



Removal of metallic cations from aqueous solutions using acorn pericarp fractions of *Quercus ilex* as new biosorbents

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Received: 11 February 2021 / Revised: 12 October 2021 / Accepted: 24 April 2022 / Published online: 22 May 2022

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Abstract

Acorn pericarps of the Algerian holm oak (*Quercus ilex*) constitute a largely underexploited forestry co-product. In the aim of valorization, adsorption efficiencies of crude, parietal, and lignocellulosic fractions of acorn pericarps were evaluated towards lead, cadmium, nickel, and copper ions. The results were modeled using Langmuir and Freundlich isotherms. The best results were obtained with the lignocellulosic fraction towards lead and cadmium with q_{\max} values of 370.37 and 303.03 mg.g⁻¹, respectively. On the contrary, crude and parietal fractions showed the highest capacities for nickel and copper, with q_{\max} values of 200 and 303.03 mg.g⁻¹, respectively. This work thus provides the first trial of acorn pericarps of oaks growing in northwest Algeria as an efficient biosorbent for the removal of metallic cations from aqueous solutions, whose adsorption capacities surpass most of the previously described biosorbents.

Keywords Adsorption · Isotherm model · Metal cations · Pericarp fraction

Introduction

Water pollution by metallic trace elements (MTE) is of great environmental concern. MTE such as cadmium, copper, mercury, lead, nickel, and zinc, present in various industrial effluents, appear on the high-priority list of hazardous pollutants in water and soil (Ahmaruzzaman and Gupta 2011; Sharma et al. 2019).

The use of agricultural and industrial wastes to purify wastewater has been the subject of several in-depth studies (Bailey et al. 1999; Mohan et al. 2014; Vikrant et al. 2018) which showed that biosorption is a cost-effective tool for wastewater treatment. These materials are inexpensive, available at large scale and reusable

(Barka et al. 2013). Successful adsorption of metal ions by agricultural waste mostly depends on their lignocellulosic content; solvent-exposed phenol and carboxylate groups of lignin constitute major fixation sites for MTE (Haroon et al. 2017). In addition, unconventional biosorbents have also been evaluated, which were obtained by chemical modification of raw materials, e.g. by increasing the number of surface carboxyl groups (Astier et al. 2010; Hachem et al. 2012; Wang et al. 2016). However, the practicality of these methods is limited by the use of toxic substances and/or organic solvents, expensive equipment, and lengthy protocols (Yeo et al. 2012). Therefore they do not offer real advantage over conventional methods.

Oaks (*Quercus*) represent an important forest resource in Algeria since they account for about 40% of the Algerian forest (Louni 1994). Among the several species of the *Quercus* genus, the dominant one in Algeria is the holm oak (*Quercus ilex*) (Hochbichler 1993; Solymos 1993). Acorns, called achenes, are made up of two starchy cotyledons which constitute the edible part. They are consumed either alone or mixed with wheat couscous semolina (Charef et al. 2008). Pericarps are considered as a waste. In the course of our studies on the valorization of natural products, we have been interested in studying acorn pericarps with the aim of developing a simple, efficient, and environmentally friendly technique for the removal of trace metals from water. The chemical composition of acorn pericarps, and more precisely their phenolic and carboxylic acid contents, highlights their high cation-exchange capacity. The present work describes for the first time

Editorial responsibility: M. Abbaspour.

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the adsorption capacities of different fractions of acorn pericarps from *Q. ilex*—the crude, parietal and lignocellulosic fractions—towards four trace metallic cations: lead, cadmium, nickel, and copper.

Materials and methods

Plant material

Due to its abundance in the North-West Algeria forest, the acorn species (*Q. ilex*) was chosen, and acorns samples were collected in December 2016 in the Saida region (34°48'45.5"N 0°09'43.5"E). After cleaning, pericarps were manually detached from acorns, then dried in a ventilated oven (40 °C), milled (particle size < 200 µm), and stored in desiccators at room temperature.

