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Research Article

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Ideal pH for the adsorption of metal ions Cr^{6+}, Ni^{2+}, Pb^{2+} in aqueous solution with different adsorbent materials

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Abstract: Industrialization increases the number of heavy metals released into the environment. Lead (Pb^{2+}), nickel (Ni^{2+}) and chromium (Cr^{6+}) are among these toxic metals and cause irreversible effects on ecosystems and human health due to their bio-accumulative potential. The decontamination through adsorption processes using lignocellulosic wastes from agricultural and/or forestry processes is a viable solution. Hence, this work aimed at studying the effect of pH on the biosorption of the metal ions using four different by-product materials: walnut shell, chestnut shell, pinewood and burnt pinewood. These experiments were conducted with solutions of the three heavy metals in which the adsorbents were immersed to measure the rate of adsorption. A range of pH values from 3.0 to 7.5 was used in the experiments, and the concentrations were determined by atomic absorption. The results showed different behaviour of the biosorbent materials when applied to the different metals. The lead adsorption had an ideal pH in the range of 5.5–7.5 when the walnut shell was used as an adsorbent, corresponding to values of adsorption greater than 90%, but for the other materials, maximum adsorption occurred for a pH of 7.5. For the adsorption of chromium, the pH was very heterogeneous with all adsorbents, with optimal values of pH varying from 3.0 (for chestnut shell) to 6.5 (for walnut shell and wood). For nickel, the best pH range was around pH 5, with different values according to the lignocellulosic material used. These results indicate that the tested biosorbents have the potential to decontaminate wastewater in variable extensions and that by controlling the pH of the solution; a more efficient removal of the heavy metals can be achieved.

Keywords: biosorption, chromium, nickel, lead, walnut shell, chestnut shell, burnt wood

1 Introduction

Heavy metals can be naturally assimilated in water environments, when present in low concentrations. However, human activities have raised these concentrations to levels considered toxic, because they surpass the natural depuration capacity of the ecosystems. According to Carvalho and Orsine (2011), industries are responsible for dumping lethal chemical waste into the environment, causing irreversible effects on ecosystems and population health due to the bioaccumulative potential of these materials. Rodrigues et al. (2016) describe that a contaminated environment directly interferes with human health and the development of living beings, besides causing an imbalance in the biosphere.

According to Penha et al. (2016), various residues, from agriculture and forestry, accumulate in large volumes without a perspective of use, becoming an environmental problem. tThus, it is essential to develop studies that result in the application and use of this waste to promote the decontamination of water resources affected by the inappropriate disposal of wastewater. Filachowski (2018) mentioned that the knowledge about the application of by-products as adsorbents is currently limited. Therefore, the study of the properties and behaviour of each material, as well as their influence on the sorption process, becomes necessary. In this way, this novel technology has the potential to be applied in large-scale treatments. Silva et al. (2013) stated that traditional techniques may be inadequate for the decontamination of significant volumes of effluents, causing low operational efficiency and high costs. Because

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of this, it is essential to search and develop new methods of treatment for contaminated water (Filachowski 2018).

Filachowski (2018) mentioned that the pH has a significant influence on the process, as it acts in the functionality and could limit the sorption rates. According to Moreira et al. (2009), one of the most important parameters in the adsorption process is the pH, since the characteristics presented by the metal in solution and the load of the active sites on the surface can change depending on this parameter.

Ofomaja and Ho (2007) stated that pH is a factor that affects dissociation, hydrolysis, complexation, precipitation and other reactions that occur with heavy metal ions in an aqueous solution. Additionally, pH influences ions' availability and speciation that affects directly the biosorption capability. Oliveira and Feris (2018) also considered that the pH has a straight influence on adsorption systems because it can modify the way that metal ions are available, favouring or not the process. According to Aguiar et al. (2002), heavy metals can be found in the water resources in the ionic form or in soluble organic or inorganic complexes, in particles or trapped in mineral or organic colloids, in sediments or incorporated into the biota. Thus, the pH directly affects the conversion process between forms.

In this way, it is considered extremely important to determine an optimum pH for the adsorption, since the electrostatic interactions that take place can be influenced by the ionic groups, changing the chemical balance of the reagents in solution (Filachowski 2018).

