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REMOVAL OF ZINC, CADMIUM AND NICKEL FROM MINING WASTE LEACHATE USING WALNUT SHELLS

The removal of heavy metals from aqueous solutions using walnut shells was investigated. The effects of pH, contact time, initial metal concentration, adsorbent concentration, and co-ions were studied in synthetic solutions. Metal uptake was found to be dependent on the initial pH of the solution; the removal rate increased upon increasing pH, showing the highest affinity at pH 5–7. The amount of metal removed improved with increasing initial concentration. Increasing adsorbent dosage enhanced removal efficiency, but reduced the amount absorbed per unit mass of walnut shells. The presence of co-ions suppressed the uptake of heavy metals, divalent ions having a more negative effect than monovalent ions. The adsorption of Zn, Cd and Ni onto walnut shells was found to fit Langmuir and Freundlich isotherms. The results obtained in the tests with mining waste leachate showed the potential use of walnut shells for the removal of heavy metals.

1. INTRODUCTION

Some of the solid wastes produced during the mining and obtaining metal concentrates may contain large amounts of hazardous substances such as Zn, Cd and Ni which are mostly dumped in the specific area. An important environmental problem is the discharge of leachates that may contaminate soil and groundwater with heavy metals [1]. The presence of these metals has a potentially harmful effect on human and other biological systems because some of them are not biodegradable and tend to accumulate in living organisms.

Conventional methods, including coagulation-flocculation, precipitation, filtration, liquid extraction, ion exchange, reverse osmosis, membrane separation, adsorption method and electrochemical treatment, have been used to remove or minimize the concentrations of heavy metal ions in industrial wastewater and municipal water supplies [2–5]. In recent years, various agricultural residues have been used as low-cost

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adsorbents to remove heavy metals from solutions [6–10]. Agriculture by-products are usually composed of lignin and cellulose as major constituents, comprising functional groups such as alcohols, aldehydes, carboxylic, phenolic and ether groups which are capable of binding to heavy metals [11]. In this study, walnut shells were used as an adsorbent for this purpose.

Most of the studies in the bibliography with other agricultural wastes have been carried out with synthetic solutions. Mine leachate presents several metallic and non-metallic ions, with different concentrations and which can compete for each other for active sites. Untreated walnut shell, after only a light grinding, can be as effective as other agricultural wastes in the adsorption of metals, being necessary, in most other wastes studied in the literature, modified for increase its adsorption capacity [10, 12–15]. Walnuts have formed a part of human nutrition since ancient times. According to the Food and Agriculture Organization (FAO), walnuts are cultivated commercially throughout southern Europe, northern Africa, eastern Asia, the USA and western South America. World production of whole walnuts was around 5 053 529 t in 2014, China being the world's largest walnut producer, producing 1 602 373 t per year [16].

The aim of this study was to investigate the feasibility of using unmodified walnut shells as a low-cost treatment for the removal of heavy metals from real wastewater: a mining waste leachate from northern Spain. The results of the removal of Zn^{2+} , Cd^{2+} and Ni^{2+} from single and multicomponent solutions have also been presented. The removal of heavy metal ions using walnut shells was studied in dependence on pH, contact time, initial concentrations, and adsorbent dosages.

2. MATERIALS AND METHODS

Materials. Walnuts (*Juglans regia*) were collected from a local market and the shells were subsequently separated, washed and dried at room temperature. They were then milled, sieved to obtain a particle size $<100\ \mu\text{m}$ and placed in sealed polyethylene bottles for preservation. The mass loss rates obtained were determined by drying at $110\ ^\circ\text{C}$ overnight and $500\ ^\circ\text{C}$ for 24 h. Walnut shells were characterized by means of various instrumental techniques: X-ray fluorescence (Phillips PW2404), X-ray diffraction analysis (Phillips X PERT PRO) and FTIR spectral analysis (Varian 620-IR). X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer ($\text{CuK}\alpha$ radiation). The diffractometer was operated at 45 kV and 40 mA, over the range of 2θ from 5° to 80° , with a detector speed of $1^\circ/\text{min}$. The real density of the walnut shells was determined using the pycnometer method (UNE Standard 80105), employing water as the immersion liquid. A gravimetric technique was used to analyze moisture, organic compounds and mineral compounds content.

All the chemical solutions used in this study were prepared using deionized water and analytical grade chemicals ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) Stock solutions were prepared to contain 1000 mg/dm^3 of cadmium, nickel, and zinc, respectively. Solutions with the desired metal concentrations ($2.5\text{--}150 \text{ mg/dm}^3$) were prepared by successive dilutions of the stock solution.

The residual leachate was collected in a mine site in northern Spain. pH, redox potential, and electrical conductivity were measured using a pH2002 meter (Crison®) (pH 5.18, 362 mV) and an EC-Meter Basic 30 device (Crison®, $518 \text{ }\mu\text{S/cm}$), respectively, and an elemental analysis was conducted by inductively coupled plasma, mass spectrometry (ICP-MS, Agilent 7700).

Batch adsorption experiments. Treatment of mining waste leachate. Batch adsorption experiments were carried out by mechanically shaking series of 100 cm^3 polyethylene bottles containing walnut shell samples and metal solutions prepared in the laboratory employing an adsorbent concentration of 10 g/dm^3 , except in the tests performed to determine the influence of the amount of adsorbent. Samples were shaken at $20 \text{ }^\circ\text{C}$ at 75 rpm, subsequently separating the two phases by filtration (Whatman 114 filter). The concentrations of metals in the resulting supernatant were analyzed by atomic absorption spectroscopy. For each metal solution, one sample was reserved for analysis to determine the initial metal concentration.

A series of experiments were carried out to determine the influence of initial pH on the removal of metal ions from the solution (50 mg/dm^3). Initial pH was adjusted from 2 to 7 using H_2SO_4 (0.01 and 0.1 mol/dm^3) and NaOH (0.01 and 0.1 mol/dm^3) solutions. A series of metal solutions (initial concentration of 50 mg/dm^3) at pH 5 mixed with walnut shell samples in 100 cm^3 polyethylene bottles were used to evaluate the effect of contact time on adsorption efficiency at time periods ranging from 5 min to 24 h. The effect of the initial concentration on metal ion uptake was investigated by varying the initial concentration of metal ions from 2.5 to 150 mg/dm^3 . The dosage effect was studied by shaking metal ion solutions of two initial concentrations (75 and 150 mg/dm^3) with various dosages of walnut shells ranging from 10 to 40 g/cm^3 .

