Agricultural wastes for wastewater treatment

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Abstract

Several dried fruits and cereals produced in Portugal originate a large amount of shells. This kind of wastes can be used as natural adsorbents in wastewater treatment, such as metals removal.

In the present study some agriculture wastes were selected, peanut shells and walnut shells to remove copper from industrial wastewater. The selected adsorbents were characterized and subjected to different treatments: washing, drying, sieving and carbonization. The experiments were carrying out in batch, varying the type and adsorbents dose with an initial Cu (II) concentration of 0.3 g L^{-1}.

The adsorption data was fitted using a Langmuir and Freundlich isotherm model. The adsorption equilibrium was best fitted by the linear and Freundlich isotherm. The results show that the values of *n* are smaller than 1 for peanut shells indicating poor sorption characteristics, for walnut results revealed that the values of *n* are greater than 2 indicating that the Cu (II) are favorably adsorbed.

Comparing the results from the two adsorbents applied to Cu (II) removal the greater removal efficiency was obtained with carbonized peanut shells.

Keywords:

Walnut shells, peanut shells, copper removal, wastewater treatment, adsorption

1. Introduction

Nowadays water protection and waste management are two extremely important issues to world population. Therefore, it is necessary reuse wastes and to find low-cost methods for wastewater treatment.

Wastes from agriculture and industry activities are a major problem caused by the increasing of food demand. These wastes contain substances with potential for affecting the public health and the environment due to the toxicity and remediation problems.

Portugal produces significant amounts of dried fruits and cereals. The annual walnuts production is more than 4,000 ton and imported 1,000 ton. The annual peanuts amount includes around 10,000 ton of importation and 2,500 ton of exportation [1]. The production of dried fruits generates large quantities of waste, particularly shells. According to INE data [1], 1 kg of walnuts or peanuts generates around 0.27 kg of shells. For 2013 the shells estimation is 1,150 ton (5,000 * 0.27) for walnuts and 2,025 ton (7,500 * 0.27) for peanuts.

Some dried fruits shells can be used in the manufacture of animal feed [2], as fertilizer or land cover [3]. There are also the applications in the manufacture of resins or activated charcoal [4].

Industrial wastewater can contain large quantities of heavy metal such as copper, cadmium, chromium, cobalt, iron, lead, nickel and zinc. Usually these wastewaters are from metal cleaning, paint, electroplating, plating baths paper and wood production, air conditions and fertilizer industries [5]. Although, some heavy metals are required by living organisms an extreme level can cause several diseases. For example copper (Cu II) can cause several problems in humans and animals such as stomach ulcer, mental retardation, brain and liver damage [5, 6]. According to EPA [7] the maximum allowable concentration for Cu (II) is 1.3 mg L^{-1} in a drinking water.

According to national legislation [8], an admissible maximum value for Cu (II) is 0.1 $mg.L^{-1}$ for minimum quality of a superficial water and 5 $mg.L^{-1}$ for an irrigation water.

The methods most used to remove heavy metals from wastewater are chemical precipitation, coagulation/flocculation, ion exchange, membrane process and adsorption [9]. Most of these methods are quite expensive for what is necessary to develop more low-cost ones. Adsorption method is referred as a simple and economical technology, due the fact that most of the adsorbents can be regenerated and reused [10].

Parameters affecting the adsorption capacity are pH, temperature, adsorbent particle size and dose, initial concentration of metal, contact time and agitation rate [11].

In last year's several studies were made concerning the adsorption of metals such us Cu (II) [12, 13, 14, 15].

Several materials can be used as adsorbent, activated carbon is the most widely used. However this adsorbent is difficult to regenerate and has high cost [16].

Amarasinghe and Williams [12] present a study to remove zinc and Cu (II) from aqueous solutions, with tea wastes as adsorbents in batch and continuous tests. The study revealed a highest removal of metal at pH 5-6.

Recently several studies presented novel adsorbents especially from agricultural wastes due to the low cost, abundance and availability [17].

