chromium (VI) ions. From this contact time on, the increase in the removal percentage is minimal, approximately 1%, until reaching equilibrium. In the first minutes, there is a greater amount of free active sites in the composites, which after being occupied, decrease the adsorption of the metal ion. The laurel composites show higher removals; however, the difference with the removals obtained with canelo is 0.3 %, and with eucalyptus 1 %. This dependence on the removal by lignocellulosic composites is related to the amount of lignin in each residue [20]. In the chromium (VI) removal tests with laurel composites, percentages of around 99% were reached. As expected, the lower the initial concentration, the shorter will be the contact time and the higher the removal percentage [7].

It should be noted that, by adsorbing the heavy metal using only magnetite nanoparticles, a 96.95% chromium (VI) removal efficiency was obtained, with a 100 min contact time and using 0.9 g of adsorbent in a 100 mL solution with initial concentration of 20 mg/L of the contaminant. Similar removal efficiencies were obtained using the lignocellulosic residues impregnated with MNP, but in a much shorter time (approximately 30 min) under the same conditions.

Figure 4. Chromium (VI) removal using composites with LR:MNP ratios of (a) 1:1 and (b) 3:1.

3.4. Adsorption isotherms

Table 2 shows the parameters for the fittings of the Langmuir and Freundlich adsorption isotherms to the data obtained when using the laurel composite adsorbents with LR:MNP ratios of 1:1 and 3:1. The model that best fits the chromium (VI) adsorption is Langmuir's. However, the difference between the correlation coefficients for the two models is not significant. This can be attributed to the surface heterogeneity of the lignocellulosic residues, which mostly generates multilayer adsorption, as well as the nanoparticles agglomerated on the surface of the residue that give rise to active sites with different adsorption energy capacity [7].

Table 2 also shows that the maximum adsorption capacity of the chromium (VI) ions on the laurel composite with MNP is around 30 mg/g. This demonstrates that there is a higher adsorption of the heavy metal with this type of adsorbent. As an example, Yuan et al. (2009) obtained a maximum chromium adsorption capacity with magnetite nanoparticles of 9.86 mg/g. With the composite material, the surface area was increased and therefore the maximum adsorption capacity of the heavy metal [18].
Table 2. Isotherm model parameters derived for the chromium (VI) adsorptive removal using laurel impregnated with MNP.

| Model             | Parameters | 1:1 Laurel : MNP ratio | 3:1 Laurel : MNP ratio |
|-------------------|------------|------------------------|------------------------|
| Langmuir isotherm | R²         | 0.9989                 | 0.9974                 |
|                   | K_L (L/mg) | 0.809                  | 0.724                  |
|                   | q_max (mg/g) | 31.44              | 30.48                  |
| Freundlich isotherm | R²   | 0.9920                 | 0.9860                 |
|                   | K_F       | 15.097                 | 13.883                 |
|                   | n         | 1.202                  | 1.172                  |

4. Conclusion
In this work we studied the removal of chromium (VI) ions from synthetic wastewaters, giving particular attention to the fraction of lignocellulosic residues used to obtain magnetic composite adsorbents. The results showed that the maximum contaminant removal is achieved in a shorter time using the composites, in comparison to the use of magnetite nanoparticles alone. The magnetic lignocellulosic composite that allowed the highest metal ion adsorption was the one made using laurel. Its high performance can be attributed to the higher content of lignin in its composition, with resulted in a removal of around 99.8 % for chromium (VI), with a 30 min contact time.

On the other hand, it was observed that there are no significant differences between the results of the adsorption tests performed using the lignocellulosic composites with 1:1 and 3:1 LR:MNP ratios. The adsorption efficiencies and capacities reached are very close. However, the role of the residue is very important since it provides a support for the highly effective magnetite nanoparticles, preventing them from excessive agglomeration while providing adsorption sites. As a result, the magnetite nanoparticles could be incorporated in relatively low fractions in magnetic lignocellulosic adsorbents, leading to more economical treatment methods. On this basis, further studies will be performed aiming to optimize the fraction of nanoparticles required to obtain highly efficient heavy metal removal.