In accordance with Zafar et al. (2015), the pH of the biosorption process is very important since it affects the adsorption efficiency, the surface chemistry of the biosorbent and metal ion specification. These authors stated that the pH significantly influences the site dissociation of the biomass surface and the chemistry of the toxic metals in the solution. Dash et al. (2009) mentioned in Zafar et al. (2015) stated that pH influences hydrolysis, complexation by organic or inorganic ligands, precipitation and biosorption availability of the toxic metals. pH also affects the degree of ionization and the activity of the functional groups in the biomass mainly the carboxylic group.

According to Esposito et al. (2002), the adsorption in each lignocellulosic material is different due to the chemical nature of the materials with different functional groups such as carboxylic, phosphate, sulphate, amino, amide and hydroxyl groups that correspond to dissimilar active sites on the cell wall.

According to Lima (2018), an adsorbent material retains pollutants by chemical, physical or ion exchange mechanisms, a process that depends directly on the pH of the medium and the characteristics of the adsorbent material. Santana et al. (2020) reported that at pH 7, there is a balance between hydroxide (OH^-) and hydronium (H_3O^+) or hydrogen (H^+) ions. In acid solution, there is a greater competition of metal ions with H^+ ions for the active spaces on the adsorbent surface (Feng et al. 2011). Thus, for low pH, the functional groups present on the surface of the biosorbent are largely associated with H^+, which disfavours the retention process, as a result of repulsion forces, since the ions of metals have positive charges (Alomá et al. 2012a). However, an increase in pH may favour adsorption, because at higher pH, the H^+ concentration is reduced. In counterpoint, the high pH can cause the precipitation of certain metals, a process that also hinders adsorption. In general, pH influences the availability and specialization of ions in the solution, which regulates retention rates. Thus, it is extremely important to know the biosorbent and its composition to understand the mechanisms of sorption that occur (Leite et al. 2017). And from that, set a pH favourable to the process. According to Silva et al. (2016), the mechanisms that take place during the retention of metals via plant biosorbent are directly related to the functional groups present in the adsorbent. These chemical groups form part of cell wall structures, encompassing cellulose macromolecules surrounded by hemicelluloses, lignin, pectin and in some cases plant proteins. Therefore, defining a pH that favours ion retention becomes essential to promote a meaningful adsorption process.

In accordance with López et al. (2000), not all the metals behave similarly with pH, in some like nickel and lead, adsorption grows with pH increase, and the highest adsorption is observed just before precipitation occurs. For the other metals, however, adsorption is not linked to precipitation like for instance chromium VI.

This work proposed the study of pH influence on the biosorption process for chromium (Cr^{6+}), nickel (Ni^{2+}) and lead (Pb^{2+}) ions in an aqueous solution, searching for a range of pH values ideal to promote the maximum removal rate of these metals, under the established conditions. In addition, four lignocellulosic materials were tested as biosorbent: walnut shell (*Carya illinoensis*), chestnut shell (*Castanea sativa*), wood (*Pinus* spp.) and burnt wood (*Pinus* spp.) which are low cost and easily obtainable agroindustrial wastes. The main objective of this work is to determine an optimal pH that could remove the maximum amount of these three pollutants using low-cost materials available in the region of Viseu, Portugal.

2 Materials and methods

The materials used in this study are Walnut Shells (*Carya illinoensis* (Wang.) K.) which are wastes produced in the company Transagri (located in Mangualde), the Chesnut Shells (*Castanea sativa* Mill.) from Agromontenegro (Carrazedo de Montenegro), based in Portugal, which are forest managements companies, the remains of burned wood are from the forests of the Viseu region, resulting from the last fires in the region, and the wood remains are waste generated in the cutting of wood.

In the first phase of this study, the adsorbent materials and aqueous solutions containing the metal ions were prepared. In the biosorbents' preparation (walnut, chestnut, wood and burnt wood), the materials were ground (Fritsch pulverisette 19 mill), sieved (Retsch AS200, 20 min at 50 rpm rotation) and dried (drying oven at 105°C for 24 h). The sieved portion used in the samples was the powder (<80 mesh). The aqueous solution containing the metal ions was prepared using the salts $Pb(NO_3)_2$, $K_2Cr_2O_7$ and $NiCl_2{\cdot}6H_2O$, which were diluted in distilled water in the necessary proportion for a stock solution of concentration 1,000 mg/L, being subsequently diluted to the concentration of 200 mg/L used for the tests.