The cereals and dried fruits shells may be employed as natural adsorbents [18]. Normally, the adsorption capacity of adsorbents is not high enough; therefore, it is necessary to use some surface modifications techniques namely chemical and physical. The chemical modifications involve acid, base and metal or metal oxide treatments. The physical modifications include especially heat and microwave treatments [10].

Usually the shells are pre-treated by washing with water to remove surface impurities and coloration, dried, shredded [19] and thermal treated at different temperatures to be activated as natural adsorbents [20].

Kazemipour et al., [14] studied several shells (e.g. walnut, pistachio and almond) as raw material for generate activated carbons with high surface areas. The application of such adsorbents to copper, zinc, cadmium and plumb removal revealed an influence of time and temperature carbonization. The copper removal was also influenced by the pH solution.

Luna et al., [17] used adlai shells as adsorbent for remove copper from solutions, with concentrations of 10, 30, 50, 70, 100 and 150 mg L^{-1}. The adlai shells were pre-treated: washed with distilled water and dried at 100 ºC for 24 h, pulverized and sieved. In addition, a chemical and physical activations were used, carbonization at 350 ºC and nitric acid solution. The study indicates that adlai shells are an effective adsorbent for Cu (II) from wastewater and that adsorptions is an endothermic process.

According to Inyang et al., [21] biochar is an alternative adsorbent to remove heavy metal from wastewater. Normally biochar is produced by a thermic treatment (e.g. pyrolysis) of carbon-rich biomass such as agricultural and forest residues, industrial wastes, municipal solid waste, tires, papers and bones. This review presents the adsorption capacities for Cu (II) with different biochars in a range of 0.4 to 52.1 mg g^{-1}. Another study also presented biochar as an effectively adsorbent for removal of copper and zinc in aqueous solutions. The biochar was produced from wood or corn straw [22]. Tong et al., [5] referred that the pulverization before pyrolysis can greatly enhance the adsorption capacity of biochars to remove Cu (II) from aqueous solution. Biochars can also be obtained from switchgrass (300 ºC) to remove uranium from groundwater [23] and pine wood (700 ºC) to remove Cu (II) [24].

A review presented by Mohan et al., [25] referred several biochar to remove Cu (II) such as: corn straw, orange waste, rice husk, olive pomace, compost, cow manure, pig manure, dairy manure, hardwood, peanut straw, soybean straw, canola straw, switchgrass, softwood and pinewood. From these biochars the cow manure, pig manure and peanut straw presented a maximum adsorption capacity of 90 mg g^{-1}.

The thermal treatment of adsorbents usually improves the adsorption capacity [10, 17]. However, it is required a huge amount of energy to produced such adsorbents. Therefore, it is necessary to develop new methodologies to apply the natural adsorbents with less pre-treatment.

In order to measure the capacity of the adsorbent for a metal equilibrium isotherms are usually applied to the results. The most common are the Langmuir and Freundlich isotherms. In Table 1 some studies concerning the Cu (II) removal are presented for Langmuir and Freundlich isotherms parameters.

Table 1 – Copper removal from wastewaters

Adsorbent type	Langmuir Model		Freundlich Model		Reference
	K_L (L mg^{-1})	q_{max} (mg g^{-1})	K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$)	**n**	
Biochar Corn straw (300 ºC)	0.682	12.52	3.71	3.605	[22]
Biochar Hardwood (450 ºC)	0.048	6.79	0.71	2.294	[22]
Biochar Olive pomace (300 ºC)	0.089	5.118	0.857	2.788	[26]
Orange waste(300 ºC)	0.077	4.921	0.783	2.827	[26]
Biochar Compost (300 ºC)	0.359	7.937	1.701	1.744	[26]
Biochar Sludge (650 ºC)	0.022	6.7	-	-	[27]
Peanut shells (W+D+M +S<30 µm)	0.022	25.39	3.09	2.97	[15]
Adlai shells (298 K)	0.3483	10.74	2.201	1.9231	[17]
Adlai shells (308 K)	0.3701	12.01	2.475	1.7473	[17]
Adlai shells (318 K)	0.6460	11.83	3.208	1.8706	[17]
Sunflower (W+D 80ºC + S < 1 mm)	0.091	9.8	0.466	3.21	[3]
Potato (W+D 80ºC + S < 1 mm)	0.023	10.5	0.141	1.66	[3]
Canola (W+D 80ºC + S < 1 mm)	0.021	11.6	0.085	1.47	[3]
Walnut shell (W+D 80ºC + S < 1 mm)	0.024	6.8	0.256	2.27	[3]
Pinion Shells	0.110	4.293	1.159	3.88	[28]