A series of binary solutions at pH 5 were prepared by mixing solutions of one of the heavy metals studied here (Zn, Cd or Ni) at an initial concentration of 50 mg/dm^3 with salts of various metals (K, Na, Cu, Ca, Mg, Zn, Cd and Ni) at concentrations ranging from 0 to 50 mg/dm^3 , to determine their effect on adsorption efficiency. The experiments were performed under similar conditions as the previous tests.

The amount of metal removed was determined by the mass balance:

$$\text{Metal}_{\text{removed}} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

The amount of metal ions removed q (mg/g) by walnut shell was calculated as

$$q = \frac{(C_0 - C_e)V}{W_s} \quad (2)$$

where W_s is the amount of adsorbent (g), C_0 and C_e the metal ion concentration (mg/dm³) before and after removal, respectively, and V is the sample volume (dm³).

Adsorption isotherms. Different metal solutions of the concentrations of 2.5, 5, 10, 20, 40, 50, 60, 100 and 150 mg/dm³ at pH 5 were shaken with walnut shell samples with an adsorbent concentration of 10 mg/dm³ for 3 h since that is the equilibrium time. The samples were subsequently filtered, and metal concentrations were determined in the liquid phases.

Treatment of mining waste leachate. Some experiments were carried out at different reaction times (0.08–3 h) with adsorbent contents of 10 g/dm³. The mixtures were shaken at 75 rpm, while other tests were performed employing different adsorbent dosages (10–80 g/dm³).

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF THE ADSORBENT

The mineral composition of the walnut shells is given in Table 1. It depends on the type of cultivar, growth conditions, soil properties [17, 18]. Ca, K, Fe and Si were the main elements (>10 wt. %) present in the walnut shells, while Al, S, Mn and Cu were found at low concentrations (<2 wt. %) and Cr, Ni, Zn, Ba, Sr and Rb, as trace elements.

Table 1

Chemical composition of the mineral matter of the walnut shells [wt. %]

K ₂ O	CaO	SO ₃	MgO	Na ₂ O	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CuO	P ₂ O ₅	MnO
30.94	36.02	3.67	0.51	2.90	10.21	11.40	1.98	1.17	0.65	0.38

The real density of adsorbent was 1.43 g/cm³, determined using the pycnometer method. The XRD patterns reveal that walnut shells are mainly amorphous and also show two peaks corresponding to the crystalline phase of cellulose (Fig. 1).

FTIR spectra were obtained for solid samples before and after the adsorption process (Fig. 2). Changes in band intensity and frequency after metal binding can be used to identify the functionalities involved in metal binding.

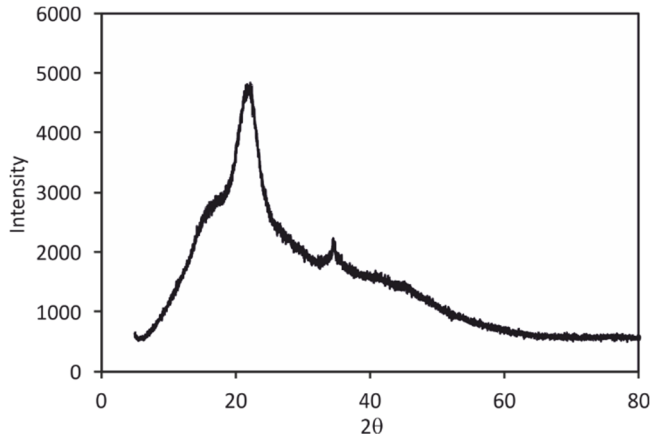


Fig. 1. X-ray diffraction pattern of walnut shells

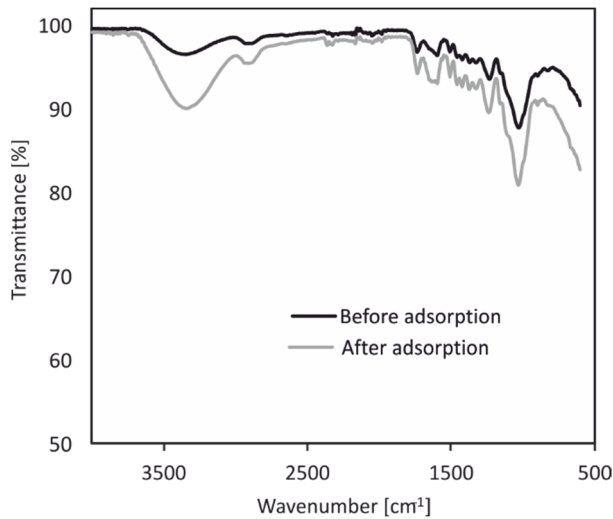


Fig. 2. FTIR spectra of walnut shells before and after being placed in contact with leachate

Figure 2 shows a broad band between 3600 and 3200 cm^{-1} including many vibration modes that may be mainly attributed to OH groups with a minor contribution of NH functional group. Solid samples containing water exhibit a band in the region of 3450 – 3300 cm^{-1} and also a band near 1650 cm^{-1} . A small broad peak between 2930 and 2887 cm^{-1} can be attributed to the asymmetric and symmetric stretching vibration of C–H bonds and the peak observed at 1734 cm^{-1} and 1655 cm^{-1} , to stretching vibration of the C=O bond due to carboxyl groups. The small peaks observed at 1594 , 1505 and 1456 cm^{-1} may be attributed to C=C stretching vibrations or asymmetric and symmetric stretching vibrations of ion carboxylic groups (1594 cm^{-1} and 1456 cm^{-1}). The peak at 1369 cm^{-1}

may be attributed to symmetric stretching of COO^- , 1230 cm^{-1} deformation vibration of C=O and stretching formation of the $-\text{OH}$ of carboxylic acids and phenols, while the peak at 1027 cm^{-1} corresponds to the C-O band in the $-\text{OCH}_3$ groups of lignin [19]. Other authors have reported similar results, using untreated coffee grounds [7] or cashew nut shell [9]. When comparing the FTIR spectra of the samples before and after being placed in contact with the leachate, it can be seen that the peaks attributed to the OH and carboxyl groups have shifted to lower frequencies and their intensity decreased. Therefore, it seems likely that these functional groups are involved in the adsorption of metals [20, 21].