Adsorption is a physical-chemical process influenced by many factors, such as the pH, which can modify the way that metal ions are available in the solution. Hence, the assays were made testing a pH range from 3.0 to 7.5, for all metals, in two or three replicates, depending on the case. The adjustment of pH values was promoted with hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions both with 0.1 M concentration, in quantity to reach the desired pH. The pH measurement was performed with a pH meter (Hach HQd Field Case). The evaluation of the metals in solution after the tests was performed by analysis in an atomic absorption spectrophotometer (Spectrum Perkin Elmer AAnalyst 300) by flame. The data evaluation was performed using the initial and final metal ions concentration in the solution, that is, the difference between the two parameters was considered as the removed or adsorbed rate.

Besides that, the other influencing factors were standardized to avoid interference in the process; thus, the tests were promoted with stirring at a constant speed, for a period of 12 h, in a horizontal stirrer (WTW OxiTop IS 12) and at environment temperature (20°C).

The ratio between biosorbent and metal solution was 100 mg of solid to 0.25 L of liquid. The Erlenmeyer flasks containing the samples were covered with aluminium paper during the stirring period, to avoid evaporation. For spectrophotometer analysis, the samples were filtered by gravity in a paper filter, after which the solutions were stored in plastic containers in a refrigerator (at a temperature of 4°C). A 10 mL aliquot was used for the evaluation and, when necessary, a dilution of the aliquot was performed.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

Lignocellulosic wastes from agricultural and/or forestry processes have the potential to act as biosorbents for heavy metals, with the advantages of being easily available, efficient and cheap. In this work, lead, chromium and nickel were removed using four by-product materials: walnut shell, chestnut shell, pinewood and burnt pinewood, using a range of pH values varying from 3.0 to 7.5. Table 1 presents the percentage of adsorbed lead from the solution, for the different biosorbents and according to the values of pH tested. The results indicated that, in general, lead retention into the adsorbent surface was favoured by increasing the initial pH of the solution (Figure 1). Hence, it can be considered that all adsorbents studied have some affinity with Pb^{2+}, since they promoted favourable adsorption, with maximums around 96% for walnut and chestnut shell, 93% for wood and 87% for burnt wood. This maximum adsorption was achieved for a pH of 7.5, although in the case of walnut shell maximum adsorption was achieved on a wide range of pH values from 5.5 to 7.5, contrarily to the other biosorbents. In the case, wood was used as an adsorbent, some increase and decrease cycles were observed, although the global trend was raising. It has been reported that for some adsorbent materials, after peak adsorption decreases, like it was observed in this case. This behaviour can be related to disparities in the biosorbent, or even, to the interference of secondary elements in solution. López et al. (2000) stated that at pH values higher than 5.0, lead may precipitate. Moreira et al. (2009) using cashew bagasse as biosorbent demonstrated that for Pb^{2+}, an increase of pH from 3 to 7 had little influence on the rate of removal. Zafar et al. (2013) studied *Azadirachta indica* (Neem) leaves biomass pretreated by chemical and physical methods and concluded that pH 5 was ideal for the removal of lead from wastewater. Similar results were presented by Zafar et al. (2019) with Trapa bispinosa's peel biosorbent chemically