W – washed with distilled water; D – dried in an oven; S – sieved

The main goal of the present study is to investigate and describe the equilibrium of sorption of metals (e.g. Cu (II) and Ni (II)) on walnut and peanut shells in order to obtain the right adsorbent amount and the suitable operating conditions.

2. Materials and Methods

2.1. Adsorbents

In the present study were selected walnut (*Juglans regia L*) shells and peanut (*Arachis hypogaea L.)* shells to be used as natural adsorbents. The walnut and peanut shells were collected from source separated domestic wastes. The wastes were characterized according to granulometric analysis and moisture, volatile matter and ash.

A portion of the natural adsorbents was subjected to different treatments as shown in Table 2. The washing of adsorbent was performed during 1 h in order to remove coloration and dust. The washed adsorbents were dried in an oven at 60 ºC for 24 h to reduce the water content. The dried adsorbents were manual crushed with a hammer and separated by sieving in different sizes (500 and 1,400 µm). The sieved fractions were used without any physical or chemical treatment. A part of natural adsorbents was carbonized at T = 550 ºC during 24 h.

Table 2 - Experimental conditions tests

Treatment	Parameter
Natural	-
Washing with distilled water and drying	Temperature: 60 ºC
Sieving	Different particles size: 0,5 and 1,4 mm
Carbonization	Temperature: 550ºC

2.2. Adsorbate preparation and analytical experiment

In order to simulate industrial wastewaters an aqueous stock solution of copper sulphate ($CuSO_4 \cdot 5H_2O$) were prepared with 5g L^{-1}. From this solution several others were prepared with the following concentrations 0.05; 0.10, 0.2, 0.3, 0.4 and 0.5 g L^{-1} for preliminary studies and chosen the concentration 0.3 mg L^{-1} adsorption tests.

The concentration of Cu (II) was determined by iodometric method with excess of potassium iodide, titration with starch as an indicator and sodium thiosulfate as titrant [29].

2.3. Adsorption tests

The adsorptions tests were carrying out in batch mode varying the adsorbents dose or the metal concentrations. The tests were carried out with a working volume of 100 to 150 mL in an orbital agitator with a mixing rate around 150 rpm [17].

The batch adsorption experiments were carried out at room temperature (between 24 to 26 ºC) at different contact times without pH adjustment; however the pH was measured at the beginning and end of each test. The contact times were 0.25, 0.5, 1 and 2 h. The pH was in the range of 4 to 5 for all adsorption tests except the thermal treated adsorbents [10 to 11].

After shaking the sample were filtrated to remove all the adsorbents and the concentration of Cu (II) was determined.

To assess the effect of particle size on Cu (II) adsorption, particles with average diameter of 0.5 mm and 1.4 mm were used with an initial Cu (II) concentration of 0.3 g L^{-1}.

The concentration of Cu (II) retained in the sorbent phase (q_e, mg g^{-1}) was calculated from equation 1, and percentage of Cu (II) removal was evaluated from equation 2.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%\,Removal = \frac{(C_0 - C_e)}{C_0} \quad (2)$$

Where: C_0 and C_e are the initial and final (equilibrium) concentration of Cu (II) in solution (mg L^{-1}); V is the volume (L) and m is the mass of the adsorbent (g).