3.2. CHARACTERIZATION OF THE LEACHATE

The physicochemical characteristics of the wastewater filtered were analyzed; pH 5.18, redox potential 362 mV and electrical conductivity $518\text{ }\mu\text{S/cm}$.

Table 2

Metal concentrations analyzed by ICP in mining waste leachate filtered

Major components, mg/dm^3	Ni	Zn	Cd	As	Na	Mg	K	Ca	
	18.1	15.3	68.19	5.8	13.31	1.58	19.38	35.98	
Minor components, $\mu\text{g/dm}^3$	Mn	Cu	Co	Se	V	Ag	Pb	Tl	Sb
	24.25	22.73	0.47	1.3	0.77	4.45	2.09	0.04	27.4
	B	Al	Ti	Cr	Mo	Sr	Sn	Ba	Fe
	20	460	0.06	11	4.7	167	0.44	4.9	0.67

Table 2 shows metal concentrations in the leachate. It contained significant amounts of heavy metals such as Cd, Ni, Zn and As ($68.19\text{--}5.8\text{ g/dm}^3$), in addition to lower amounts of Pb, Cu, Se, Mn, Cr and Mo ($24.25\text{--}1.3\text{ }\mu\text{g/dm}^3$).

3.3. BATCH ADSORPTION EXPERIMENTS

pH dependence of the amount of metal ions removed (mg/g) is shown in Fig. 3. As can be seen, the metal ion uptake by the walnut shells increased upon increasing pH from 2 to 5. In acidic media ($\text{pH} = 2$), the values of removal percentages are low (only 0.16 mg/g , 0.05 mg/g and 0.07 mg/g of Zn^{2+} , Cd^{2+} and Ni^{2+} , respectively). The efficiency of the metal ion uptake was not significantly affected in the 5–7 pH range. The final pH of the solution after treatment had barely changed (Fig. 4). For solutions with the initial pH of 4 or higher, the final pH falls within the 5.5–6 range for Ni and Zn, being slightly lower for Cd. pH of the solution has a significant impact on the uptake of heavy metals, as it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The FTIR analysis shows that hydroxyl and carboxyl groups

are involved in almost all the potential binding mechanisms. At lower pH, these groups become protonated as follows:

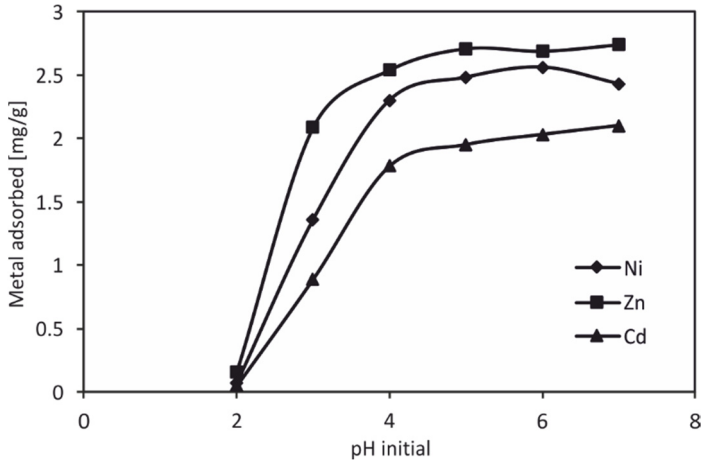
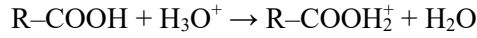


Fig. 3. Metal removal onto walnut shells versus initial pH; $C_0 = 50 \text{ mg/dm}^3$, adsorbent concentration = 10 g/dm^3 , $t = 3 \text{ h}$, $T = 20 \text{ }^\circ\text{C}$

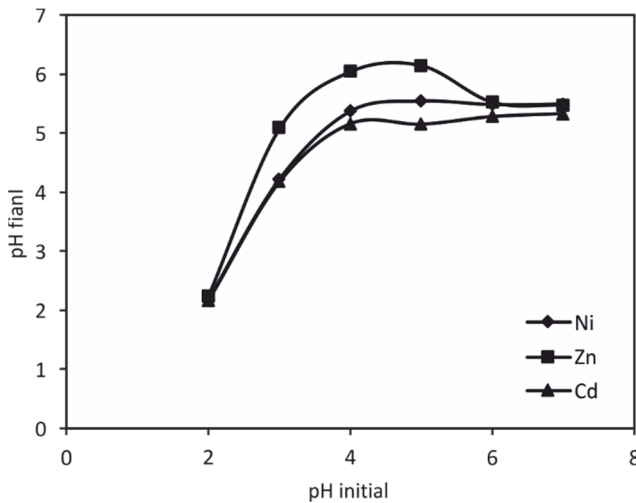


Fig. 4. Final pH versus initial pH in metal removal onto walnut shells; $C_0 = 50 \text{ mg/dm}^3$, adsorbent concentration = 10 g/dm^3 , $t = 3 \text{ h}$, $T = 20 \text{ }^\circ\text{C}$

The adsorbent surface area and metal ions in solution are positively charged. Hence, as there is electrostatic repulsion between metal ions and active sites, there is almost no adsorption. At higher pH, however, carboxyl and hydroxyl groups are deprotonated

($R-COO^-$), active sites are negatively charged and, therefore, electrostatic attraction of Cd^{2+} , Zn^{2+} and Ni^{2+} ions do exist [7, 22, 23]. A similar pH dependence has been previously reported for heavy metals adsorbed onto walnut shells and other agricultural waste [7, 12]. The data shown in Fig. 3 suggest that the initial pH equal to 5 is optimal. As the leachate to be treated in this study has pH of around 5, the following tests were conducted at this pH.