Table 1: Residual concentration of lead

Target initial pH	Walnut shell		Chestnut shell		Wood		Burnt wood	
	Range of pH[a]	$[Pb^{2+}]$[b] (mg/L)	Range of pH[a]	$[Pb^{2+}]$[b] (mg/L)	Range of pH[a]	$[Pb^{2+}]$[b] (mg/L)	Range of pH[a]	$[Pb^{2+}]$[b] (mg/L)
3.0	3.07–3.08	99.2 ± 7.3	3.00–3.45	93.6 ± 4.2	3.05–3.62	68.8 ± 4.5	3.06–3.41	123.4 ± 1.0
3.5	3.53–3.16	93.7 ± 5.9	3.50–3.57	65.6 ± 2.6	3.50–3.93	51.9 ± 4.6	3.47–3.53	112.1 ± 6.3
4.0	4.11–3.44	73.4 ± 2.2	4.00–3.65	57.3 ± 4.4	3.88–3.98	37.1 ± 10.5	4.05–3.84	119.9 ± 9.4
4.5	4.51–3.67	54.8 ± 2.6	4.50–3.62	50.7 ± 8.6	4.40–3.92	64.6 ± 0.9	4.46–3.97	120.9 ± 10.0
5.0	5.05–3.91	31.8 ± 5.0	5.00–3.66	55.9 ± 1.3	5.16–4.00	37.0 ± 5.7	4.92–4.09	120.7 ± 9.1
5.5	5.57–4.46	13.2 ± 3.4	5.50–3.65	61.6 ± 2.8	5.49–4.31	26.2 ± 4.4	5.46–4.17	130.5 ± 8.9
6.0	6.02–5.13	8.0 ± 1.4	6.00–3.79	44.0 ± 5.9	5.97–4.31	37.6 ± 2.2	5.98–4.42	110.4 ± 8.6
6.5	6.58–5.46	14.6 ± 1.7	6.50–3.75	30.5 ± 4.4	6.50–4.54	39.1 ± 4.7	6.45–4.64	97.9 ± 6.2
7.0	7.02–5.35	8.7 ± 0.4	7.00–4.12	20.1 ± 3.9	6.97–4.79	23.0 ± 2.9	9.65–4.78	76.2 ± 19.6
7.5	7.58–5.54	16.8 ± 0.4	7.50–4.67	8.0 ± 1.0	7.43–4.91	14.2 ± 3.4	7.46–5.03	25.7 ± 5.9

[a] Range of pH: initial and final values of pH (mean values of three assays). [b] Concentration of lead at the end of the assay for an initial concentration of 200 mg/L (mean value ± standard deviation of three assays).

treated to enhance adsorption capacity for Pb(II) where the best pH was 5 for all the chemical treatments tested.

The biosorbent burnt wood presents a constant removal rate at pH from 3.0 to 5.5, being considerably lower than other biosorbents, but tends to raise after that, particularly after a pH of 7.0, achieving a maximum removal rate for pH 7.5, comparable with that of the other biosorbents tested. Aguiar et al. (2002) studied aluminosilicates as adsorbents and concluded that between pH 4.0 and 7.0, the removal of lead ions experienced an insignificant variation. According to Feng et al. (2011) at pH values above 6.0, Pb^{2+} species such as $Pb(OH)_2$ could be generated, making the adsorption process more difficult. In this way, they concluded that the best rates of biosorption by copolymerization-modified orange peel for Pb^{2+} were at pH 5.5. For pH values of 7.0 or higher (alkaline), the adsorption rate greatly increased, corresponding to the region where chemical adsorption occurs.

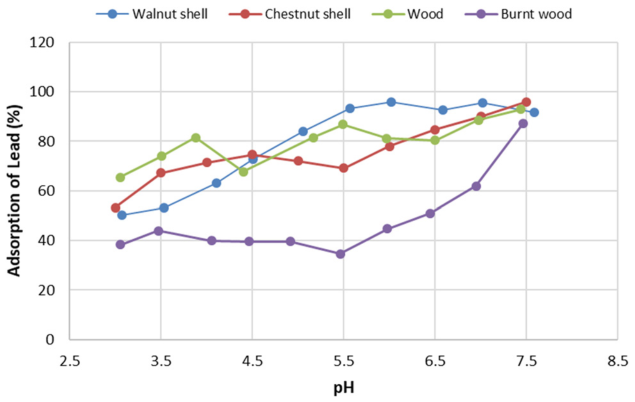

Figure 1: Adsorption of lead at different pH values.

Pierangeli et al. (2001) evaluated the adsorption of lead in soils and concluded that the amount adsorbed increased with an increase in pH and considered that this increase in adsorption was related to the decrease in the concentration of H^+ and the increase in negative charges due to the deprotonation of OH^- groups.

Table 2 shows the residual concentration of lead for all assays performed, i.e., with four different biosorbents and for pH values varying from 3.0 to 7.5. Considering that the initial lead concentration as 200 mg/L, the residual concentration was greatly decreased in some cases, like for example to 8.0 ± 1.0 mg/L (using chestnut shell and pH of 7.5), 8.0 ± 1.4 mg/L (walnut shell/pH 7.0) and 8.7 ± 0.4 (chestnut shell/pH 7.0). The assays in which the final lead concentration was higher were for burnt wood and on the pH range from 3.0 to 6.0 (concentration varying between 110.4 ± 8.6 and 130.5 ± 8.9 mg/L).