Preparation of the biosorbents

Parietal (R_1) and lignocellulosic (R_2) fractions were isolated from pericarps (R_0) according to the methods of Bailey 1967 and Carpita 1984 (Fig. 1). Briefly, the milled powders were subjected to 80% ethanol (v:v) extraction at 90 °C with continuous stirring for 20 min. The solid residue (parietal fraction R_1) consisted of cellulose, pectin, hemicelluloses, and lignin. Pectins were removed from R_1 by two successive extractions, first with H_2O at 100 °C for 20 min, and then with 1% ammonium oxalate at 85 °C for 2 h. R_2 , the lignocellulosic fraction of pericarps, was finally obtained after removal of hemicelluloses from R_1 by two successive extractions, first with 4.3 M KOH and then

4.3 M NaOH at 22 °C for 24 h. During all these fractionation steps, the same method of separation of the solid residue from the solution was used: filtration on sintered glass (porosity 3).

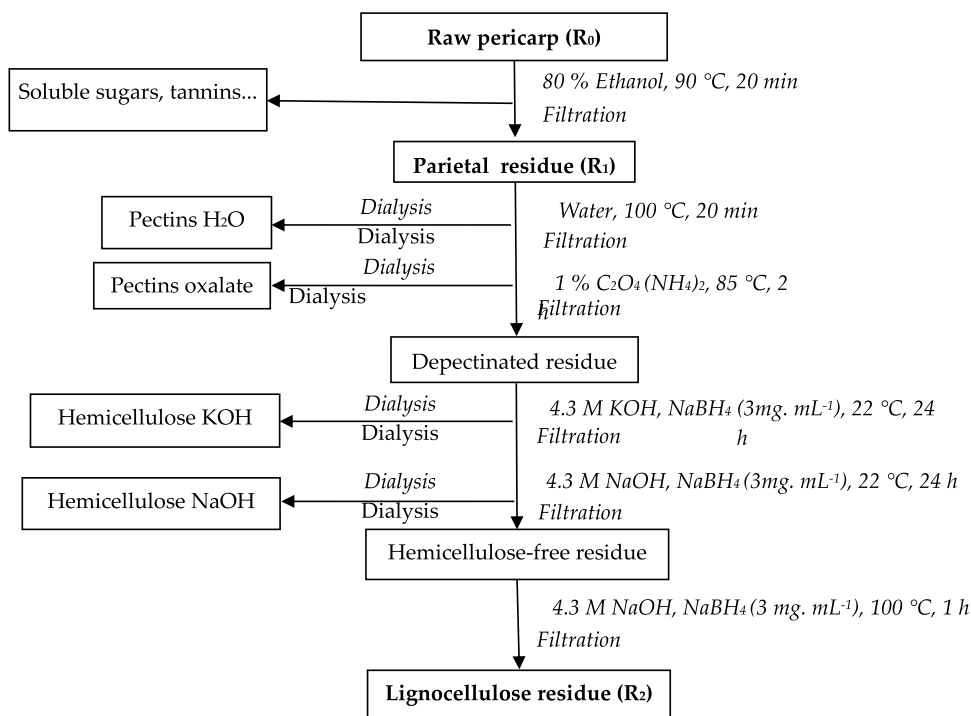
Batch biosorption experiments

Solutions of MTE were prepared by dissolving cadmium nitrate ($Cd(NO_3)_2$), lead nitrate ($Pb(NO_3)_2$), copper nitrate ($Cu(NO_3)_2$), and nickel nitrate ($Ni(H_2O)_6(NO_3)_2$) in Milli-Q deionized water (Millipore system). Adsorption experiments were conducted by stirring 0.1 g of each fraction (crude, parietal or lignocellulosic fraction) with 50 mL MTE cation solution in the following concentration ranges: 0–2,000 $mg.L^{-1}$ for Pb(II), and 0–1,000 $mg.L^{-1}$ for Cd(II), Ni(II) and Cu(II). The pH of these solutions was adjusted to 5.0 by dropwise addition of 0.1 N HNO_3 . The flasks were placed on an orbital shaker platform and shaken at 250 rpm. After 2 h of equilibration at room temperature, the biosorbent was separated from the solution by vacuum filtration through a sintered glass filter (porosity 3).

