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Agro-Industrial Waste as Potential Heavy Metal Adsorbents and Subsequent Safe Disposal of Spent Adsorbents

Daiana Simón [1], Cristina Palet [2], Agustín Costas [3] and Adrián Cristóbal [1,*]

[1] Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Universidad Nacional de Mar del Plata (UNMdP)–Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Mar del Plata 7600, Argentina
[2] GTS–UAB Research Group, Department of Chemistry, Faculty of Science, Edifici C-Nord, Universitat Autònoma de Barcelona, Carrer dels Til·lers, 08193 Bellaterra, Spain
[3] Centro Biotecnológico Fares Taie, Mar del Plata 7600, Argentina
* Correspondence: acristobal@fi.mdp.edu.ar

Abstract: Water pollution is an environmental problem that affects the ecosystem and living beings. Adsorption is one of the best technologies for the removal of heavy metals. Since waste recovery is the basis of the Circular Economy, agro-industrial waste is emerging as low-cost adsorbents for these pollutants from wastewater. Residues of pine sawdust, sunflower seed hulls and corn residues mix were evaluated as adsorbents of synthetic aqueous solutions of Ni(II), Zn(II) and Cd(II). These residues were characterized to determine their structure and composition, and to understand the adsorption mechanism. Adsorption efficiencies and capacities for the adsorbents and adsorbates were determined and compared. From the obtained results, it is possible to affirm that all biomasses used are good alternatives to the synthetic materials, with adsorption efficiencies greater than 50%. The order of adsorption was Cd > Zn > Ni. At the concentration range checked, adsorption efficiencies decreased in sawdust when a mixture of all metals together was considered (as present in real sewage). Finally, the heavy metals were immobilized, with efficiencies over 88.5%, in clay ceramics (as brick's precursors). This procedure would help to minimize the contamination that could be generated by the disposal of spent adsorbents, rarely explored in the literature.

Keywords: heavy metals; agro-industrial waste; adsorption; wastewater treatment; contaminant immobilization

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1. Introduction

Water pollution is a serious world environmental problem mainly caused by the climate change, rapid urbanization and advance of industrialization [1,2]. Heavy metals are among most released pollutants or contaminants into the water and are not biodegradable; therefore, they accumulate in living organisms entering in the food chain, also through the consumption of water and other contaminated products, producing corresponding pollution biomagnification [3,4]. These metals are an environmental and public health concern, not only because of their persistence and concentration that influence exposure, but also because of their toxicity, and their mobility in the environment that determines their bioavailability, which is given by the type of compound or metabolite that each metal can form, and also by the characteristics of each the specific environment [5,6].

Nickel, zinc and cadmium are common and relevant heavy metals in the environment [4,7]. Electroplating, metallurgical and batteries industries are some of the anthropogenic sources of nickel, zinc and cadmium contamination [8,9]. Also, nickel and zinc can easily leach due to mineral weathering [10]. Ni(II) and Zn(II) are essential elements and, in low concentrations, they are necessary for the metabolic development of humans, plants or animals. However, these elements can be toxic and harmful to health effects when exposure/assimilation exceeds the upper limit of the physiologically required range [11–13].

For example, high exposure to nickel can cause cancer, dry cough and lung problems, dermatitis, nausea, gastrointestinal and kidney problems in humans, and high exposure to zinc can cause fever, vomiting, anemia, and skin problems in humans [7,8]. Cd(II) is a highly toxic metal, even at very low concentrations, and is a non-essential element because it has no known benefit to human health or other living beings [6,10]. Cadmium is a human carcinogen as established by The International Agency for Research on Cancer (IARC) and can cause kidney problems, hypertension, stomach irritation, among others, and its chronic exposure can lead to the development of "Itai-Itai" disease [11,14].

In the province of Buenos Aires, Argentina, the permitted maximum discharge limits of these heavy metals in sewers, surface water or stormwater conduits and the open sea vary from 2 to 3 mg/L for Ni, 2 to 5 mg/L for Zn and 0.1 to 0.5 mg/L for Cd [15]. Industrial effluents generally can contain concentrations of heavy metals above the maximum permissible limits; therefore, industries must treat their effluents before discharging them into the environment [13,14]. There are conventional technologies for treating wastewater and minimizing heavy metal pollution (e.g., chemical precipitation, coagulation/flocculation, membrane filtration, electrochemical technologies, ion exchange), however they can be expensive, and can generate by-products or sludge, involving complicated procedures [8,16]. Adsorption is considered one of the best options for heavy metal removal due to its flexibility in operation and design, low energy consumption, minimization of sludge and by-products, possibility of regenerating adsorbents, and high removal efficiency even at a very low metal concentrations [17,18]. Activated carbon (AC) is the most used and recognized heavy metal adsorbent but it is expensive due to its preparation process and the impossibility of its regeneration, which limits its use at large-scale application [19,20].

For developing countries, the application and development of heavy metal removal technologies represents a challenge [20]. In recent years, agro-industrial residues have emerged as low-cost adsorbents, also for heavy metals, due to its availability and abundance, allowing to apply processes under the bases of the Circular Economy (which corresponds to the recovery and reuse of wastes) [7,10]. Every year, worldwide, tons of waste are produced from the agro-industrial sector that are stored in the open air and disposal in landfills, causing negative environmental impacts due to leachates and gases, following with the CO_2 generation with their burning [21]. Literature examples of agro-industrial residues used as heavy metal adsorbents are: cow dung [5], potato peel [22], cucumber peel [23], groundnut husk [24], eggshells [25], pine and modified pine [26], rice and rapeseed [27], coffee husk and lignin [28], among others. All the plant-based wastes are made up of hemicellulose, cellulose and lignin, and has a wide variety of functional groups (e.g., aldehydes and ketones, carboxyl groups, phenolics, hydroxyls, methyls, ethers, amides, aminos, etc.) that can interact with pollutants through various mechanisms [7,8].

As reported by the national government in 2020, in Argentina agro-industrial is really important and constitutes the 25% of the manufacturing industry and represents the 40% of exports. Among the agro-industrial residues, sawdust constitutes from 9 to 15% of the forest biomass discarded by sawmills and comes mainly from pine and eucalyptus plantations [29]. Sunflower crop is one of the most important in Argentina with a production of 3.5 million tons of seeds per year, obtaining 50% by weight of discarded hulls per seed [30]. On another hand, the corn production extends over a large area of the country and generates a great volume of biomass when compared to others such as wheat or barley [31].

This paper focuses the study of adsorption processes of Ni(II), Zn(II) and Cd(II) by using pine sawdust, sunflower seeds hulls and corn residues mix as adsorbents. A comparison of these three agro-industrial wastes as adsorbents is here presented, by checking firstly each individual heavy metal adsorption process, and secondly the influence of the mixture of these three heavy metals on their adsorption (as they are present in real sewage all together), by corresponding adsorption experiments. Later, such biomass residues containing heavy metals are immobilized in clay ceramics (as brick's precursors), to here propose an environmentally safe way to dispose the spent adsorbents together

with adsorbates (heavy metals). This procedure would help to minimize the secondary contamination that could be generated by the disposal of spent adsorbents, which is rarely explored in the adsorption literature and is fundamental for the real application of the adsorption from low-cost materials.

2. Materials and Methods

2.1. Chemicals and Reagents

All reagents used were of analytical grade. Stock solutions of concentration 1000 mg/L of individual heavy metals ions, Ni(II), Zn(II) and Cd(II), were prepared dissolving adequate amounts of $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$ and $Cd(NO_3)_2.4H_2O$ (all from Panreac, Castellar del Vallès, Spain), respectively. From these solutions the corresponding dilutions used in the adsorption experiments were prepared and the pH (Omega 300 pH meter, Crison Instruments, S.A, Barcelona, Spain) was adjusted with HNO_3 70% (Panreac, Spain). Solutions were prepared with Milli-Q water.