2.4. Adsorption calculations

The adsorption equilibrium can be described by a number of models available in the literature, but as evident from the literature, Langmuir and Freundlich are the most widely used isotherm models [10].

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy. This model is expressed by equation 3.

$$q_e = q_{max} \frac{K_L C_e}{1 + k C_e} \quad (3)$$

Where q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L is the Langmuir constant that is related to the affinity of binding sites and is related to the energy of sorption, (L mg^{-1}).

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model is represented by equation 4.

$$q_e = K_F {C_e}^n \quad (4)$$

Where K_F ((mg g^{-1})(L $mg^{-1})^{1/n}$) and n are Freundlich constants related to capacity and intensity of adsorption, respectively. The magnitude of n gives an indication of ability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [30].

The applicability of Freundlich and Langmuir isotherms to the equilibrium sorption was studied using standard straight line equations. The generalized linear form of the Langmuir isotherm is represented by the equation 5 and linear form of Freundlich isotherm is represented by the equation 6.

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (5)$$

$$log\ q_e = \frac{1}{n} log\ C_e + log\ K_F \qquad (6)$$

3. Results and discussion

3.1 Characteristics of adsorbents

In the preliminary adsorbents characterisation it was estimated the amount of shells produced per kilogram of walnuts or peanuts. The results showed a significant difference from those presented by INE for walnuts with 0.56 kg of shells per kg adsorbent. For peanut the results was similar 0.26 kg of shells per kg.

Results of granulometric analysis of peanut and walnut shells waste are in Table 3. The granulometric analysis shows that most of the particles, 94.09 % by weight of walnut shell, has an equivalent diameter greater than 2 mm, this percentage decreases slightly to the sample of peanut shell (80.72%). This fact may mean a low adsorbent power because smaller particle size has the higher the surface area per unit weight of adsorbent and hence higher percentage of metal removal expected [12, 31]. However some studies showed that for very porous materials, particles size has not greatly influence in adsorption capacity [32].

The moisture content was 5.56 % of weigh for peanut shells and a double value was obtained for walnut shells (10.52 %) (Table 4). This low moisture content facilitates the preparation of this solid as adsorbent and means a small mass loss on drying. However both types of shells have a high percentage of organic matter, which means a high weight loss in carbonization treatment. This result was expected since the shells have a high concentration of cellulose, lignin, proteins and lipids [10, 11]. Low ash content, may mean a rich source for activated carbon generation [10].

Table 3 - Peanut and walnut shells granulometric analysis

Size	Fraction (%)	
(mm)	Peanut	Walnut
>2	80.72	94.09
1.40	8.72	3.56
1.00	2.81	1.06
0.50	3.98	0.82
0.25	1.48	0.25
<0.25	2.28	0.21

Table 4 - Peanut and walnut shells characteristics

Shells	% weight		
	Moisture	Volatile matter	Ash
Peanut	5.56	94.28	5.38
walnut	10.52	99.01	0.89

3.2. Effect of particle size

The effect of particle size on Cu (II) removal was studied on walnut and peanut shells washed, dried in an oven at 60 ºC sieved with a diameter of 0.5 and 1.4 mm. These studies were carried out to the initial concentration of 0.3 mg L^{-1} Cu (II). Fig. 1 and 2 show the percentage removal of Cu (II) by walnut and peanut shell at different particles diameter. It was found that increase in the particles diameter, from 0.5 mm to 1.4 mm, causes a decrease of adsorption efficiency for Cu (II) by walnut and peanut shells. This result was expected since the adsorbent surface area per unit weight decreases when the particle diameter increases [11, 31].