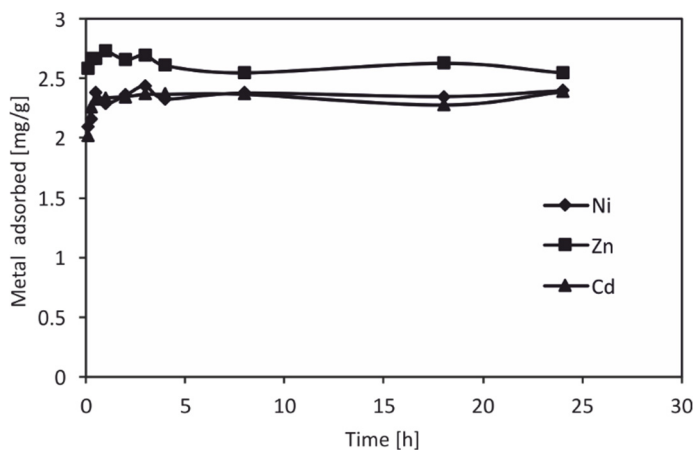


Fig. 5. Metals adsorption onto walnut shells versus contact time; $C_0 = 50 \text{ mg/dm}^3$, adsorbent concentration = 10 g/dm^3 , $T = 20 \text{ }^\circ\text{C}$, $\text{pH} = 5$

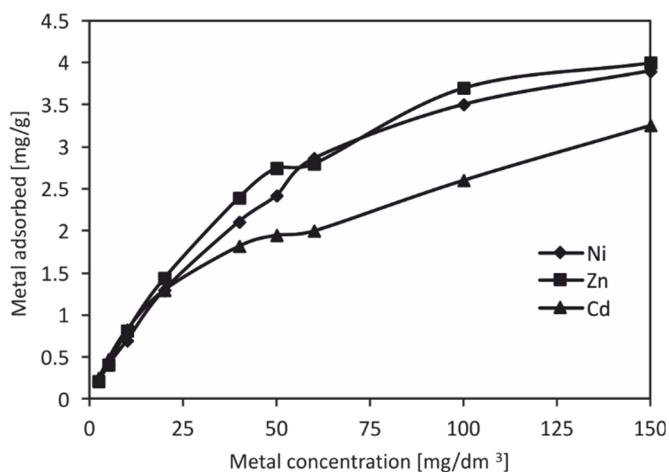


Fig. 6. Effect of initial concentration on the adsorption of metals; adsorbent concentration = 10 g/dm^3 , $t = 3 \text{ h}$, $T = 20 \text{ }^\circ\text{C}$, $\text{pH} = 5$

The dependence of metal ions uptake on the contact time is shown in Fig. 5. The experiments showed that it is a two-step process. The removal of metal ions starts

shortly after stirring and increases over time. In the first 5 min it was found to be 2.1, 2.59 and 2.02 mg/g for Ni^{2+} , Zn^{2+} and Cd^{2+} , respectively, reaching equilibrium values of 2.44 mg/g, 2.7 mg/g and 2.37 mg/g after 3 h. No further adsorption above the equilibrium concentration was observed within the following 24 h. The explanation for this behavior is that all the sites on the surface of sorbent are initially vacant, but upon increasing contact time, there is a progressive increase in the bonds between the active sites and heavy metal ions and the metal uptake process become less efficient [7, 9].

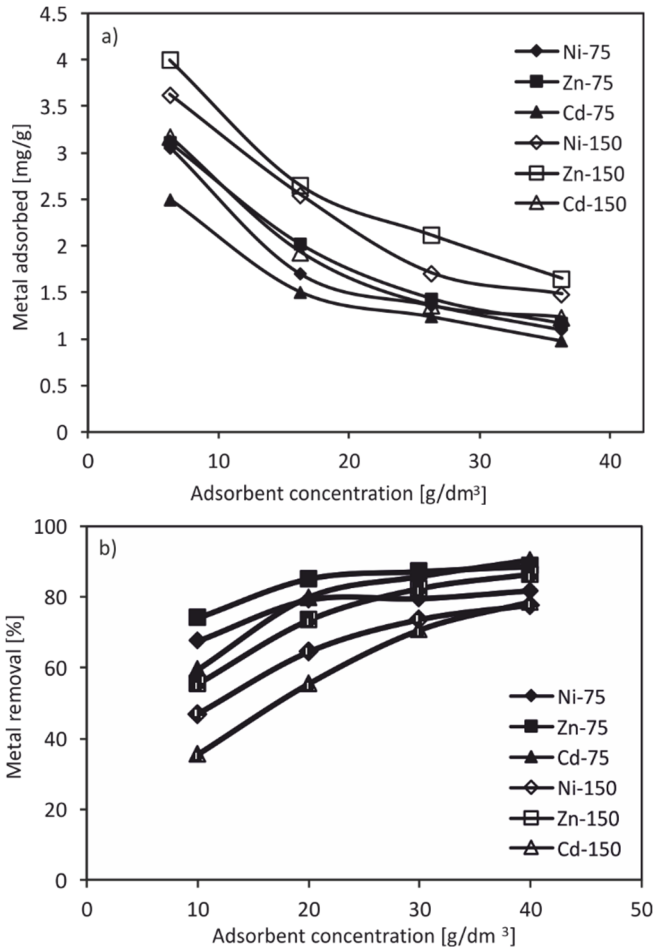


Fig. 7. Effect of walnut shell dosage on the removal of Ni^{2+} , Zn^{2+} and Cd^{2+} :
 a) metal adsorbed, b) % of metal removal;
 $C_0 = 75$ and 150 mg/dm^3 , $t = 3 \text{ h}$, $T = 20 \text{ }^\circ\text{C}$, $\text{pH} = 5$

The adsorption of metals onto walnut shells was found to be strongly dependent on the initial concentration. As can be seen in Fig. 6, the amount of adsorbed metal ions

increased upon increasing initial concentration. Metals removal reached 0.25 mg/g for the initial concentration of 2.5 mg/dm³, increasing to 4, 3.9 and 3.25 mg/g for Zn²⁺, Ni²⁺ and Cd²⁺, respectively, when employing an initial concentration of 150 mg/dm³. The results indicate that the percentage of metal uptake decreases with increasing initial concentration. This can be explained by the fact that the adsorbent has a limited number of activate sites and, above a certain concentration, becomes saturated [7].