2.2. Biomass

The biomasses of sawdust, sunflower and corn were selected according to the reasons already mentioned. The pine (*Pinus elliottii*) sawdust residues were provided by a sawmill in the province of Corrientes, Argentina, and corresponded to the main cutting process of the wood, before any addition. Sunflower seed hulls (*Helianthus annuus*) were provided by a company located in the province of Santa Fe, Argentina, dedicated to the oilseed market, and were obtained from the processing of sunflower grains. The corn residues mix (*Zea mays var. saccharata*) were kindly provided by the National Institute of Agricultural Technology (INTA), and corresponded to the harvest stage.

The development of the adsorbents included the collection of the biomass, grinding with a knife mill (IKA A10) and sieving to a particle size of less than 1 mm to promote adsorption. The waste did not receive additional processing (chemical or thermal treatment) to make it as friendly as possible to the environment and reduce costs. Figure 1 shows the macroscopic appearance of the used waste, after grinding and sieving.

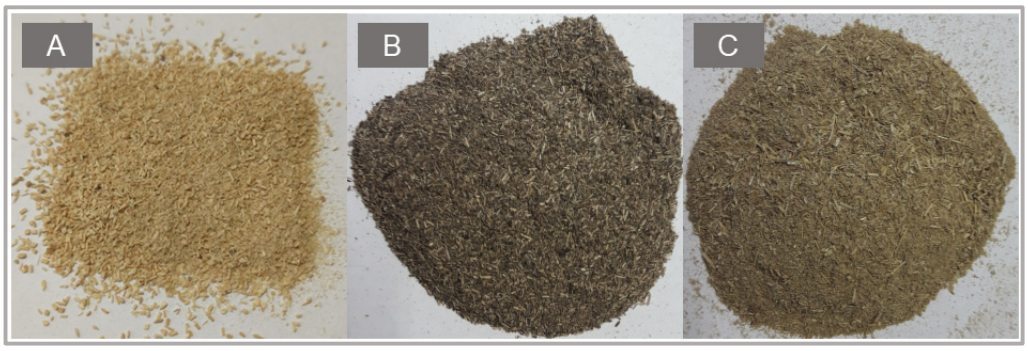

Figure 1. Ground and sieved residues (**A**) pine sawdust, (**B**) sunflower seed hulls and (**C**) corn residues mix.

2.3. Biomass Characterization

Physicochemical properties of adsorbents contribute to the process of adsorption of contaminants. Characteristics of potential adsorbents were determined from a number of techniques, that included the Brunauer-Emmett-Teller (BET) (Micromeritics Accusorb, model 2100), Scanning Electron Microscopy (SEM) (ZEISS EVO® MA 10 at the UAB Microscopy Service and FEI ESEM Quanta 200), Energy-Dispersive X-ray Spectroscopy (EDS) (Oxford SDD X-Act, software: AZTecOne), Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Nicolet 6700, Thermo Electron Corp. equipment, Waltham, MA, USA), X-ray Fluorescence (XRF) (PW4024 Minipal2 PANalytical X-ray spectrometer with copper anode and operating conditions nitrogen flow, voltage 20 kV, current 5 mA and time 100 s), and Differential Thermal Analysis (DTA) and Thermogravimetric

Analysis (TGA) (Shimadzu TGA-50 and Shimadzu DTA-50 instruments, with TA-50 WSI analyzer and operating conditions air, heating rate of 10 °C/min to 1000 °C and approximately 20 mg of mass). The mineral content of biomass it was determined following the guidelines of the ASTM E1755-01 standard [32]. In addition, the possible changes produced in the biomasses after the adsorption experiments were analyzed.

2.4. Batch Adsorption Experiments

The removal of heavy metals by means of the aforementioned agro-industrial residues was carried out under batch adsorption experiments at room temperature. A volume of 10 mL of a mono-metal solution, of Ni(II), Zn(II) or Cd(II) of 0.18 mmol/L, or a multi-metal solution of all together with a concentration of 0.18 mmol/L for each heavy metal was placed in contact with 0.1 g of adsorbent in tubes. The pH of the solutions was initially adjusted to 4–5 following previous literature [26,33]. The system was stirred at 40 rpm in a rotary mixer (CE 2000 ABT-4, SBS Instruments SA) for 24 h to ensure that equilibrium was reached. The liquid phase was filtered through 0.22 µm filters (Millex-GS, Millipore, Burlington, MA, USA). The metal concentration in the aqueous solution (not adsorbed) was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (XSERIES 2 ICP-MS, Thermo Scientific, Waltham, MA, USA) from the Autonomous University of Barcelona. The adsorption of each heavy metal was expressed as adsorption percentage (A%), calculated from Equation (1), and the adsorption capacity of each adsorbent (q_e) was calculated from Equation (2):

$$A\%\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e \left(\frac{mmol}{g}\right) = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 and C_e (mmol/L) are the initial and equilibrium concentrations of heavy metal in solution, respectively, V (L) is the volume of the heavy metal solution, and m (g) is the mass of the adsorbent [34,35]. Adsorption experiments are prepared by duplicate and the average results are reported.

2.5. Spent Adsorbents Disposal in Clay Ceramics

Safe disposal of spent adsorbents is necessary to minimize secondary contamination, especially if large-scale adsorption technology implementation is considered. Pine sawdust, sunflower seed hulls and corn residues mix, after being used as adsorbents, were added to the clay, and clay ceramics were prepared with the aim of immobilizing adsorbed heavy metals.

The amount of residue contaminated with Ni(II), Zn(II) and Cd(II) that was used in the clay ceramics corresponded to 20% in volume with respect to the volume of clay, in accordance with what was observed by the authors in previous studies [36]. For this reason, adsorption experiments were previously carried out scaling 20 times the amount of adsorbent (2 g) and 20 times the moles of metal ion (3.6×10^{-5}). As a consequence of the increase in adsorbent mass, the solution volume had to be increased to 40 mL so that the liquid covers the entire surface of the biomass.

The methodology used in the preparation process of the clay ceramics is detailed in Figure 2 and it was designed considering the characteristics of the raw materials, the pressure and firing conditions used in the brick factory. The clay was provided by a local brick factory and is the same that the manufacturer uses in the hollow brick production process. Firing of clay ceramic was carried out in an electric oven INDEF 332.

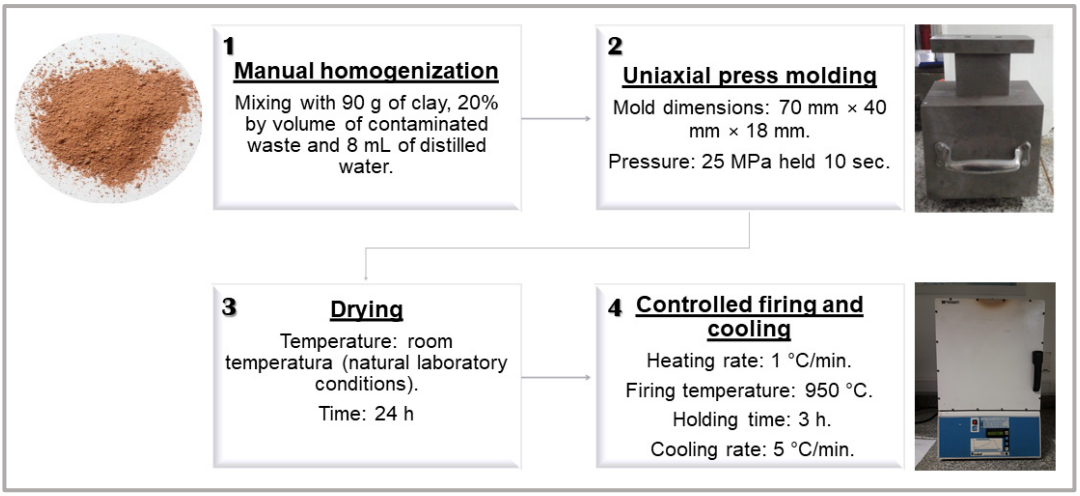

Figure 2. Clay ceramics preparation process.