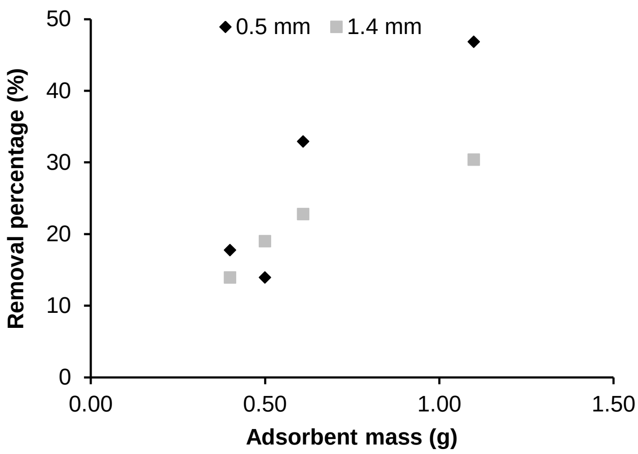

Fig 1 - Influence of particle size on the adsorption efficiency of Cu (II) onto dry peanut shells at 60 ºC with a contact time = 15 min

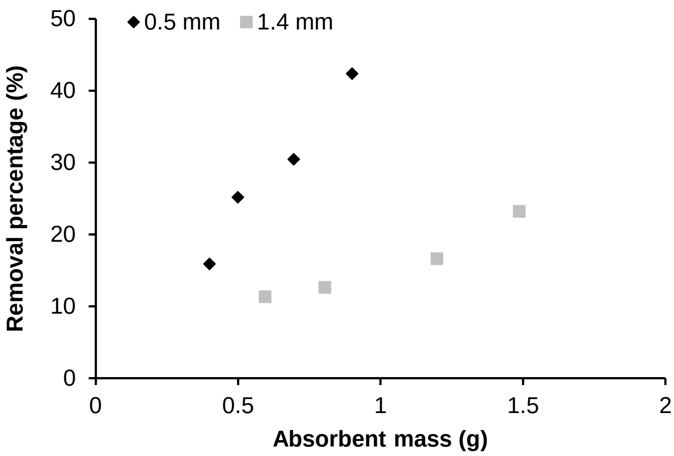

Fig 2 - Influence of particle size on the adsorption efficiency of Cu (II) onto dry walnut shells at 60 ºC with a contact time = 30 min

3.3. Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Cu (II), with peanut and walnut shells washed, dried in an oven at 60 ºC and sieved with a diameter of 0.5 and 1.4 mm, is shown in Fig 1 and Fig 2 respectively.

The results clearly show an increase of Cu (II) removal with growth in dose for both adsorbents used. The observed enhancement in adsorption yield with increasing adsorbent concentration could be due growth in the number of possible binding sites and surface area of the adsorbent [12, 15].

3.4. Effect of adsorbent type

Comparing the Cu (II) removal using walnut shells and peanuts shells under the same conditions (dry shells at 60 ºC with a C_0 = 0.3 g L^{-1}; contact time = 30 min and T = 25.5 ºC) was found that the percentage removal is greater for peanut shells as show in Fig 3.

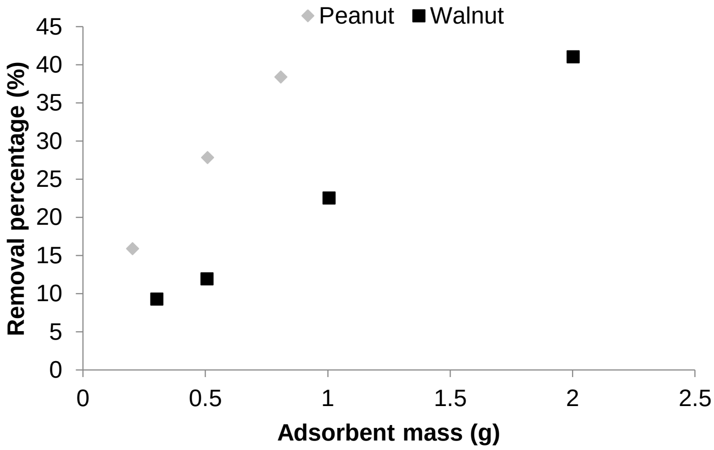

Fig 3 - Influence of adsorbent type on the adsorption efficiency of Cu (II) onto dry shells at 60 ºC

3.5. Effect of time

A higher contact time increases the removal efficiency as represent in Fig 4 and Fig 5. Comparing the percentage removal of dry walnut shells at the same condition (60 ºC with a C_0 = 0.3 g L^{-1}; and T = 25.5 ºC). For example, with an adsorbent mass of 1.5 g it was found that increase in contact time induce a growth of percentage removal from 11.4% to 23.2%.