Metal ion quantification

Residual MTE concentrations infiltrates were determined by flame atomic absorption spectrometry with a Perkin Elmer Analyst 400 spectrophotometer; wavelength was set at 217.0, 228.8, 341.1, and 216.6 nm for lead, cadmium, nickel, and copper, respectively. Standards were made up in the following concentrations ranges: lead: 0.5–10 $mg.L^{-1}$ cadmium: 0.5–3 $mg.L^{-1}$, nickel: 1–15 $mg.L^{-1}$.

Fig. 1 Isolation of the lignocellulosic fraction residue from acorn pericarp



L^{-1} , copper: 0.5–5 $mg.L^{-1}$. Adsorption capacity was obtained from Eq. 1 (Hameed et al. 2008)

$$qe = \frac{(C_i - C_e)V}{W} \quad (1)$$

where qe is the equilibrium adsorption capacity expressed in mg of cation per g dry weight of biosorbent ($mg.g^{-1}$), V is the volume of the heavy metal solution (L), C_i and C_e are the initial and final free heavy metal concentration ($mg.L^{-1}$) before and after incubation, respectively, and W is the dry weight of biosorbent (g).

Results and discussion

Yield of pericarp fractions

The results obtained show that the yield of parietal residues or cell wall residue from pericarp is important since it represents 88.9% of the dry mass of the *Q.ilex* pericarps (Table 1). The lignocellulosic residue remains the major component of the cell wall (nearly half of the initial dry mass), confirming the secondary nature of the walls. Our previous work indicated that the cell wall of the holm oak pericarp contains also pectins and hemicelluloses (Mébarki et al. 2019a). The biosorption phenomenon is generally presented as an exchange between the metal cations present in solution and protons of the solvent-exposed surface of lignocellulosic or polysaccharidic materials such as the carboxylic acid functions of pectins (Thakur et al. 2019), or the phenolic functions of condensed tannins (Qiu et al. 2019) and lignins (Li et al. 2016). Other constituents might also be involved, notably hemicelluloses or cellulose (Dhabhai et al. 2018).

Batch biosorption studies

Biosorption isotherms

The experimental isotherm at adsorption equilibrium is represented by plotting the adsorbed quantity q_e ($mg.g^{-1}$) against C_e ($mg.L^{-1}$) at constant temperature. The isotherms of metallic cation adsorption on the crude, parietal, and lignocellulosic fractions of the pericarp of *Q.ilex* are shown in Fig. 2. According to the classifications proposed

by Brunauer et al. (1940), the adsorption isotherms obtained with the different fractions, whatever the MTE studied are of types II and III, and they are generally observed for adsorbents with a wide range of pore sizes. For each system, there is a continuous progression with the creation of adsorption multilayers. This is due to capillary condensation in the mesopores. It could also be mentioned that an absorption process might occur and so could contribute to the retention of MTE by the biosorbent. Brunauer et al. (1940) proposed a classification of physical adsorption isotherms into five classes, based on van der Waals' theory of adsorption. Class I corresponds to the so-called "Langmuir isotherm" and type II and III to the "sigmoid" isotherm (Balbuena and Gubbins 1992). A quick analysis could result in misinterpretation of the results. Indeed, if at first sight, the curves described differ only moderately, the mathematical interpretation of these data according to the Langmuir and Freundlich models allows the characterization of the adsorption mode of each one of the different cations on the different residues of pericarps.

Isotherm models

Isotherm models are generally studied to describe the adsorption process and the related mechanisms (Haroon et al. 2017). Langmuir and Freundlich are two widely used models of isotherms.

The Langmuir adsorption model (Langmuir 1918) assumes that ligands adsorb as a monolayer at active homogeneous sites on the adsorbent surface and that these adsorbed ligands do not interact with each other. Langmuir's Eq. (2) and its linearization (3) are as follows:

$$qe = \frac{q_{max} \cdot K_L \cdot Ce}{1 + K_L \cdot Ce} \quad (2)$$

$$\frac{1}{qe} = \frac{1}{q_{max}} + \frac{1}{K_L \cdot q_{max}} \cdot \frac{1}{Ce} \quad (3)$$

where: qe : the amount of trace element adsorbed by the adsorbent at equilibrium (mg of ions per g of biosorbent); q_{max} : the maximum adsorption capacity (mg of ions per g of biosorbent); K_L : the Langmuir equilibrium constant that reflects the affinity between adsorbent and the ligands ($L.mg^{-1}$); C_e : the concentration of metal ions in solution at equilibrium ($mg.L^{-1}$).