The average values of chromium adsorption are presented in Figure 2. Regarding the effect of pH on the adsorption rate, no specific trends were observed, contrary to what had been described above for lead. Instead, there were variations between the materials with peaks of adsorption at different values of pH. Thus, an ideal range of pH for chromium adsorption is not defined as it varies depending on the adsorbent used and its interactions with the aqueous solution. However, the results allowed us to identify more favourable values of pH to obtain a higher degree of water purification. In this way, greater adsorption was observed with chestnut shell at pH 3.0 (71.8%), with walnut shell and wood at pH 6.5 (52.3 and 41.8%, respectively) and with burnt wood at pH 5.5 (34.2%).

Although the behaviour of chromium was found to be heterogeneous according to the type of adsorbent, a

Table 2: Residual concentration of chromium

Target initial pH	Walnut shell		Chestnut shell		Wood		Burnt wood	
	Range of pH[a]	**$[Cr^{6+}]$**[b] **(mg/L)**	**Range of pH**[a]	**$[Cr^{6+}]$**[b] **(mg/L)**	**Range of pH**[a]	**$[Cr^{6+}]$**[b] **(mg/L)**	**Range of pH**[a]	**$[Cr^{6+}]$**[b] **(mg/L)**
3.0	3.01–5.65	103.1 ± 27.3	3.00–6.53	56.5 ± 28.2	2.92–4.26	148.4 ± 26.8	2.96–4.72	135.9 ± 10.5
3.5	3.49–5.62	124.4 ± 9.2	3.50–6.60	107.6 ± 21.3	3.48–4.81	135.6 ± 15.9	3.47–5.28	160.6 ± 42.1
4.0	3.95–5.79	163.4 ± 32.4	4.04–6.71	100.4 ± 1.3	4.06–5.00	141.3 ± 19.1	3.98–5.43	174.9 ± 27.4
4.5	4.46–5.86	99.7 ± 18.8	4.45–6.67	129.5 ± 12.0	4.48–5.01	160.0 ± 11.0	4.50–5.26	142.5 ± 15.1
5.0	4.97–5.70	140.9 ± 13.8	4.90–6.71	71.9 ± 44.9	5.02–5.16	176.7 ± 11.0	4.98–5.60	155.1 ± 35.6
5.5	5.48–6.06	118.8 ± 54.9	5.50–6.63	83.3 ± 16.8	5.44–5.31	145.0 ± 32.2	5.56–5.81	131.6 ± 6.1
6.0	5.95–6.19	112.3 ± 6.6	6.01–6.91	112.3 ± 67.9	5.98–5.94	158.1 ± 1.0	6.02–6.10	147.3 ± 17.8
6.5	6.51–6.43	95.5 ± 20.4	6.55–7.18	80.3 ± 33.7	6.50–6.19	116.4 ± 2.1	6.46–6.50	182.3 ± 11.7
7.0	7.04–6.64	136.5 ± 8.8	6.91–7.28	173.1 ± 5.1	7.03–6.61	155.4 ± 6.4	6.94–6.95	164.4 ± 28.1
7.5	7.52–6.93	146.7 ± 0.4	7.50–7.11	144.7 ± 34.8	7.54–6.85	154.2 ± 12.2	7.48–7.19	154.1 ± 41.1

[a] Range of pH: initial and final values of pH (Mean values of two assays). [b] Concentration of chromium at the end of the assay for an initial concentration of 200 mg/L (Mean value ± standard deviation of two assays).

greater affinity was identified with chestnut shell, particularly in the range of pH from 3.0 to 6.5, allowing higher retention (up to around 70%). For wood and burnt wood, a consistently low removal rate was observed over the entire pH range studied (values between 10 and 40%). In fact, for chromium, these two biosorbents showed worse performance in relation to the walnut or chestnut shells. Tests made by Esteves et al. (2017) with untreated and heat-treated pine wood at temperatures from 180 to 210°C showed that the best pH for untreated wood was 2 with around 50% adsorption, while for heat-treated wood, the best pH was pH 3 with adsorption of almost 100%. Clearly burnt pinewood showed much worse adsorption rates than heat-treated wood probably due to the heterogeneity between completely burnt parts and unburned ones. For chromium in an aqueous solution, Oliveira and Feris (2018) observed that a decrease of removal may occur with an increase in the pH level, due to the anionic form of chromium in an aqueous solution being favourable to adsorption because it has a surface containing a large amount of H^+ ions due to the acidified pH. This behaviour was verified in the adsorption with the chestnut shell, whereas for the other materials employed, the highest adsorption was verified at pH above 4.5.