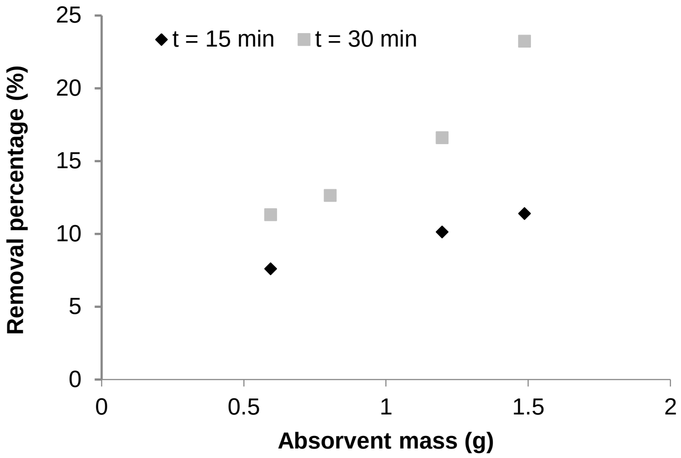

Fig 4 - Influence of time on the adsorption efficiency of Cu (II) onto dry walnut shells

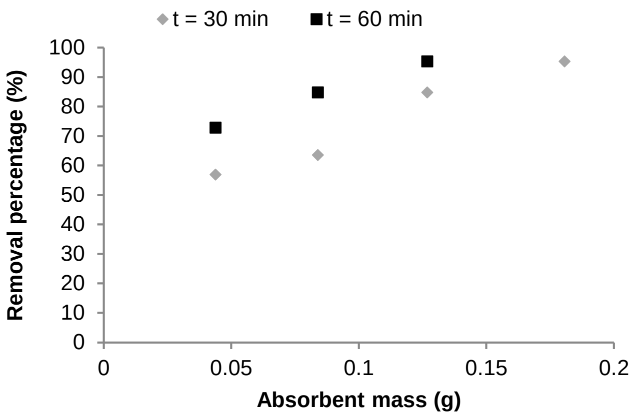

Fig 5 - Influence of time on the adsorption efficiency of Cu (II) onto peanut carbonized

3.5. Effect of adsorbent treatment

Thermal treatment (carbonized peanut shells) have higher adsorption capacities compared to untreated material as shown in Fig 6 which compares adsorption efficiency of Cu (II) with dry peanut shells, with identic condition (t = 30 min and C_0 = 0.3 mg L^{-1}). The carbonized treatment created changes in nature and concentration of surface functional groups of adsorbent. It can increase the surface area and porosity of some adsorbents resulting in increased adsorption capacity [10, 17]. However, treatments increase the cost and should be taken into account.

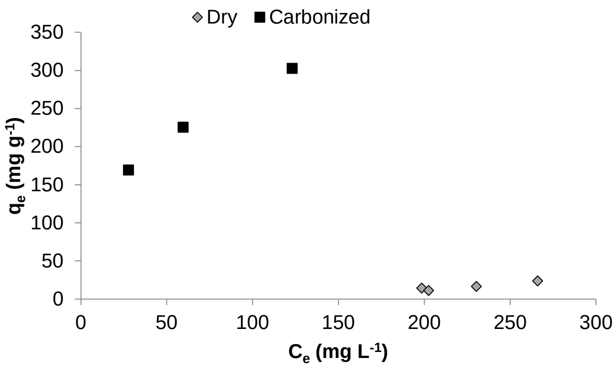

Fig 6 - Influence of treatment on the adsorption efficiency of Cu (II)) onto carbonized and dry peanut shells

3.6. Adsorption isotherm of Cu (II)

Adsorption isotherms describe the relationship between adsorbed component retained in the sorbent phase (q_e, mg g^{-1}) and the equilibrium concentration (Ce). Determination of equilibrium parameters provides important information that allows for future design of adsorption systems.