Another useful parameter in Langmuir equation is R_L , the degree of suitability, that describes the properties of the equation. R_L is defined by Eq. (4):

$$R_L = \frac{1}{1 + K_L \cdot C_i} \quad (4)$$

The value of R_L is representative of the state and quality of the adsorption isotherm model. If $R_L > 1$, $R_L = 0$, $R_L = 1$ and $0 < R_L < 1$, the process is considered to be unfavorable, irreversible, linear or favorable, respectively (Foroutan et al. 2019; Vafakhah et al. 2016).

Table 1 Fraction yields from acorn pericarp of *Q.ilex*

	Residue of cell wall (R_1)*	Lignocellulosic residue (R_2)**
Yields (%)	88.9 ± 2.30	48.9 ± 8.5

*Percentage weight of the 15 g starting pericarps powder (dry weight)

**Weight % from the cell wall residue

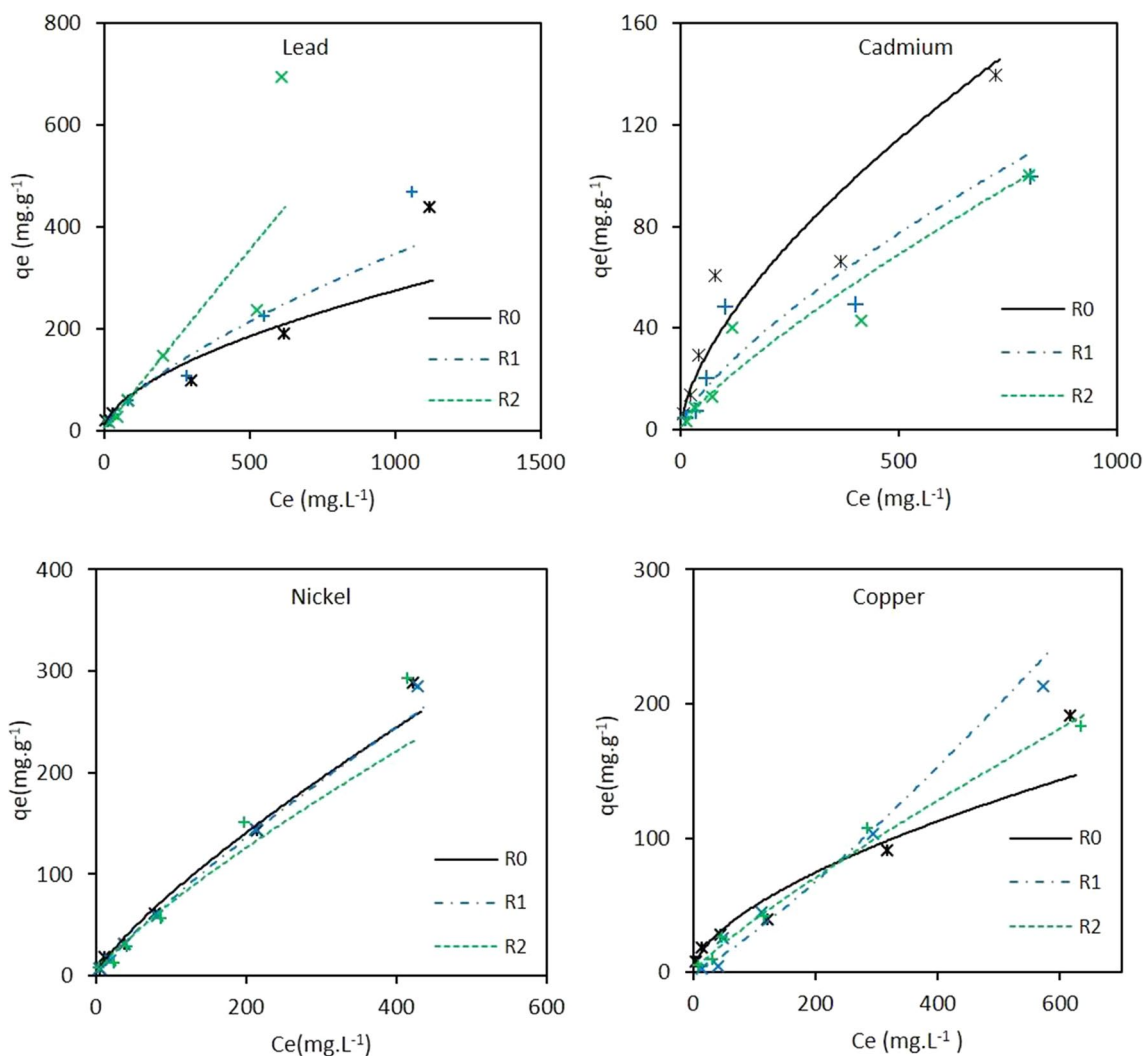


Fig. 2 Lead, cadmium, nickel and copper adsorption isotherms on crude (R_0), parietal (R_1) and lignocellulosic (R_2) fractions of acorn pericarp of *Quercus.ilex*

The Freundlich isotherm is frequently used to describe adsorption on heterogeneous surfaces (Freundlich, 1906). It is described by the following equation:

$$qe = K_F \cdot Ce^{1/n} \quad (5)$$

where qe ($\text{mg} \cdot \text{g}^{-1}$) is the amount of trace element adsorbed at equilibrium, Ce ($\text{mg} \cdot \text{L}^{-1}$) is the concentration of the metal ion in solution at equilibrium. K_F and n are indicators of adsorption capacity and intensity, respectively (Vafakhah et al. 2016). K_F and n can be determined from the linearized plot of $\log qe$ versus $\log Ce$ as follows:

$$\log qe = \log K_F + \frac{1}{n} \log Ce \quad (6)$$

Figures 3 and 4 show the Langmuir and Freundlich equilibrium diagrams obtained from lead, cadmium, nickel, and copper

adsorption on the different residues. The values of the constants and other parameters of the two models are listed in Table 2.

The results obtained showed that in the cases of lead and cadmium, the highest value of the retention capacities (q_{\max}) was obtained with the lignocellulosic residue, ($370.37 \text{ mg} \cdot \text{g}^{-1}$ and $303.03 \text{ mg} \cdot \text{g}^{-1}$, respectively). These results surpass those obtained by Hachem et al. (2012) in the same experimental conditions with Douglas fir barks whose measured q_{\max} were $213.37 \text{ mg} \cdot \text{g}^{-1}$ (lead) and $67 \text{ mg} \cdot \text{g}^{-1}$ (Cadmium) after chemical modifications. Furthermore, these results surpass those of Li et al. 2016 who have reported maximum adsorption capacities of 325.2 and $257.2 \text{ mg} \cdot \text{g}^{-1}$ for these two ions, respectively, with thiosemicarbazide-modified chitosan.

On the contrary, for nickel, the highest q_{\max} value, $200 \text{ mg} \cdot \text{g}^{-1}$, was obtained with the crude residue, these results remain high compared to those obtained by Siti et al. (2013) with nickel on banana peel, rice straw, and tea waste with 6.88 , 35.08 and $15.26 \text{ mg} \cdot \text{g}^{-1}$