It is essential to evaluate the mobility of heavy metals present in manufactured clay ceramics to determine the feasibility of immobilize these contaminants in the ceramic structure. Leaching tests were carried out based on EPA method 1311 [37], which is a method accepted by Argentine laws for hazardous waste.

Clay ceramics prepared from spent adsorbents were crushed and sieved to a particle size of less than 9.5 mm. In beakers, crushed clay ceramics were mixed with leaching solution in a 1:20 solid-liquid ratio. According to the alkalinity of the ceramic, an extraction fluid of pH 4.93 ± 0.05 was prepared from 5.7 mL of acetic acid, 64.3 mL of sodium hydroxide 1 mol/L and completing with distilled water up to 1 L. The covered beakers were shaken at 100 rpm in an orbital shaker (SK-0330-Pro) for 22 h. The mixtures were then filtered through filter paper washed with 1 mol/L nitric acid and rinsed with distilled water. The TCLP extracts of the solid phases were acidified with concentrated nitric acid until pH < 2 and stored refrigerated at 4 °C. Finally, the extracts were analyzed by Atomic Absorption Spectrophotometry (AAS) (Shimadzu 6800 with flame) from the Fares Taie Biotechnological Center. The results of the leaching tests were compared with the estimated initial mass of heavy metals in the clay ceramics. In this way, the retention efficiency was calculated according to Yilmaz et al. [38].

3. Results and Discussion

3.1. Biomass Characterization

The phenomena that occur in an adsorbent are related to its specific surface and, therefore, to the total volume of pores and their dimensions, that influence the interaction with the adsorbate and the obtained adsorption efficiency. Table 1 shows the results obtained from the BET analysis for pine sawdust, sunflower seed hulls and corn residues mix. All biomasses showed the presence of mesopores and the surface area values are in agreement with those reported in the literature for adsorbents of lignocellulosic origin [34,39]. Corn biomass presented a higher surface area, total pore volume, and mean pore size comparing with the other two biomass residues (pine sawdust and sunflower seed hulls). Bilal et al. [7] reported that the adsorption of contaminants increases with the increase in the surface area of the adsorbent, since the adsorption process is a surface phenomenon.

Table 1. BET analysis results of surface area, total pore volume and mean pore size for biomass residues.

Biomass	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Mean Pore Size (nm)
Pine sawdust	1.1	0.003	9.4
Sunflower seed hulls	0.7	0.0009	4.9
Corn residues mix	1.5	0.006	14.9

SEM images allow to obtain information about the morphological characteristics (texture, topography and surface characteristics) of the adsorbents. So, the SEM images of the three studied agro-industrial wastes are presented in Figure 3. Biomass analyzed particles showed an elongated shape and a fibrous microstructure. An irregular and rough surface with cavities can be observed in all cases, which forms a network of holes and fibers. These characteristics can facilitate the adsorption of heavy metals [40]. No appreciable changes were detected in the morphology of the adsorbents related to the interaction with metal ions, as reported by Zhang et al. [33], after the adsorption of heavy metals. The combination of SEM with EDS detector and analyzer system allowed to obtain the distribution of heavy metals on the biomasses after adsorption by mapping. As shown in Figure 4, the distribution, and therefore adsorption, of nickel, zinc and cadmium in the adsorbents was across the entire surface.

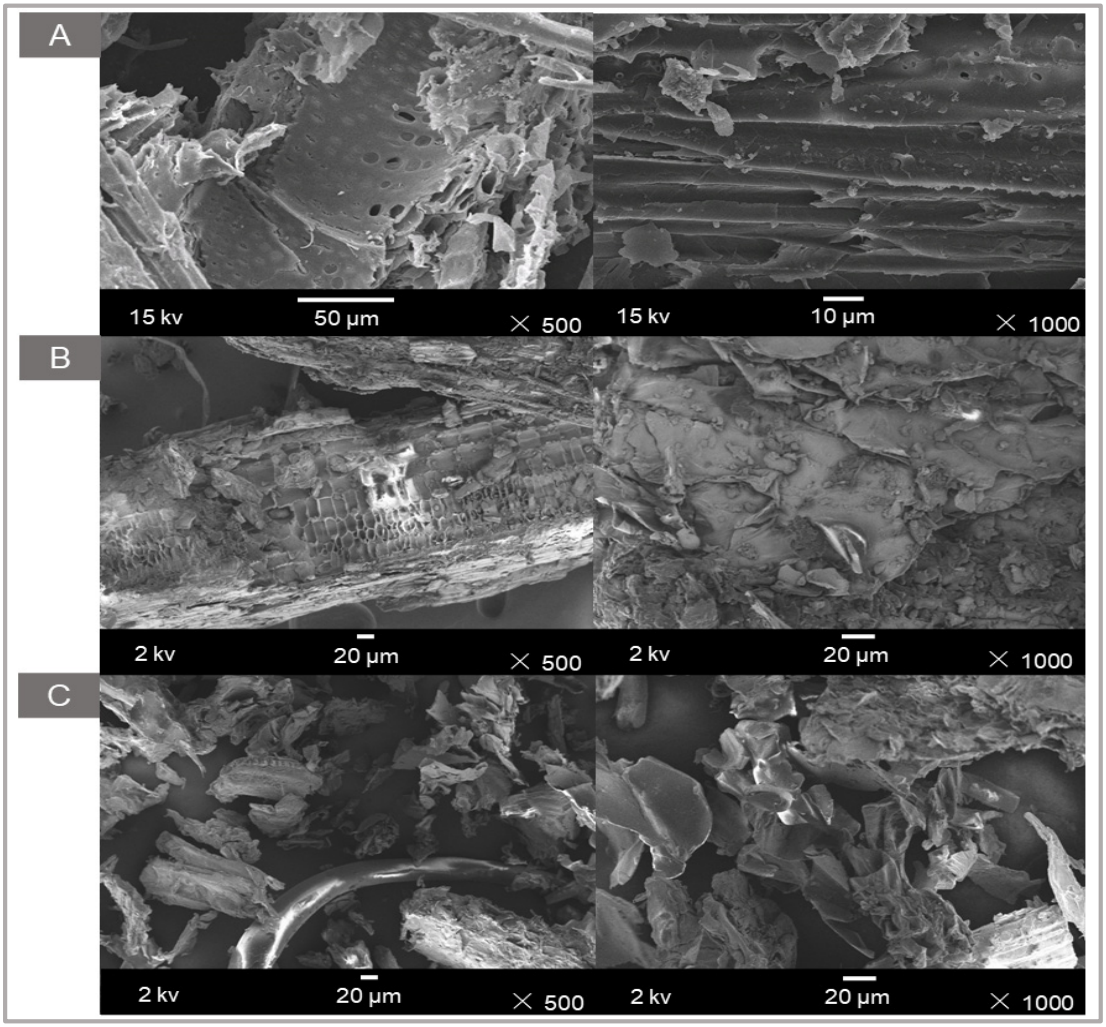

Figure 3. SEM images of: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix.