The experimental equilibrium data obtained were fitted with Langmuir model (equation 5) and Freundlich model (equation 6). The parameters of Langmuir and Freundlich models used to describe metal sorption are showed in Table 5 for peanut shells and in Table 6 for walnut shells.

Table 5 – Isotherms for peanut shells

Adsorbent	Time (min)	Freundlich isotherm			Langmuir isotherm		
		K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$)	n	R^2	K_L (L mg^{-1})	q_{max} (mg g^{-1})	R^2
Natural (Ø = 1,4 mm)	30	0.061	0.585	0.935	-	-	-
Drying (Ø = 1,4 mm)	30	0.188	0.857	0.940	-	-	-
Carbonized	30	1.274	0.539	0.974	5.523	263.15	1
	60	1.491	0.546	0.886	0.152	303.03	0.918

Table 6 – Isotherms for walnut shells

Adsorbent	Time (min)	Freundlich isotherm		
		K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$)	n	R^2
Natural (Ø = 1,4 mm)	30	0.968	2.77	0.998
Drying (Ø = 1,4 mm)	15	1.246	1.97	0.998
	30	9.985	6.79	0.895

In this study the Freundlich model describe more often the adsorption data than Langmuir model, with high correlation coefficients values (R^2 > 0,89). The fact that Langmuir isotherm failed to apply in this case could indicate that the adsorption of Cu (II) ions was not limited to a monolayer mechanism [30]. Identical results were obtained for Cu (II) by other studies [17, 30, 33].

The good correlation of the Freundlich model to the experimental data can be explained by the fact that this model can frequently be applied for small concentration of adsorbed component [26, 30] and for highly heterogeneous sorbent systems [34].

The values of K_F and n obtained in the experiment tests with peanut shells are smaller than the values obtained with walnuts, indicating an increased adsorption capacity and adsorption intensity.

The result shows that the values of n are smaller than 1 for peanut shells indicating poor sorption characteristics (Table 5), for walnut result shows that the values of n are greater than 2 indicating that the Cu (II) are favorably adsorbed [30].

The obtained n values for peanut are generally lower than those reported in other studies (Table 1) however, it should be noted that adsorption characteristics largely depend on many parameters such as particle size, pH of the solution [11, 33].

As described by several other studies [3, 5, 6, 12, 15-17, 22, 27, 28] and in recent reviews [10, 21], it was found that the adsorption capacity is highly dependent on the system conditions: adsorbent type and dose, size of adsorbent, contact time and type of treatment.

The highest Cu (II) removal percentage were obtain when using the carbonized peanut shells. Only with these conditions the Cu (II) concentration was below the recommended values by EPA [7] and national legislation [8].

4. Conclusions

The study aimed to selected, prepare and characterize natural adsorbents in order to evaluate their adsorption performance. The results revealed that the selected adsorbents remove Cu (II) from water.

For all conditions the highest Cu (II) removal percentage were obtain when using the carbonized peanut shells. However, the carbonized treatment increases the cost to prepare the adsorbents to industrial scale and should be taken into account.

Therefore it was necessary to optimize the conditions to obtain a good removal with lower costs, for example to further reduce the adsorbents size. It was found that the amount of Cu (II) adsorbed increased under the condition that the particle size of the sorbent decreased.

Regarding the adsorption equilibrium was best described by the Freundlich isotherms.

The work is still in progress with other metals and shells, preliminary assays were carried out in order to select the adequate adsorbents and conditions.

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To the several agriculture industries for wastes assignment.

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