As can be seen in Fig. 7a, the amount of adsorbed metal (mg/g) decreased progressively with increasing adsorbent concentration. The explanation for this is that the adsorption of metal is subject to the “particle concentration effect” as a result of flocculation of the solid phase, with the resulting decrease in available surface area. Employing an adsorbent concentration of 10 g/dm³ and initial concentrations of 150 mg/dm³, the amount of metal adsorbed per gram was 4 mg/g, 3.18 mg/g and 3.63 mg/g for Zn²⁺, Cd²⁺ and Ni²⁺, respectively, whereas the amount of metal adsorbed per gram decreased to 1.65 mg/g, 1.23 mg/g and 1.48 mg/g when employing an adsorbent concentration of 40 g/dm³. In the case of lower initial concentrations (75 mg/dm³), Zn removal reached 3.11 mg/g and 1.17 mg/g for an adsorbent concentration of 10 g/dm³ and 40 g/dm³, respectively. These results are consistent with the gradual increase in the percentage of metal removal as the dosage of adsorbent increased from 10 to 40 g/dm³ (Fig. 7b). The latter value is optimum for the process. Enhancements in adsorption with increasing dosage can be attributed to the availability of more binding sites for adsorption [7, 9].

Several researchers have studied the uptake of metals from single metal solutions onto walnut shells as adsorbent [10, 13, 21, 24], though less attention has been paid to the adsorption of multimetal systems. Mining waste leachate contains several metal ions at different concentrations. A series of trials were performed to investigate how the presence of other metal ions affects the removal of one metal ion.

The adsorption capacity of walnut shells in a binary system mainly depends on the initial concentration of the primary ion, and the initial concentration of other ions in solution (Fig. 8). The adsorption of Zn, Cd and Ni decreased in the presence of other metal ions. The adsorption of metal ions decreased when increasing the concentration of second ions. This is because more ions can compete for the active sites on the walnut shell's surfaces.

The presence of alkaline ions (Na⁺ and K⁺) was not found to have a significant effect on the removal of heavy metals. Comparing trials with mono-metallic solutions (100 mg/dm³) with bi-metallic trials (50 mg/dm³ + 50 mg/dm³ second ion), Cu and Cd were found to be the metals that reduce adsorption the most. The amount of Zn removed by walnut shells in the single metal solution was 3.7 mg/g, while the uptake of Zn decreased to only 1.16 mg/g and 1.39 mg/g in the presence of Cu and Cd second ions, respectively. Similar behaviour was obtained for Ni, the amount of Ni uptake with the bimetal solution being 0.92 mg/g and 0.94 mg/g for Cu and Cd, respectively.

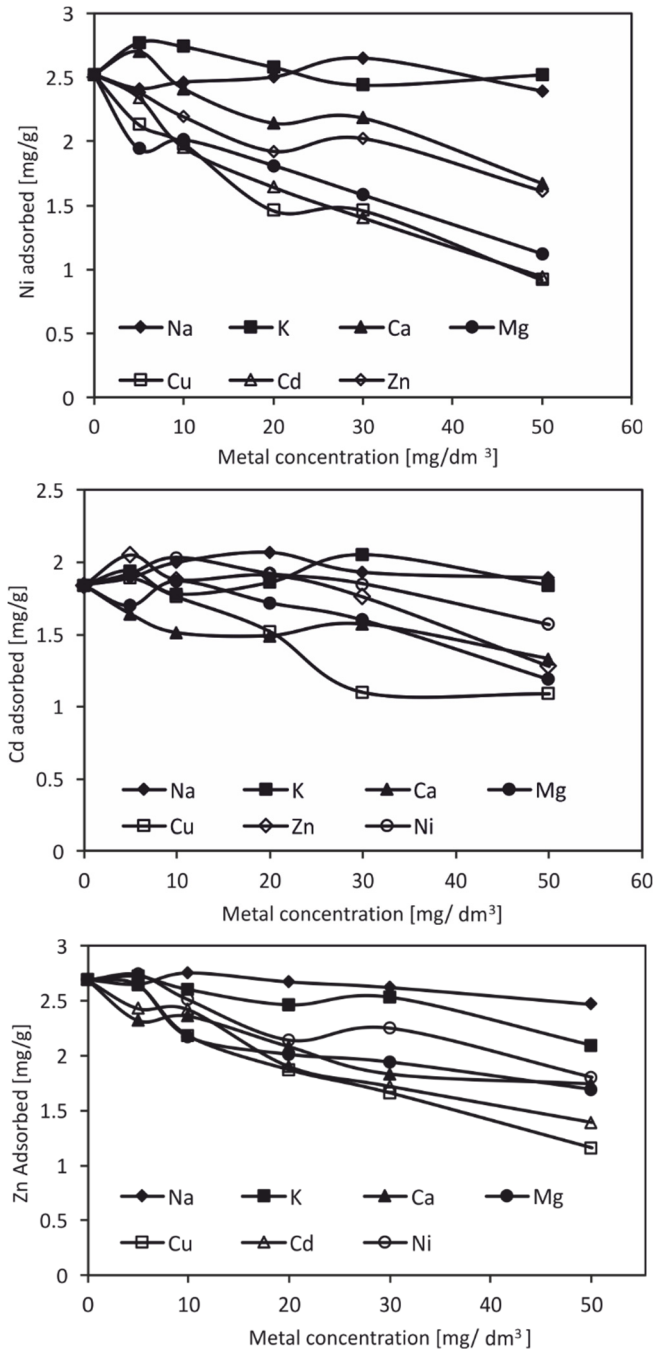


Fig. 8. Influence of other metal ions on Zn, Cd and Ni removal; adsorbent concentration = 10 g/dm³, $t = 3$ h, $T = 20$ °C, pH = 5

The negative effect of other ions on metal uptake followed the order shown below:

Zn removal: Cu > Cd > Mg ≈ Ca ≈ Ni > K > Na,

Cd removal: Cu > Mg > Zn > Ca > Ni > K ≈ Na,

Ni removal: Cu ≈ Cd > Mg > Zn ≈ Ca > Na > K.