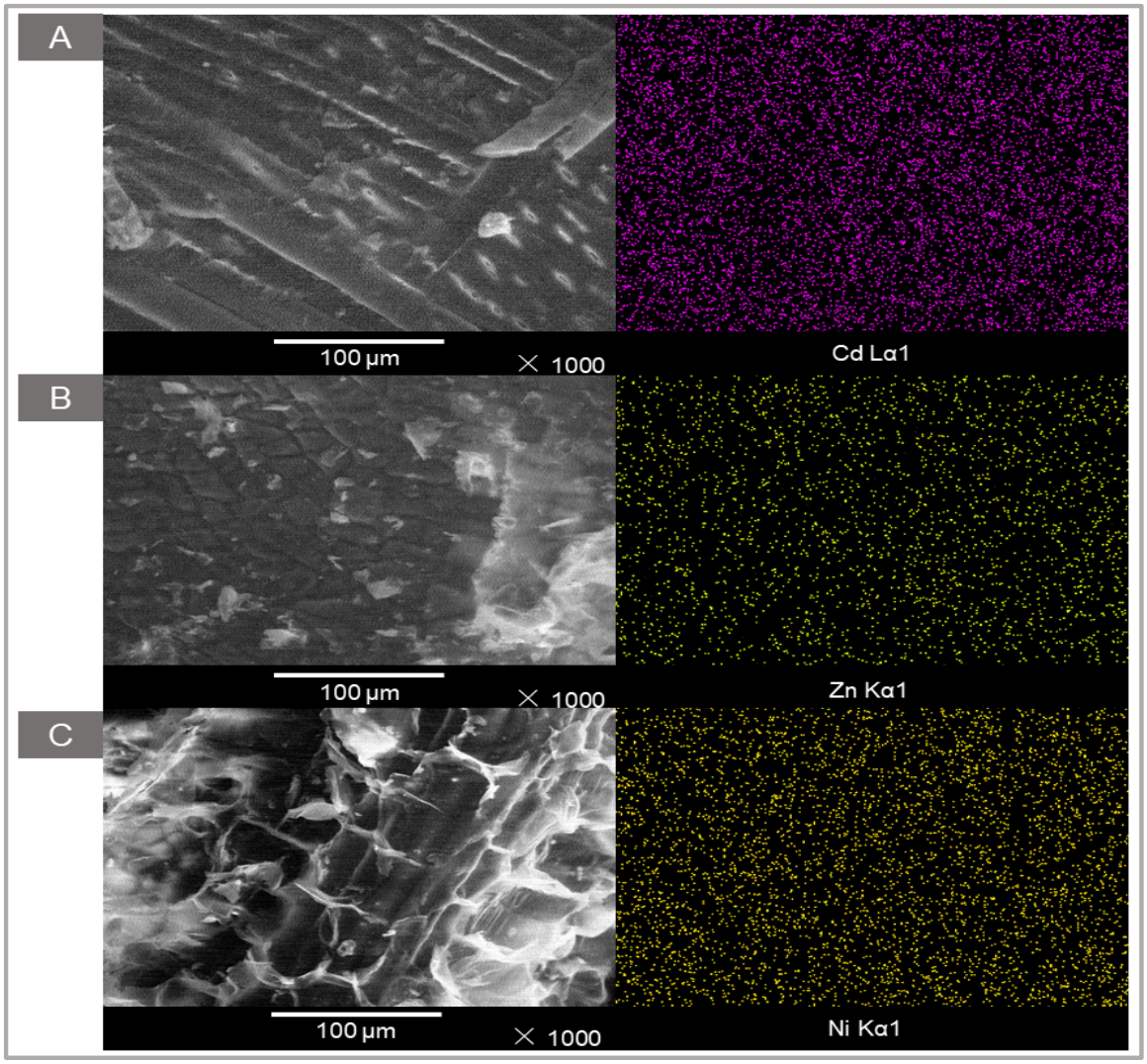

Figure 4. Elemental distribution obtained by SEM-EDS by mapping analysis for (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix, after adsorption of Cd(II), Zn(II) and Ni(II), respectively.

ATR-FTIR made it possible to determine the presence of functional groups in biomass responsible for the metal adsorption mechanism, for example, either by electrostatic forces or complexation. ATR-FTIR spectra for the biomass residues studied here are shown in Figure 5. The large number of IR bands was associated with the typical complex nature of agro-industrial biomasses [41–43]. The assignment of the main IR bands at the respective approximate wavelengths are summarized in Table 2. The great similarity between the ATR-FTIR spectra of sawdust, sunflower and corn was due to the fact that the composition of these three biomasses is based on cellulose and lignin.

The presence of numerous functional groups in biomass facilitates the adsorption of heavy metals [7]. A comparison of the ATR-FTIR spectra of the biomasses before and after the adsorption of the heavy metals is also shown in Figure 5, being both spectra were very similar in each biomass case. However, slight differences were observed, such as a shift of the band at 1603–1624 cm^{-1} in the three biomasses, and shift of the band at 1224–1238 cm^{-1} in the pine sawdust and corn residues, after the contact with heavy metals. These results may be indicative that carboxyl, alcohol, phenol, amide, and other functional groups could provide possible adsorption sites for the retention of the studied heavy metals, and were similar to those found in previous works in the literature [44,45].

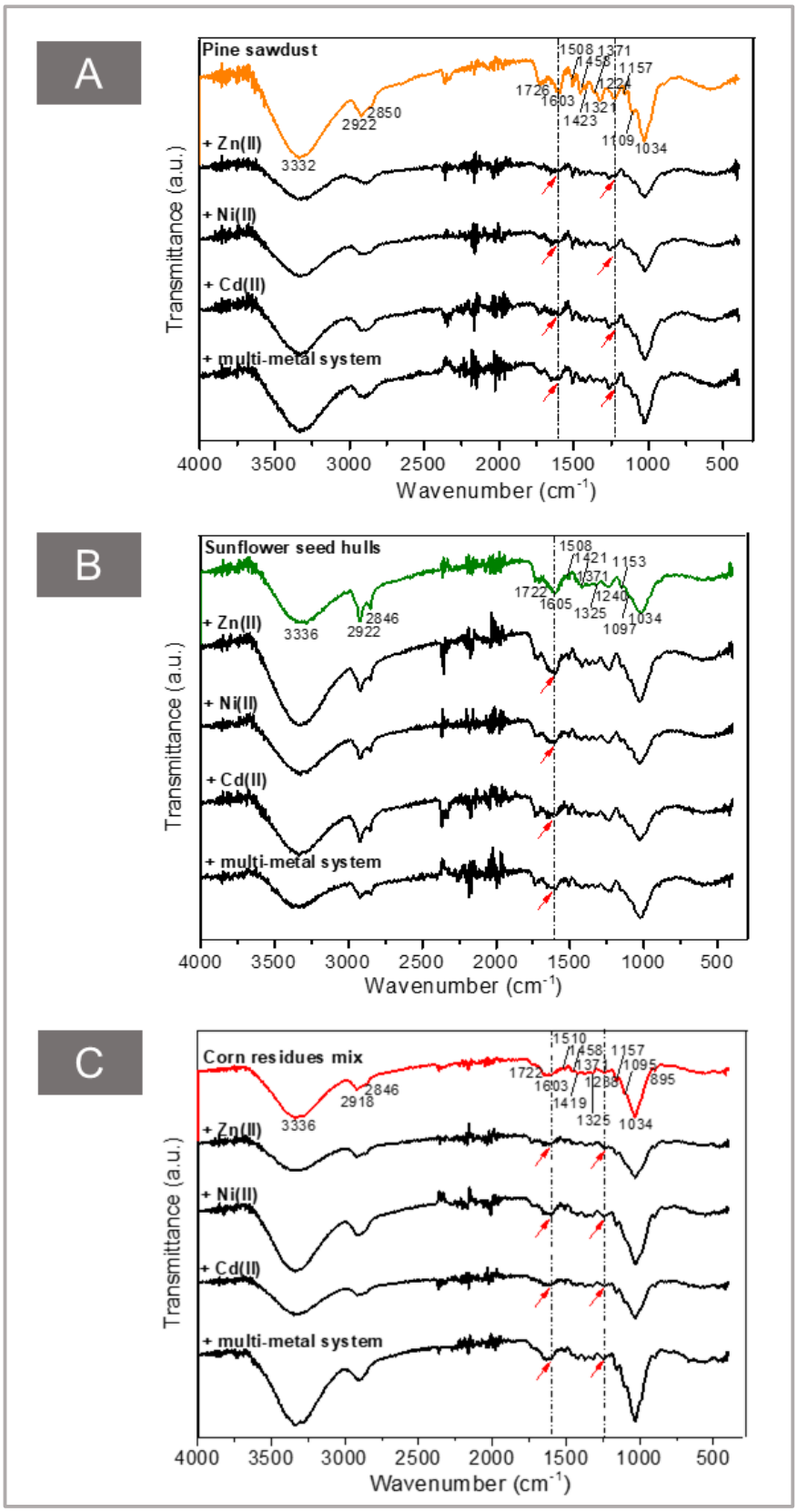

Figure 5. ATR-FTIR spectra of: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix, before and after the adsorption process.