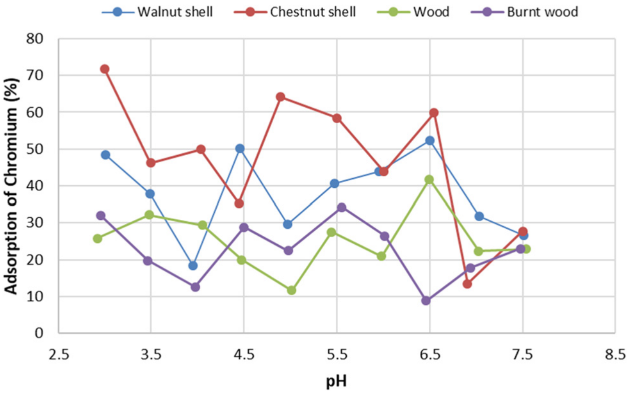

Figure 2: Adsorption of chromium at different pH values.

According to Souza et al. (2009), pH determines the proportion of chromium removal, as it limits the formation of surface charges favourable to the retention of the ions, determining the ionic form of this element in the solution. Blázquez et al. (2009) considered that the pH and the oxidation are the main factors that limit the process. These authors reported that two main mechanisms take place, simultaneously, in the sorption of Cr^{6+}: the reduction of Cr^{6+} to Cr^{3+} (in acidic media) and the retention of both into the biosorbent surface. Blázquez et al. (2009) also stated that the percentage of Cr^{6+} removed was greater than 80% when in very acid pH conditions (2.0 or lower), while at higher pH, this ratio decreased to 15% or even less. These findings are in line with the results obtained in our study, although the lowest range of pH values was not tested.

Souza et al. (2009), in tests with activated carbon, observed that the percentage of removal of chromium showed a brief increase with an increase in pH reaching 98% at pH 6.0, followed by a gradual decrease in adsorption rate. This decrease at higher pH values can be attributed to a significant reduction in the concentration of positive charges on the surface of the adsorbent by the deprotonation of acid groups and the competitiveness between chromium species and OH^- ions for sites on the adsorbent. Blázquez et al. (2009) described that Cr^{6+}

species formed in aqueous solution ($HCrO_4^-$ and CrO_4^{2-}) have negative charges. Thus, decreasing the pH value makes the biosorbent positively charged. So, while the pH increases, the H^+ concentration decreases, and the surface becomes negative. This explains a decrease in Cr^{6+} adsorption when an increase of pH values occurs.

The residual concentrations of chromium are presented in Table 2, for different biosorbents and pH values. As compared with lead, the adsorption of chromium is not so efficient, and remarked differences were found between the biosorbents, being the walnut and chestnut shells considerably better when compared with wood or burnt wood. The minimum residual concentration was 71.9 ± 44.9 mg/L at pH 5.0 using chestnut shell and 95.5 ± 20.4 mg/L for walnut shell at pH 6.5. These values still represent a decrease to under 50% of the initial amount of chromium present (200 mg/L). When wood or burnt wood were used, the concentration decreased much less to 116.4 ± 2.1 and 131.6 ± 6.1, respectively, for wood/pH 6.5 and burnt wood/pH 5.5.