The affinity of metal ions for walnut shells could be attributed to different ionic characteristics of metal ions such as ionic radius, electronegativity, the energy of hydration and covalent index. Cu is the metal that most inhibits the removal of Cd, Zn and Ni. This may be because Cu²⁺ ion has a 0.73 Å radius, similar to those of Zn²⁺ (0.74 Å) and Ni²⁺ (0.69 Å) and slightly smaller than that of Cd²⁺ (0.95 Å). It has similar electronegativity to that of Ni²⁺ (1.9 in Pauling scale) and slightly higher than those of Cd²⁺ (1.69) and Zn²⁺ (1.65). The hydration energy of Cu²⁺ ion (−2099 kJ/mol) is similar to that of Ni (−2096 kJ/mol) and higher than that of Zn (−2047 kJ/mol) and Cd (−1809 kJ/mol). The covalent index of Cu (46) is the same as that of Zn (46), slightly lower than that of Ni (48) and higher than that of Cd (37).

3.4. ADSORPTION ISOTHERMS

In order to describe the behavior of metal ion adsorption on walnut shells, the isotherm data thus obtained were fitted to Langmuir and Freundlich adsorption models. The Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir isotherm is represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{b a_{\max}} + \frac{C_e}{a_{\max}} \quad (3)$$

where C_e is the equilibrium concentration of metal ions in solution (mg/dm³), q_e the amount of metal adsorbed at equilibrium (mg/g), while b (dm³/mg) and a_{\max} (mg/g) are the Langmuir constants related to the binding constant and the maximum adsorption capacity, respectively. The values were estimated from the intercept and slope of the regression line for various initial metal concentrations.

The essential feature of the Langmuir isotherm can be expressed in terms of the dimensionless separation parameter, R_L , which is indicative of the isotherm shape that predicts whether an adsorption system is favorable or unfavorable. R_L is defined as:

$$R_L = \frac{1}{n(1 + bC_0)} \quad (4)$$

where b is the Langmuir constant, and C_0 is the initial concentration. The R_L value indicates the character of the isotherm as follows: unfavorable ($R_L > 1$), linear, favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The adsorption data were also fitted using the Freundlich isotherm equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (5)$$

where q_e is the amount of metal ions adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the metal ion in solution (mg/dm³), K ((mg/g)·(dm³/mg)^{1/n}), the equilibrium constant indicative of adsorption capacity, and n is the adsorption equilibrium constant. If the value $1/n$ is below unity, this implies that the sorption process is chemical, if it is above unity, sorption is a favorable physical process [25]. The Freundlich model is applicable to sorption on heterogeneous surfaces with non-energetically equivalent sites. Adsorption parameters are given in Table 3. The results showed that adsorption data could fit both equations, according to the coefficient of determination for the heavy metals studied here, although the data for Cd gave a slightly better fit to the Freundlich isotherm.

Table 3

Langmuir and Freundlich adsorption isotherm constants

Metal	Langmuir			Freundlich		
	a_{\max} [mg/g]	b [dm ³ /mg]	R^2	K [(mg/g)(dm ³ /mg) ^{1/n}]	n	R^2
Ni	4.28	0.31	0.983	0.434	1.963	0.989
Zn	4.29	0.41	0.992	0.494	1.982	0.969
Cd	3.18	0.32	0.947	0.737	3.424	0.993

Adsorbent dose 10 g/dm³, t = 3 h, T = 20 °C, pH = 5.

Table 4

Adsorption capacities of various agricultural adsorbents [mg/g]

Adsorbent	Cd	Ni	Zn	Reference
Rice husk ash	2.86	4.07	5.07	[15]
Coffee grounds	5.96	7.51	10.22	[6]
Walnut shell	4.29	3.18	4.29	present study

The maximum adsorption capacity onto walnut shells for heavy metals, a_{\max} , follows the order: Zn(II) > Ni(II) > Cd(II). The R_L was found to fall within a similar range for the three cations studied and, therefore, represents a favorable adsorption. The $1/n$ values for adsorption were found to be below 0.5 that implies chemical process. The same conclusions were drawn using different agricultural wastes. Table 4 shows adsorption capacities of various agricultural adsorbents.

3.5. TREATMENT OF MINING WASTE LEACHATE

The wastewater used in this study contained $18.1 \text{ Ni}^{2+} \text{ mg/dm}^3$, $15.3 \text{ Zn}^{2+} \text{ mg/dm}^3$ and $68.19 \text{ Cd}^{2+} \text{ mg/dm}^3$, in addition to other ions such as Ca, Na, K, Mg, etc. (Table 2).

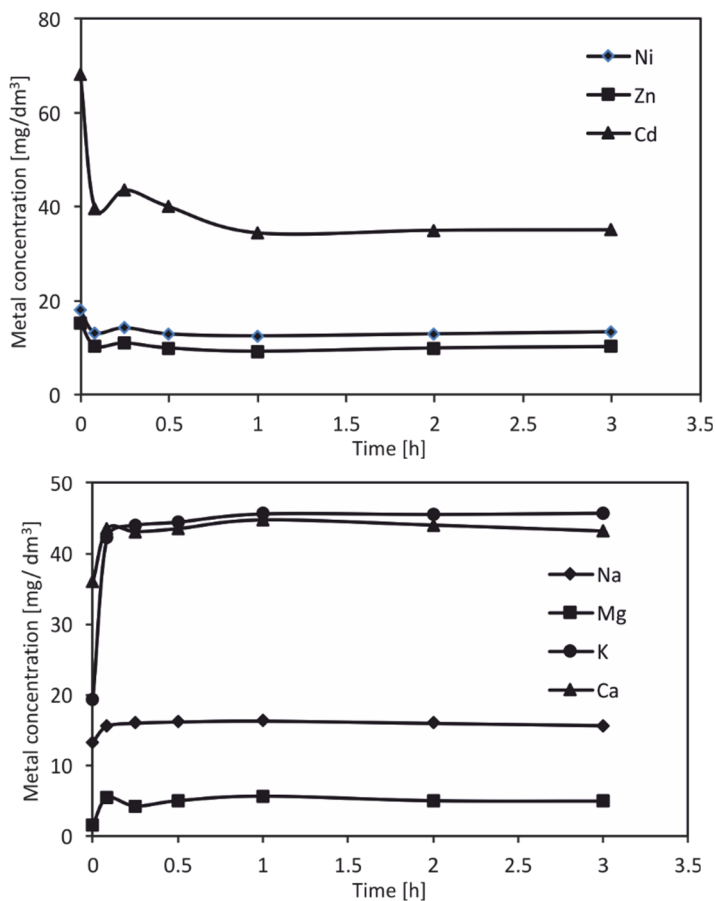


Fig. 9. Time effect on treatment of leachate with walnut shells; adsorbent concentration 10 g/dm^3 , $T = 20 \text{ }^\circ\text{C}$, $\text{pH} = 5.18$

The amount of Zn, Cd, Ni ions adsorbed onto walnut shells increased with time (Fig. 9). The concentration of Cd in the leachate was found to be 39.6 mg/dm^3 in the first 5 min, reaching 35 mg/dm^3 after 1 h. The concentrations of Ca, K, Na and Mg increased after treatment, suggesting ion exchange mechanisms between protons, alkali and alkaline earth metals and Zn^{2+} , Ni^{2+} and Cd^{2+} .