Table 2. Assignment of the main bands obtained by ATR-FTIR for biomass residues.

Wavenumber (cm^{-1})	Assignment
3332–3336	O-H stretching of carboxylic acids and alcohols/phenols, and N-H of amino and amide groups
2918–2922	Asymmetric C-H stretching of CH_3
2846–2850	Symmetric C-H stretching of CH_2 and stretching of methoxy groups
1722–1726	C-O stretching of carbonyl, C=O of acetyl, carboxyl, aldehydes and aromatic/conjugated esters
1603–1624	COO- stretching of carboxyl groups, C=C of the aromatic ring, and C=O, C-N, C-N-H stretching of amides, and O-H bending
1508–1510	C=C stretching of aromatic ring, N-H bending
1458	C=C aromatic, C=O stretching and symmetric bending of C-H, O-H
1419–1437	O-H bending of acids, vibrations of aromatic rings and bending of CH_2 and aromatic functional groups such as C=C and C=O
1371	Asymmetric C-H bending of CH_3, CH_2
1321–1325	O-H bending of phenol group, C–N groups
1224–1240	C-O stretching of phenols and carboxylic acids, and alkyl aryl ether bonds
1153–1157	Asymmetric stretching of the C-O-C pyranose backbone
1095–1109	C-OH and C-H stretching
1034–1036	C-O stretching in carboxyl group, C-O-C, dialkyl ether, C-H of aromatics, and C=C and C-C-O
874–895	Changes in aromatic structures such as C–H stretching of aromatics

The XRF analysis for the biomasses before and after the adsorption of heavy metals is presented in Figure 6. The Cr peaks come from the tube used as the source of the equipment (anode). Signals corresponding to Cl, K, Ca, Mn and Fe were observed, although the intensities varied according to the residue. The presence in biomasses of Ni, Zn and Cd was observed after adsorption (Cd signals were detected in the Ca and K energy zone), associated with the decrease in the intensities of elements such as Ca and K, mainly.

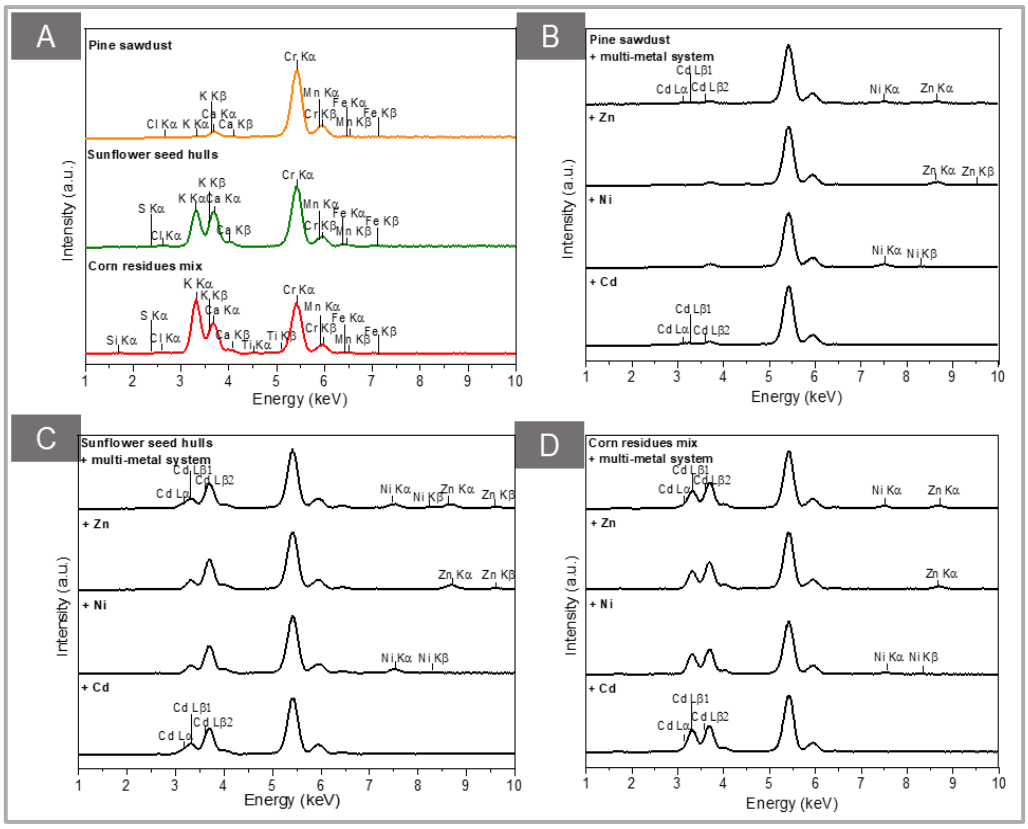

Figure 6. XRF of: (**A**) biomasses before the adsorption process, and after adsorption process with (**B**) pine sawdust, (**C**) sunflower seed hulls, (**D**) corn with adsorbed heavy metals.

The percentage of ash obtained was 0.2%, 2.0% and 10.2% for pine sawdust, sunflower seed hulls and corn residues mix, respectively. The XRD patterns of the biomasses (Figure S1 of the supplementary material) evidenced the presence of a significant amount of amorphous phase, in agreement with the mentioned results. The XRF equipment used does not allow the measurement of elements lighter than Na, and H, C and O are part of hemicellulose, cellulose and lignin as the main components of the biomasses. For that reason, the composition of the corresponding ashes was also analyzed by XRF (results collected in Figure 7). Differences in mineral content and composition were observed. Probably potassium, calcium, magnesium and phosphorus are involved in the adsorption of heavy metals through ion exchange mechanism, as reported previously [46].

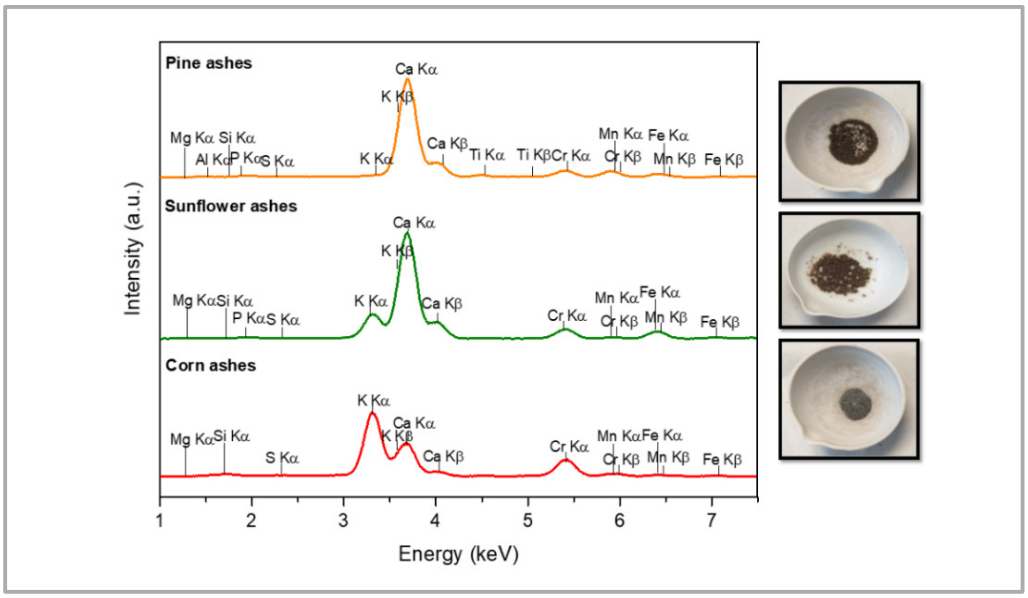

Figure 7. XRF of pine ashes, sunflower ashes and corn ashes.