In Figure 3, the average adsorption of nickel is presented, as a function of pH. The maximum nickel adsorption was obtained at pH 5 The highest adsorption was obtained with chestnut shell, reaching 75%. With the other adsorbents, the maximum adsorption was a little lower, being 45% adsorption for wood and 71% for the walnut shell. The lowest adsorption was obtained for burnt wood (64%). Thus, under the proposed conditions, pH around 5 can be considered as favourable for Ni^{2+} adsorption, higher pH values decreased the adsorption of nickel ion as can be seen in Figure 3. These results are in line with what was described in the literature for the adsorption of nickel by other types of biosorbents. The remaining differences may, however, be associated with the biosorbents used. Jimenez et al. (2004) described that there was an increased retention of nickel as pH increased and the more acidic the solution, the greater the competition between H^+ ions. Monteiro et al. (2008) verified, in a study carried out with green coconut shell as adsorbent, that the process of adsorption of Ni^{2+} was favoured with the increase of pH. This result was also verified by Moreira et al. (2009). Alomá et al. (2012b) observed that increasing the pH, the retention of Ni ions by sugarcane bagasse also increased. The greatest increase was identified when the pH raised from 3.0 to 5.0. This way, pH around 5.0 was indicated as optimum for Ni^{2+} biosorption by sugarcane bagasse. Xu et al. (2006) found that increasing the pH, the retention of nickel by aerobic granules of sludge also increased. The best rates were performed at pH 3.0 to 6.0; thus, the optimum value for Ni^{2+} adsorption by this material was about 6.0. Similar to the study by Nadeem et al. (2014) for NaOH pretreated *Mangifera indica* waste biomass, Zafar et al. (2009, 2007) showed that rice bran presented the best biosorption rates for a nickel at pH 6.0. Around pH 7.0, the sorption capacity was reduced, probably caused by chemical precipitation. In contrast, in this study, the highest adsorption occurred in acidic pH 5. One of the reasons for the somewhat different ideal pH for adsorption between this study and the study promoted by Zafar et al. (2009) might be the alteration of pH along the adsorption test since only the initial pH was controlled. Alomá et al. (2012b) described that at pH 5.0, Ni^{2+} ions are predominant, and the use of a higher pH

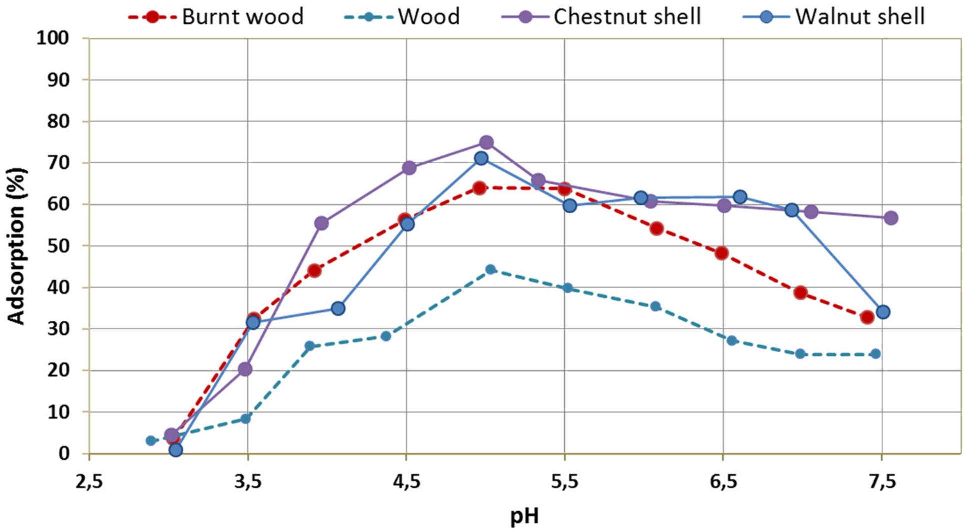

Figure 3: Adsorption of nickel at different pH values.

is not recommended, due to precipitation. This conclusion is in accordance with the results obtained here. Naturally, once the adsorption process depends on the biosorbent used, the divergence in the behaviour of lignocellulosic materials might be due to their different structures and chemical composition, which can promote or hinder the adsorption of ions according to the interactions between the limiting factors (Gouveia 2006).

Table 3 represents the residual concentration of nickel for the different operating conditions assayed. The adsorption of nickel promoted by the biosorbents was not so intense as it happened with lead, but it was considerably better as compared with chromium. Low retention was found for wood or burnt wood, like in the case of chromium adsorption, and the best biosorbents for nickel were also the walnut and chestnut shells giving the lowest concentrations equal to 57.8 ± 0.1 mg/L (at pH 5.0) and 50.3 ± 0.1 mg/L (at pH 5.0), respectively. The lowest concentration achieved with burnt wood was 72.1 ± 0.2 mg/L (at pH 5.0), and for wood, the value was much higher 111.6 ± 0.1 mg/L (at pH 5.0). On the other hand, at pH 3, the adsorption is almost zero with concentrations higher than 190 mg/L showing that a very acidic pH is unfavourable for nickel adsorption. Similar results were reported by Zafar et al. (2009). Although Moreira et al. (2009) reported that an increase in the pH from 3.0 to 7.0 did not produce considerable effects on the removal of nickel, our results show that adsorption increases until pH 5 decreasing afterward. This different behaviour can result from several factors, such as the composition of the solid material, secondary components present in the solution and other conditions which may significantly impact the adsorption of the metal. Gouveia (2006) observed that pH influences the cation complexation process, varying according to the metallic species, and the dependence on the availability of the metal is related to the functional groups present in the adsorbent and to the chemistry of the metal in aqueous solution. At reduced pH, functional groups present in cell walls are tightly associated with H^+, avoiding the cation approach because of repulsive forces (Xu et al. 2006).