5. References
[1] Vareda J P, Valente A J M and Durães L 2019 Assessment of heavy metal pollution from anthropogenic activities and remediation strategies: A review J. Environ. Manage. 246 101–18
[2] Shukla A, Zhang Y-H, Dubey P, Margrave J . and Shukla S S 2002 The role of sawdust in the removal of unwanted materials from water J. Hazard. Mater. 95 137–52
[3] Zhang J, Li Y, Zhou J, Chen D and Qian G 2012 Chromium (VI) and zinc (II) waste water co-treatment by forming layered double hydroxides: Mechanism discussion via two different processes and application in real plating water J. Hazard. Mater. 205–206 111–7
[4] Stoica-Guzun A, Stroescu M, Jinga S I, Mihalache N, Botez A, Matei C, Berger D, Damian C M and Ionita V 2016 Box-Behnken experimental design for chromium(VI) ions removal by bacterial cellulose-magnetite composites Int. J. Biol. Macromol. 91 1062–72
[5] Zamora-Ledezma C, Negrete-Bolagay D, Figueroa F, Zamora-Ledezma E, Ni M, Alexis F and Guerrero V H 2021 Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods Environ. Technol. Innov. 22 101504
[6] Aftabtalab A, Sadabadi H, Chakra C, Rao K and Mahofa E 2014 Magnetite nanoparticles (Fe3O4) synthesis for removal of Chromium (VI) from waste water Int. J. Sci. Eng. Res. 5 1419–23
[7] Kapur M and Mondal M K 2016 Magnetized sawdust for removal of Cu (II) and Ni (II) from aqueous solutions Desalin. Water Treat. 57 12620–31
[8] Castro D, Rosas-Laverde N M, Aldás M B, Almeida-Naranjo C E, Guerrero V H and Pruna A I 2021 Chemical Modification of Agro-Industrial Waste-Based Biosorbents for Enhanced Removal of Zn(II) Ions from Aqueous Solutions Materials (Basel). 14 2134
[9] Lasheen M R, El-Sherif I Y, Sabry D Y, El-Wakeel S T and El-Shahat M F 2014 Removal and
recovery of Cr (VI) by magnetite nanoparticles Desalin. Water Treat. 52 6464–73

[10] Padmavathy K S, Madhu G and Haseena P V 2016 A study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles Procedia Technol. 24 585–94

[11] Kumar B, Smita K, Galeas S, Sharma V, Guerrero V H, Debut A and Cumbal L 2020 Characterization and application of biosynthesized iron oxide nanoparticles using Citrus paradisi peel: A sustainable approach Inorg. Chem. Commun. 119 108116

[12] Kumar B, Smita K, Cumbal L, Debut A, Galeas S and Guerrero V H 2016 Phytosynthesis and photocatalytic activity of magnetite (Fe3O4) nanoparticles using the Andean blackberry leaf Mater. Chem. Phys. 179 310–5

[13] Cheng Z, Gao Z, Ma W, Sun Q, Wang B and Wang X 2012 Preparation of magnetic Fe3O4 particles modified sawdust as the adsorbent to remove strontium ions Chem. Eng. J. 209 451–7

[14] Abas S N A, Ismail M H S, Kamal M L and Izhar S 2013 Adsorption process of heavy metals by low-cost adsorbent: A review World Appl. Sci. J. 28 1518–30

[15] Afkhani A, Saber-Tehrani M and Bagheri H 2010 Modified maghemite nanoparticles as an efficient adsorbent for removing some cationic dyes from aqueous solution Desalination 263 240–8

[16] Adeli M, Yamin Y and Faraji M 2017 Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples Arab. J. Chem. 10 S514–21

[17] Gupta V K and Nayak A 2012 Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe2O3 nanoparticles Chem. Eng. J. 180 81–90

[18] Yuan P, Fan M, Yang D, He H, Liu D, Yuan A, Zhu J X and Chen T H 2009 Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions J. Hazard. Mater. 166 821–9

[19] Devaraj N K, Ong B H and Matsumoto M 2008 Yield control of chemically-synthesized magnetite nanoparticles Synth. React. Inorganic, Met. Nano-Metal Chem. 38 208–11

[20] Lee B G and Rowell R M 2004 Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers J. Nat. Fibers 1 97–108

[21] Yaseminin B and Zeki T 2007 Removal of heavy metals from aqueous solution by sawdust adsorption J. Environ. Sci. 19 160–6

[22] Petcharoen K and Sirivat A 2012 Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 177 421–7

[23] Slavov L, Abrashev M V., Merodiiska T, Gelev C, Vandenberghe R E, Markova-Deneva I and Nedkov I 2010 Raman spectroscopy investigation of magnetite nanoparticles in ferrofluids J. Magn. Magn. Mater. 322 1904–11

[24] Panneerselvam P, Morad N and Tan K A 2011 Magnetic nanoparticle (F3O4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution J. Hazard. Mater. 186 160–8

[25] Sundrarajan M, Ramakishkmi M and Nadu T 2012 Novel Cubic Magnetite Nanoparticle Synthesis Using Room Temperature Ionic Liquid 9 1070–6

[26] Nethaji S, Sivasamy A and Mandal A B 2013 Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr(VI) Bioresour. Technol. 134 94–100

Acknowledgments
The authors acknowledge the support provided by the project grant PIGR-19-05, from the Escuela Politécnica Nacional.