Biomasses of plant origin are mainly composed of lignin and cellulose, as mentioned above, together with hemicellulose, low molecular weight compounds, lipids, proteins, starch, water, etc. [7]. The DTA-TGA profiles were obtained for the three biomasses here selected, and provided a description of the thermal behavior and an estimated percentage composition of biomasses, which was in agreement with the literature [47,48]. As seen in Figure 8, TGA analysis, the total weight loss was 96% for pine sawdust, 97% for sunflower seed hulls, and 86% for corn residues mix, and was divided into three stages. The first weight loss stage (up to 230 °C) was 7% for pine sawdust, 12% for sunflower seed shells and 10% for corn residues mix. This stage was related to the loss of moisture, which was characterized by an endothermic peak at 52 °C in pine sawdust and at 60 °C in sunflower seed hulls. The degradation of low molecular weight compounds was identified with an exothermic peak at 263 °C, and was observed in sawdust. The second weight loss stage was 48% for sawdust (up to 311 °C), 56% for sunflower (up to 297 °C) and 50% for corn (up to 338 °C). This stage could be related to the degradation of hemicellulose and pectin into volatile compounds of lower molecular weight. Finally, the third weight loss stage was 41% (up to 500 °C), 29% (up to 460 °C) and 26% (up to 508 °C) for biomasses of pine sawdust, sunflower seed hulls and corn, respectively, and it could be related to the degradation of cellulose and lignin into CO_2, H_2O and ashes. From the TGA analysis, the final residue corresponds to the mineral content and was higher for corn than for sawdust and sunflower, in accordance with the results obtained following the guidelines of the ASTM E1755-01 standard. The two large exothermic peaks in the three DTA curves were assigned to the decomposition of the biopolymers present in the biomass: such as hemicellulose, cellulose and lignin. Since these biopolymers are closely related in the biomass structure, the thermal degradation of each biopolymer cannot be clearly defined independently, probably being

hemicellulose responsible of the first peak and cellulose and lignin together of the second peak [30].

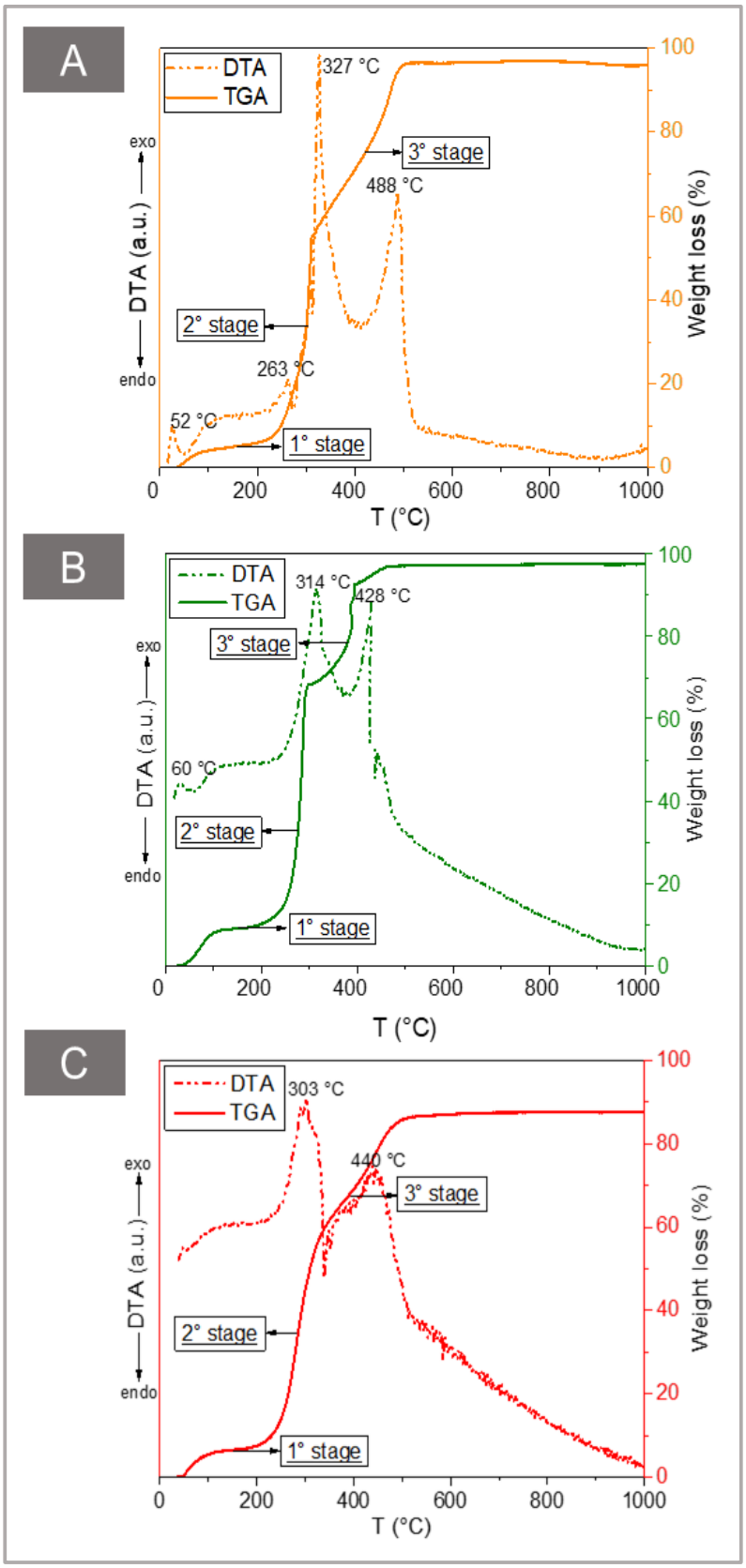

Figure 8. DTA-TGA of: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix.

3.2. Adsorption Process Characterization

Biomasses of pine sawdust, sunflower seed hulls and corn residues mix were evaluated as adsorbents of mono-metal aqueous solutions of Ni(II), Zn(II) and Cd(II). The results obtained are shown in Figure 9.

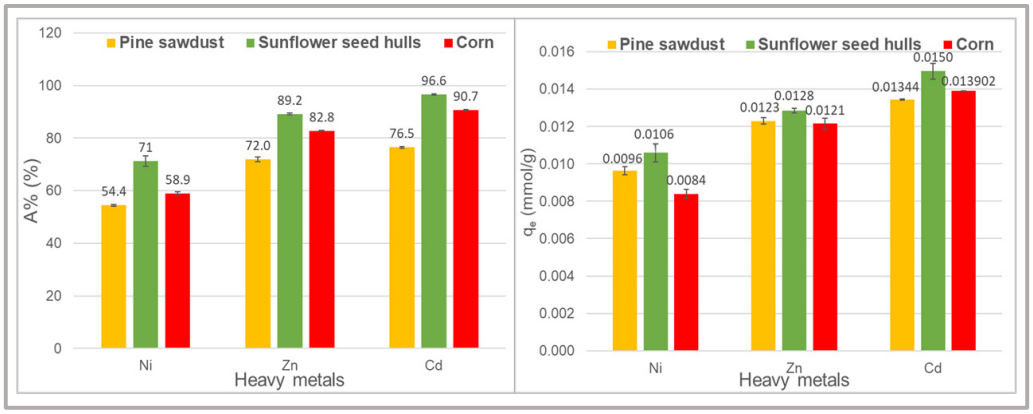

Figure 9. Comparison of the adsorption of mono-metal solutions of Ni(II), Zn(II) and Cd(II) on pine sawdust, sunflower seed hulls and corn residues mix.