The obtained results confirmed that the adsorption capability depends on the solution pH as stated by Souza et al. (2009). According to López et al. (2000), metals can be divided into two main groups when it comes to pH: in the first group, adsorption grows with pH increase, and the greatest accumulation is verified before precipitation occurs (Ni^{2+} and Pb^{2+} are part of this group). On the other hand, in the second group, accumulation is not linked with precipitation (Cr^{6+} is included in this last group).

4 Conclusions

It was possible to observe a different behaviour between the adsorbent materials when in contact with different metallic solutions. For the adsorption of lead, the ideal pH was in the range between 5.5 and 7.5 when using walnut shells or 7.5 for the other three biosorbents tested, comprising adsorption greater than 90% in all cases. With regards to the adsorption of chromium, the most favourable pH for adsorption was heterogeneous among the materials: for walnut and wood, the ideal pH was 6.5,

Table 3: Residual concentration of nickel

Target initial pH	Walnut shell		Chestnut shell		Wood		Burnt wood	
	Range of pH[a]	$[Ni^{2+}]$[b] (mg/L)	Range of pH[a]	$[Ni^{2+}]$[b] (mg/L)	Range of pH[a]	$[Ni^{2+}]$[b] (mg/L)	Range of pH[a]	$[Ni^{2+}]$[b] (mg/L)
3.0	3.05–4.19	198.2 ± 0.1	3.02–3.77	190.9 ± 0.1	2.89–3.66	194.1 ± 0.1	3.03–5.34	192.8 ± 0.1
3.5	3.54–4.60	136.8 ± 0.1	3.48–4.30	159.4 ± 0.1	3.49–4.23	183.3 ± 0.1	3.54–5.73	135.0 ± 0.1
4.0	4.07–4.54	130.1 ± 0.1	3.97–4.39	89.2 ± 0.1	3.90–4.53	148.4 ± 0.1	3.92–6.05	111.8 ± 0.1
4.5	4.51–4.93	89.3 ± 0.1	4.52–4.39	62.4 ± 0.1	4.38–4.52	143.6 ± 0.1	4.49–6.34	87.4 ± 0.1
5.0	4.97–4.87	57.8 ± 0.1	5.01–4.79	50.3 ± 0.1	5.04–4.56	111.6 ± 0.1	4.96–6.19	72.1 ± 0.1
5.5	5.53–4.78	80.5 ± 0.1	5.33–4.90	68.4 ± 0.1	5.52–4.77	120.4 ± 0.1	5.50–6.27	72.4 ± 0.1
6.0	5.98–4.78	76.8 ± 0.1	6.04–4.64	78.3 ± 0.1	6.08–4.81	129.4 ± 0.1	6.08–6.33	91.6 ± 0.1
6.5	6.61–4.80	76.4 ± 0.1	6.51–4.87	80.5 ± 0.1	6.56–4.86	145.6 ± 0.1	6.49–6.38	103.6 ± 0.1
7.0	6.93–4.88	82.8 ± 0.1	7.06–5.17	83.4 ± 0.1	6.99–5.24	152.2 ± 0.1	6.99–6.39	122.6 ± 0.1
7.5	7.51–5.05	113.8 ± 0.1	7.56–5.50	86.6 ± 0.1	7.47–5.60	152.1 ± 0.1	7.41–6.41	134.4 ± 0.1

[a] Range of pH: initial and final values of pH (Mean values of two assays). [b] Concentration of nickel at the end of the assay for an initial concentration of 200 mg/L (Mean value ± standard deviation of two assays).

for chestnut was 3.0 and for burnt wood was 5.5. Finally, the test made with nickel, indicated that the most adequate pH for adsorption was 5 for the biosorbents under analysis.

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