Comparing the data obtained with single metal solutions of similar concentrations with those of the leachate, it was found that the total amount of Zn, Cd and Ni adsorbed

was 4.425 mg/g (1.3 mg Ni²⁺/g, 1.125 mg Zn²⁺/g, 2 mg Cd²⁺/g) in single metal solutions, while the total amount of Zn, Cd and Ni adsorbed in the test with mining leachate was 4.274 mg/g (0.464 mg Ni²⁺/g, 0.5 mg Zn²⁺/g, and 3.31 mg Cd²⁺/g).

Table 5

Released cations due the adsorption of Zn²⁺, Cd²⁺ and Ni²⁺ onto walnut shells [meq/g]

Total metal bound			Amount of cation released					$R_{b/r}$
Zn ²⁺	Cd ²⁺	Ni ²⁺	Al ³⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
0.0153	0.0589	0.0158	0.0050	0.0103	0.0675	0.0359	0.0277	0.671

$R_{b/r}$ – ratio of metal bound to cation released.

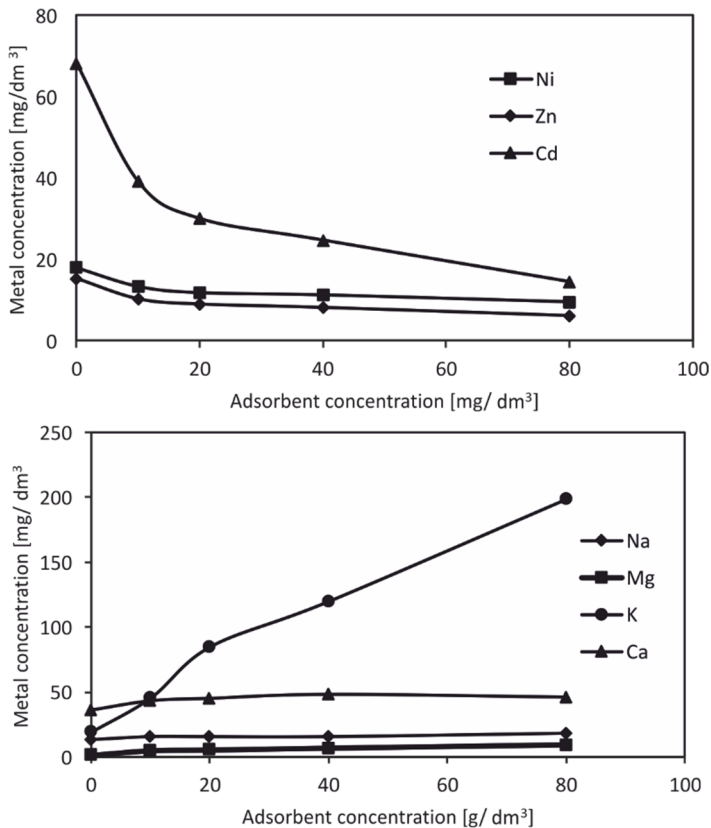


Fig. 10. Effect of dosage on the treatment of mining leachate using walnut shells; $t = 3$ h, $T = 20$ °C, $\text{pH} = 5.18$

These results show that the presence of other ions in the leachate exhibits inhibitory (antagonistic) sorption for Ni and Zn, thereby resulting in a lower sorption yield. However, the presence of other ions in the solution exerts a synergistic effect by increasing

the removal of Cd. Srivastava et al. [15] reported similar results for Ni and Zn adsorption onto rice husk ash. These authors suggest that there is a variety of adsorption binding sites on the adsorbent surface exhibiting partially specific affinity for the individual metal ions.

In order to confirm the ion exchange mechanisms, the amount of Na^+ , K^+ , Ca^{2+} and Mg^{2+} released due to the sorption process was calculated by subtracting the amount of these metals in the supernatant and the amount of these metals present in the leachate. Table 5 shows the amount of cations which passed into solution after the treatment of the leachate with walnut shells, as well as the amount of Zn^{2+} , Cd^{2+} , Ni^{2+} and Al^{3+} removed.

The total amount of cations released was found to be 0.1414 meq/g and the uptake, 0.095 meq/g. The ratio of metal bonded to cation released $R_b/r < 1$; hence the ion exchange mechanism is not the only one involved in the removal of heavy metals. The ion exchange mechanism was suggested by other authors, in addition to some other types of interactions such as physical force and/or chelation in metal biosorption. Walnut shells have functional groups (alcohol, ketone and carboxylic) that may be involved in complexation reaction with metal ions.

Figure 10 shows the results obtained employing different amounts of adsorbent. The heavy metals concentration can be reduced by increasing the adsorbent dosage. The amount of Cd remaining in the leachate was 14.4 mg/dm³ using an adsorbent concentration of 80 g/dm³. 79% of the Cd present in the leachate was removed, mainly believed to be due to the exchange with K^+ ions (Table 4).

4. CONCLUSIONS

The present study demonstrated that walnut shells can be used as adsorbents for Zn^{2+} , Ni^{2+} and Cd^{2+} removal from synthetic solutions and from real wastewater. Metal adsorption is highly dependent on pH, maximum removal taking place at $\text{pH} > 5$. Metal uptake was found to be very rapid and heavy metal concentration can be reduced by increasing the adsorbent dosage.

The adsorption data could be fitted to the Langmuir and Freundlich models, demonstrating that both monolayer and heterogeneous surface adsorption occur during the treatment with walnut shells. Furthermore, maximum Zn, Ni and Cd uptake of 4.29, 4.28 and 3.18 mg/g, respectively, were obtained when using an adsorbent concentration of 10 g/dm³, $t = 3$ h, $T = 20$ °C, $\text{pH} = 5$.