According to the results of adsorption percentage (A%) and adsorption capacity (q_e) obtained, Ni(II) presented a lower adsorption, compared to Zn(II) and Cd(II), in all the biomasses studied. The adsorption follows the order: Ni(II) < Zn(II) < Cd(II), as shown in Figure 9, for sawdust, sunflower and corn, as it was also reported for other waste of lignocellulosic origin, such as coffee residues, rice husks, cocoa husks, and paper manufacturing wastes [49,50]. This behavior is related to the different characteristics and affinity of the metal ions for adsorbent adsorption sites [51]. Comparing the values of the hydration energies (Ni(II): −2106 kJ/mol, Zn(II): −2044 kJ/mol and Cd(II): −1806 kJ/mol), related to hydrolysis of metal ions, the nickel ion has a higher hydration energy than the zinc and cadmium ions and, therefore, it is less easy to lose its water molecules from its coordination sphere, which would prevent it from being adsorbed by the adsorbent through complexation or ion-exchange mechanisms. According to Mahmood-ul-Hassan et al. [52] and Qu et al. [53], smaller ions are more hydrated than larger ones, which could hinder adsorption.

The higher surface area, pore volume and mineral fraction in corn residues could have positively contributed to the adsorption of heavy metals. However, the differences in the adsorption results are not too significant between the three biomasses.

The obtained results are of the same order as results reported in the literature for batch adsorption experiments of Ni(II), Zn(II) and Cd(II) using sawdust, sunflower and corn residues (Table S1, supplementary material). However, the differences between the results of adsorption percentage (A%) are not only due to the characteristics of the biomass adsorbent but were also due to the concentration of contaminant, dosage of the adsorbent, pH of the solution, temperature, contact time, among others, that are factors that can affect the adsorption process [7]. Some of these factors were evaluated by the authors in previous work on the adsorption of heavy metals on adsorbent materials of plant origin [26,46,54,55].

The determination of the adsorption of heavy metals of a mixing metal solutions represents a closer situation to a real effluent. The competition between the metal ions for the adsorption sites occurs due to the saturation of the adsorption sites of the adsorbent whose dosage remains fixed to that of the individual systems [7]. Figure 10 compares the results of A% for the adsorption of mono-metal aqueous solutions of Ni(II), Zn(II) and Cd(II), and the multi-metal aqueous solution made up of heavy metals mentioned above with a concentration of 0.18 mmo/L of each of them. At this initial concentration, the results of A% for each of the heavy metals were similar when the adsorption was carried out separately and when it was carried out within the mixture, on sunflower seed

hulls and corn residues mix. However, the adsorption of heavy metals in pine sawdust was lower for the multi-metal aqueous solution than for each metal separately, being the nickel ion the most affected by the competition with the other two heavy metals for the adsorption sites of the adsorbent, as expected (as Ni was the less adsorbed, as seen in Figure 9). Zhao et al. [46], also reported a lower performance of sawdust as an adsorbent when comparing the results of A% obtained for the adsorption of a mixture consisting of Cr(III), Cd(II), Cu(II) and Pb(II), on poplar sawdust and two other agricultural residues.

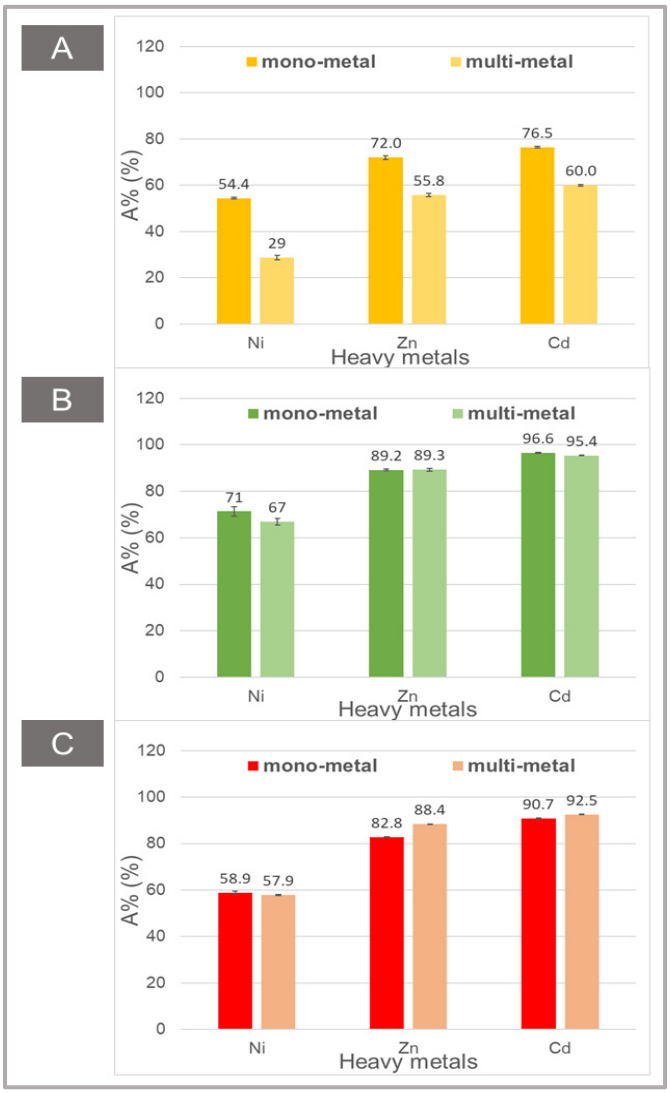

Figure 10. Comparison of the adsorption percentage (A%) of Ni(II), Zn(II) and Cd(II) in mono-metal and multi-metal solutions on: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix.

3.3. Spent Adsorbent Disposal

There is limited information available in the literature on the toxic effects of spent adsorbents, and their regeneration decreases their performance and generate new contaminant materials. The safe disposal of used and/or spent adsorbents is nowadays raising as a need to consider it for a more sustainable processes that can help to preserve the environment [56]. Based on the previous experience of the authors [54,55], the local production of ceramics for bricks construction is presented as a possible alternative for the safe disposal of spent adsorbents that would contribute to the real applicability of them as metal adsorbents.

In Figure 11, the adsorption percentages obtained from the experiments using 0.1 g of adsorbent and 1.8×10^{-6} moles of each of the heavy metals in the multi-metal system

are compared with those results obtained by increasing the residue mass by 20 times to 2 g and moles of adsorbate to 3.6 × 10^{-5} moles. As can be seen, by maintaining the adsorbent/adsorbate ratio constant, the adsorption percentage remained constant. These results were considered in the preparation of clay ceramics with 20% by volume of contaminated biomass with respect to the volume of clay.