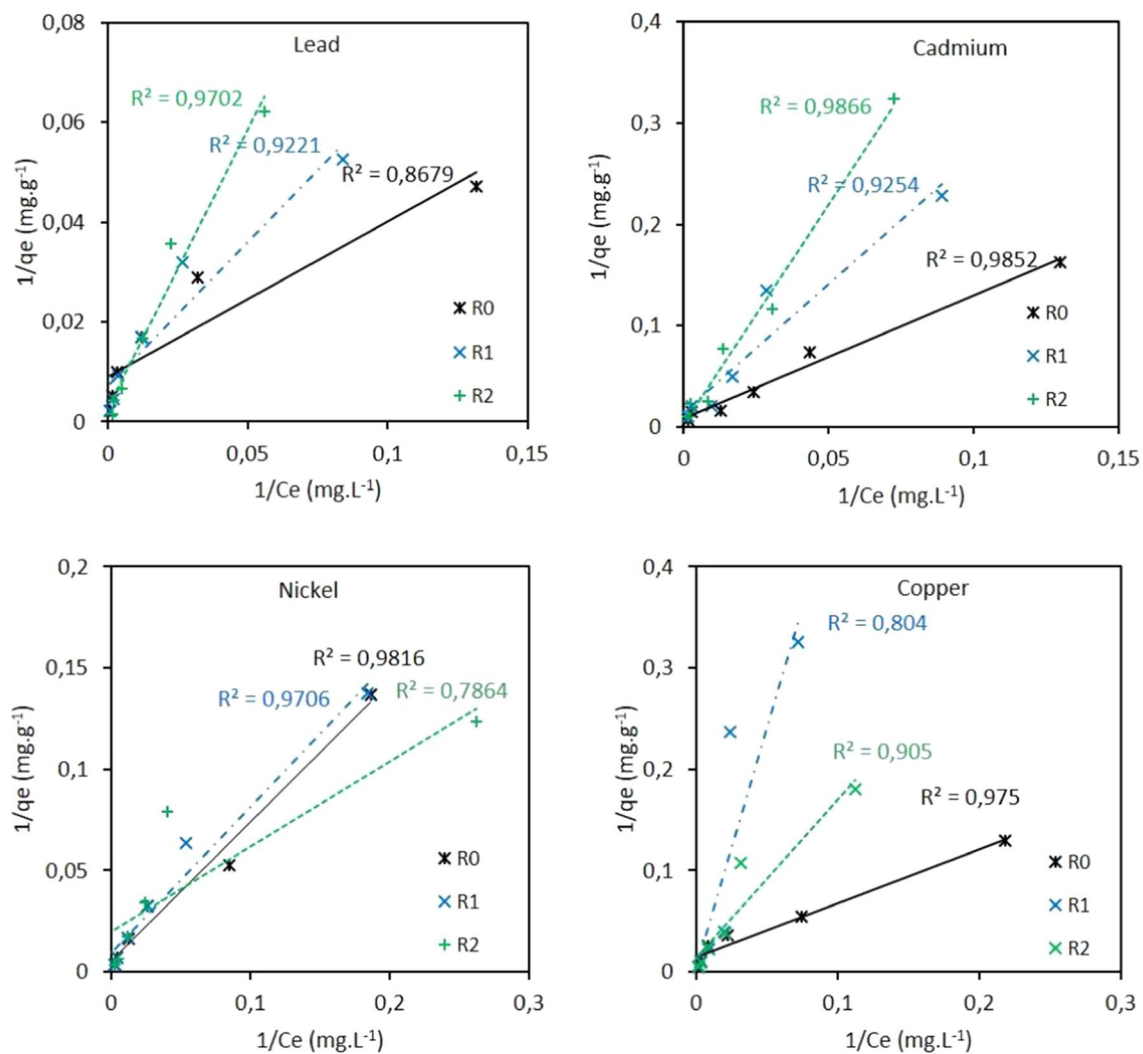


Fig. 3 Langmuir linearization of lead, cadmium, nickel and copper adsorption on the crude (R_0), parietal (R_1), and lignocellulosic (R_2) fractions of acorn pericarp of *Quercus ilex*

respectively. Adsorption capacities of copper were the highest on parietal residues with $q_{max} = 303.03$ mg.g⁻¹; this value was much higher than those recently achieved with other adsorbents for the removal of copper from aqueous solutions (Mébarki et al. 2019b; Moreira et al. 2019; Roozegar and Behnam 2019), with adsorption capacities ranging from 12.58 to 53.76 mg.g⁻¹.

In the present study, adsorption capacities were overall higher than those reported for other biosorbents cited in the literature (Table 3).

The R_L values displayed in Table 2 (ranging from 0.27 to 0.80) for the different residues (crude, parietal and lignocellulosic fractions) of pericarp acorn indicate that these materials are favorable for adsorption of the metallic trace element ($0 < R_L < 1$). In terms of affinity, the values (K_L) between 0.005 and 0.047 L.mg⁻¹ are broadly similar.