The presence of other cations significantly reduced metals adsorption, divalent cations having a more negative effect than monovalent ones.

The release of alkaline and alkaline earth ions from walnut shells due to the uptake of Zn, Cd and Ni indicates that ion exchange takes place in the adsorption process.

Freundlich isotherm parameter $1/n$ is below unity, this implies that the sorption process is chemical.

The results obtained in this study demonstrate that walnut shells can be used to treat mining waste leachate.

Untreated walnut shells, with only a light grinding, can be as effective as other agricultural wastes in the adsorption of metals, being necessary, in most other wastes studied in the literature, modified for increase its adsorption capacity.

Furthermore, the walnut shell is able to capture metals from the leachate without modifying the pH of the leachate. Therefore, no type of preparation or previous treatment of leachate is necessary.

REFERENCES

- [1] OWSIANIAK M., HOLM P.E., FANTKE P., CHRISTIANSEN K.S., BORGGAARD O.K., HAUSCHILD M.Z., *Assessing comparative terrestrial ecotoxicity of Cd, Co, Cu, Ni, Pb, and Zn. The influence of aging and emission source*, Environ. Pollut., 2015, 206, 400.
- [2] AYALA J., FERNÁNDEZ B., *Bayer electrofilter fines as potential Se(VI) adsorbents*, JOM, 2015, 67, 2727.
- [3] COMAN V., ROBOTIN B., ILEA P., *Nickel recovery/removal from industrial wastes. A review*, Res. Cons. Rec., 2013, 73, 229.
- [4] FU F., WANG Q., *Removal of heavy metal ions from wastewaters. A review*, J. Environ. Manage., 2011, 92, 407.
- [5] LI L., TAKAHASHI N., KANEKO K., SHIMIZU T., TAKARADA T., *A novel method for nickel recovery and phosphorus removal from spent electroless nickel-plating solution*, Sep. Purif. Techn., 2015, 147, 237.
- [6] AYALA J., FERNANDEZ B., *Treatment of mining waste leachate by the adsorption process using spent coffee grounds*, Environ. Techn., 2018, 15, 1.
- [7] AZOUAOU N., SADAOUI Z., DJAAFRI A., MOKADDEM H., *Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics*, J. Hazard. Mater., 2010, 184, 126.
- [8] BAYO J., *Kinetic studies for Cd(II) biosorption from treated urban effluents by native grapefruit biomass (Citrus paradisi L.). The competitive effect of Pb(II), Cu(II) and Ni(II)*, Chem. Eng. J., 2012, 191, 278.
- [9] KUMAR P.S., RAMALINGAM S., SATHYASELVABALA V., KIRUPHA S.D., MURUGESANAND A., SIVANESAN S., *Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell*, Korean J. Chem. Eng., 2012, 29, 6, 756.
- [10] SAADAT S., KARIMI-JASHNI A., *Optimization of Pb adsorption onto modified walnut shell using factorial design and simplex methodologies*, Chem. Eng. J., 2011, 173, 743.
- [11] MARTÍNEZ NIETO L., BEN DRISS S., HODAIFA G., FAUR C., RODRÍGUEZ S., GIMÉNEZ J.A., OCHANDO J., *Adsorption of iron on crude olive stones*, Ind. Crops Prod., 2010, 32, 467.
- [12] KAMAR F.H., NECHIFOR A.C., ALWAN G.M., CRACIUN M.E., *Comparative removal of lead, copper and cadmium ions from wastewater in single and ternary batch biosorption systems onto dry walnut shells*, Rev. Chim. (Bucharest), 2015, 66 (8), 1083.
- [13] GALA A., SANAK-RYDLEWSKA S., *A comparison of Pb²⁺ sorption from aqueous solutions on walnut shells and plum stones*, Polish J. Environ. Stud., 2011, 20 (4), 877.
- [14] SAHOO P.K., TRIPATHY S., PANIGRAHI M.K., EQUENUDDIN S.M., *Evaluation of the use of an alkali modified fly ash as a potential adsorbent for the removal of metals from acid mine drainage*, Appl. Water Sci., 2013, 3, 567.

- [15] SRIVASTAVA V.C., MALL I.D., MISHRA I.M., *Equilibrium modeling of ternary adsorption of metal ions onto rice husk ash*, J. Chem. Eng. Data, 2009, 54, (3), 705.
- [16] Food and Agricultural Organization (FAO), <http://faostat.fao.org/site/339/default.aspx> (accessed on 22.12.16).
- [17] LAVEDRINE F., RAVEL A., VILLET A., DUCROS V., ALARY J., *Mineral composition of two walnut cultivars originating in France and California*, Food Chem., 2000, 68 (3), 347.
- [18] ÖZCAN M.-M., İMAN C., ARSLA D., *Physicochemical properties, fatty acid and mineral content of some walnuts (Juglans regia L.) types*, Agric. Sci., 2010, 1 (2), 62.
- [19] SOCRATES G., *Infrared and Raman characteristic group frequencies. Tables and Charts*, 3rd Ed., Wiley, Chichester 2001.
- [20] IQBAL M., SAEED A., ZAFAR S.I., *FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ removal by mango peel waste*, J. Hazard. Mater., 2009, 164, 161.
- [21] KAMAR F.H., NECHIFOR A.C., *Removal of copper ions from industrial wastewater using walnut shells as a natural adsorbent material*, U.P.B. Bull. Series B, 2015, 77 (3), 141.
- [22] PARCK D., YUN Y., PARCK J.M., *The past, present and future trends of biosorption*, Biotechnol. Bioproc. Eng., 2010, 15, 86.
- [23] SAEED A., IQBAL M., AKHTAR M.W., *Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk)*, J. Hazard. Mater., 2005, 117, 65.
- [24] FEIZI M., JALALI M., *Removal of heavy metals aqueous solutions using sunflower, potato, canola and walnut shell residues*, J. Taiwan Inst. Chem. Eng., 2015, 54, 125.
- [25] CRINI G., BADOT P.M., *Sorption processes and pollution. Conventional and non-conventional sorbents for pollutant removal from wastewaters*, Presses universitaires de Franche-Comté, Besançon 2010.