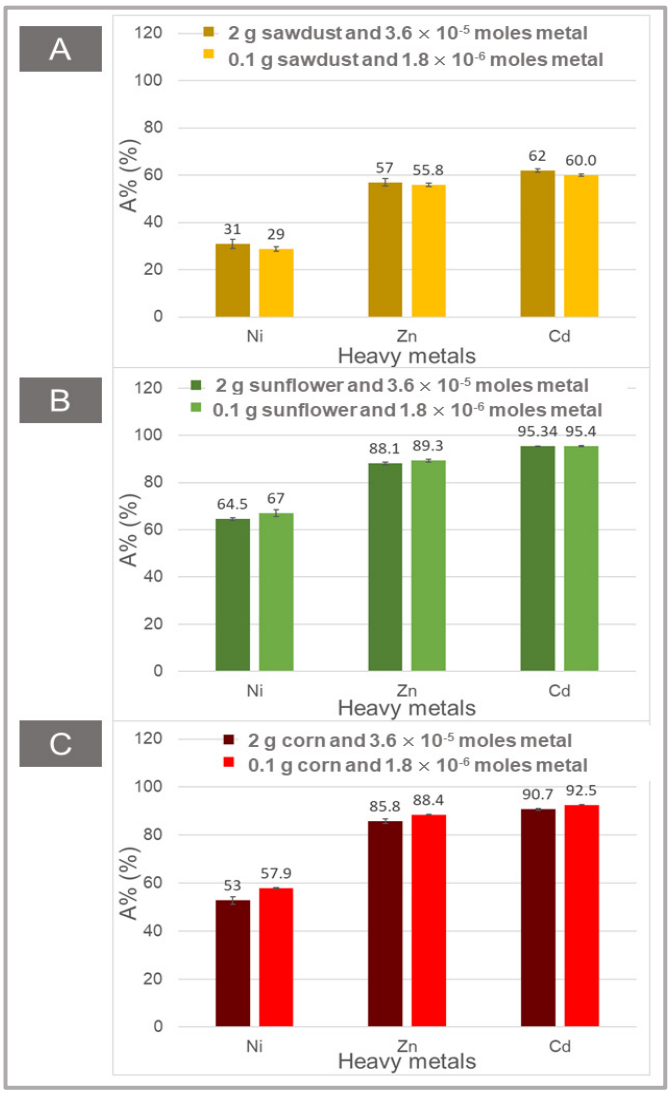

Figure 11. Comparison of the percentage of adsorption (A%) when increasing 20 times the mass of adsorbent and moles of adsorbate in the multi-metal system of heavy metals for: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix.

The macroscopic appearance of the clay ceramics is shown in Figure 12. All the samples presented a reddish color due to the Fe content of the natural clay and a porous surface according to the TGA and DTA results of the included lignocellulosic residues. As can be seen in Figure 8, at the ceramic firing temperature (950 °C), the added biomass burned out creating pores and releasing gases in the clay ceramics matrix.

Leaching tests based on EPA Method 1311 were performed to determine the possible leaching levels of Ni(II), Zn(II) and Cd(II) from the clay ceramics prepared with the addition of each of the spent adsorbents. Heavy metal concentrations were not detected in the TCLP extracts of the ceramic matrices because they were below the detection limits of the equipment used (Ni(II) < 0.05 mg/L, Zn(II) < 0.02 mg/L and Cd(II) < 0.05 mg/L, by AAS). For this reason, they were lower than the permissible limits of Argentina (nickel 5 mg/L and cadmium 1 mg/L, zinc not reported) [57].

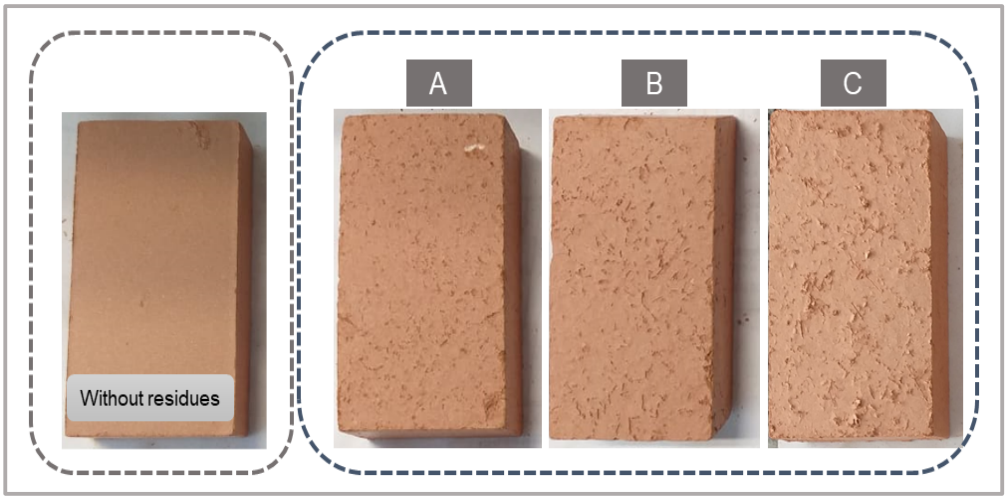

Figure 12. Macroscopic appearance of clay ceramics including spent biomass of: (**A**) pine sawdust, (**B**) sunflower seed hulls, (**C**) corn residues mix, and comparison with a sample without residue addition.

Table 3 shows the retention efficiency calculated for each one clay ceramics matrices. It was calculated from the mass of each of the heavy metals added in the ceramic (included in the spent adsorbent) and in the TCLP extract obtained for each tested ceramic. Based on these results, with heavy metal retentions above 88.5% in all cases, we can propose such clay ceramics prepared with added spent adsorbents with potential use in construction, and useful for the stabilization and immobilization of heavy metals together with the corresponding spent adsorbents. At firing temperatures in the followed leaching tests (EPA Method 1311), the organic residues can burn out and the heavy metals would be able to form stable phases with the clay minerals, which would decrease their bioavailability [58].

Table 3. Heavy metal retention efficiency for clay ceramics prepared from spent adsorbent with the mixture of heavy metals.

Clay Ceramics	Retention Efficiency (%)		
	Ni(II)	Zn(II)	Cd(II)
Pine sawdust	>88.5	>98.2	>97.1
Sunflower seed hulls	>95.9	>99.1	>98.5
Corn residues mix	>93.4	>98.7	>97.9

According to Mohajeran et al. [59], the particle size of the sample determines the contact surface with the leaching solution and therefore influences the concentration of heavy metals detected. This fact is important because in the leaching tests the clay ceramics were used crushed, but in practice the clay bricks will be used whole, so the leaching may be even lower, even there is still no legislation that imposes a test and limits on the leaching of heavy metals in construction materials [60].

4. Conclusions

One of the challenges of these times is the minimization of waste generated by agro-industrial activities and/or the reuse of this waste in applications that improve the quality of life. In this sense, considering that there is still no universal process to remove heavy metals from wastewater and effluents, adsorption from agroindustry residues is emerging as a simple, low-cost and efficient alternative.

Agro-industrial residues such as pine sawdust, sunflower seed hulls and corn residues mix, without any additional treatment, are characterized. These results are correlated with the performance of these materials as adsorbents of heavy metals such as Ni(II), Zn(II) and

Cd(II). In addition, SEM-EDS and XRF confirmed the presence of these heavy metals in the residues after the adsorption process.

Batch adsorption experiments from aqueous mono-metal solutions of nickel, zinc and cadmium ions, with concentrations of 0.18 mmol/L, with all three biomass residues selected showed promising results, with adsorption percentages greater than 50%. Ni(II) presented the lowest adsorption percentages and adsorption capacities compared to Zn(II) and Cd(II), possibly due to the higher hydration energy that could hinder its accessibility to the adsorbent. At this concentration, in a multi-metal solution, the decrease in adsorption due to the competition of heavy metals for the limited adsorption sites of pine sawdust determined that it is necessary to study multi-component systems to evaluate the actual performance of the adsorption process in practice.

Sawdust, sunflower and corn residues could be used as an alternative to traditional synthetic materials to remove heavy metals from wastewater given their properties, low cost and availability. However, more research is needed for the scale-up and possible commercial application of these agro-industrial residues as adsorbents of toxic metals from industrial wastewater.

Furthermore, a solution to the safe disposal of such biomass adsorbents after the adsorption process (containing heavy metals as pollutants) was proposed in this research work. The stabilization of these spent adsorbents in clay ceramics with possible use in construction is presented as an alternative for the immobilization of Ni(II), Zn(II), Cd(II) and their mixture. The heavy metal leaching tests of the ceramic matrices prepared with added spent adsorbents confirmed an effective immobilization for all heavy metals, whose concentrations were found to be below the permissible limits. The clay ceramics showed retention efficiencies over 88.5%.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14203298/s1, Figure S1: XRD patterns of pine sawdust, sunflower seed hulls, and corn residues mix; Table S1: Main results of literature studies about the adsorption of Ni(II), Zn(II) and Cd(II) on sawdust, sunflower and corn. References [44,52,61–67] are cited in the "supplementary materials".

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