The variability of retention capacity as a function of the residue and the metal cation tested attests to sorbent selectivity which may

rely on the physical and chemical characteristics of metal cations (ionic radius, polarizability, hydration energy). According to the HSAB theory (Pearson 1987) lead is considered as a medium-strength acid and cadmium as a soft acid. The latter therefore has a stronger affinity for hydroxyl functions as compared with lead, which in turn has a stronger affinity for medium sites such as aromatic rings, which is why the interaction with lignocellulosic residues is more favorable in the case of lead than in the case of cadmium. However the lead cation has an ionic radius of 0.132 nm while those of the Cd, Cu, and Ni ions are 0.097, 0.096, and 0.069 nm respectively (Panayotova and Velikov 2002), so the latter (Ni) can more easily access the more congested sites. The structure of the crude fraction (R_0) is denser and probably less porous than those of the parietal and the lignocellulosic fractions. This is why the retention capacities of Ni are higher than those of the other three cations.

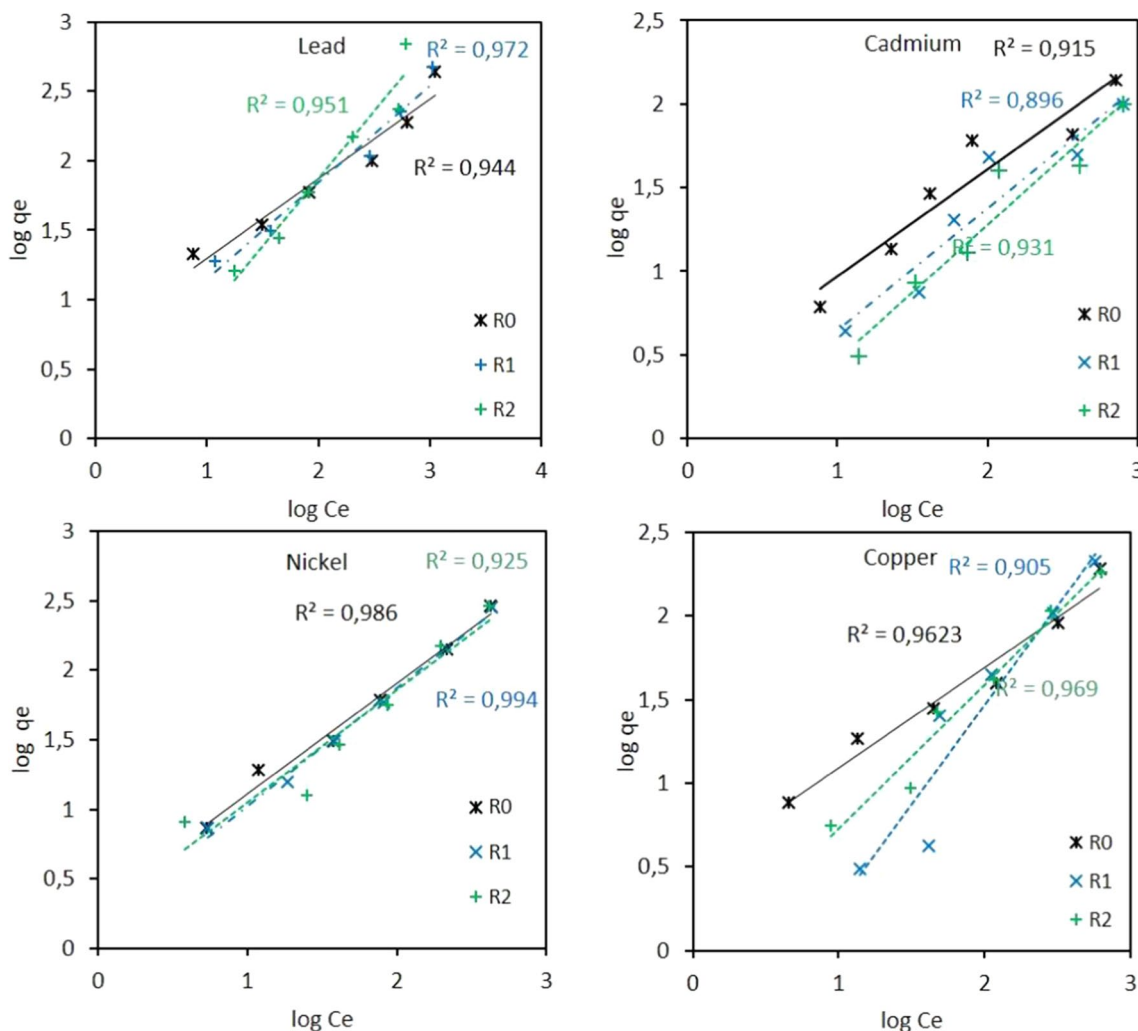


Fig. 4 Freundlich linearization of lead, cadmium, nickel and copper adsorption on crude residue (R_0), parietal residue (R_1), and lignocellulosic residue (R_2) of acorn pericarp of *Quercus.ilex*

Table 2 Langmuir and Freundlich parameters for MTE adsorption with the different fractions (crude, parietal and lignocellulosic fractions) of pericarp acorns of *Q.ilex*

Metals	Biosorbent	Langmuir isotherm			Freundlich isotherm				
		q_{max} (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R^2	R_L	K_F	$1/n$	n	R^2
Lead	R_0	111.11	0.029	0.86	0.40	5.24	0.57	1.74	0.94
	R_1	142.85	0.012	0.92	0.62	2.81	0.69	1.44	0.97
	R_2	370.37	0.022	0.97	0.47	0.85	0.97	1.03	0.95
Cadmium	R_0	119.04	0.006	0.98	0.76	2.08	0.64	1.56	0.91
	R_1	66.66	0.005	0.92	0.80	0.82	0.72	1.38	0.89
	R_2	303.03	0.007	0.98	0.74	0.48	0.80	1.25	0.93
Nickel	R_0	200	0.007	0.98	0.74	1.99	0.80	1.25	0.98
	R_1	106.38	0.013	0.97	0.60	1.44	0.85	1.17	0.99
	R_2	50	0.047	0.78	0.29	1.69	0.81	1.23	0.92
Copper	R_0	69.44	0.027	0.97	0.42	3.09	0.59	1.69	0.96
	R_1	303.03	0.006	0.80	0.76	0.12	1.18	0.84	0.90
	R_2	71.94	0.008	0.90	0.71	0.74	0.86	1.16	0.96

The maximum value obtained for each element either for Q_{max} (Langmuir isotherm) or K_F (Freundlich isotherm) are indicated in bold

Table 3 Main characteristics, and uptake capacities of various biosorbents used for the removal of metallic cations from aqueous solutions

Biosorbents	Metallic cations	Adsorbent dose (g/L)	Initial concentration (mg/L)	Sorption capacities (mg/g)	References
Peat moss	Lead	1	500	40	McLellan and Rock (1988)
	Cadmium	1	500	5.8	
	Copper	1	500	23	
Blast furnace sludge	Lead	50	48–7,100	64.17	López- Delgado, et al. (1998)
	Cadmium	50	5.1–970	6.74	
	Copper	50	4.5–3,000	16.07	
<i>Citrus limetta</i> leaves	Lead	1	5–100	69.82	Aboli et al. (2020)
	Nickel	1	5–100	58.139	
Marine macrophyte, <i>Cymodocea nodosa</i>	Cadmium	2	100	11.6	Moawad et al. (2020)
	Nickel	2	100	16.7	

Based on the correlation coefficients (R^2) presented in Table 2, it can be concluded that the Freundlich model is adequate to model the isotherms of copper, nickel and lead adsorption on the different residues of the pericarps, (R^2) ranges between 0.90 and 0.99. Therefore, among the two models used, the Freundlich isotherm model better matched experimental data, since the correlation coefficients R^2 ranged from 0.78 to 0.98 with the Langmuir model.

The highest of the 8 calculated K_F values were recorded with the crude fraction of acorn pericarp which reached $5.24 \text{ mg} \cdot \text{g}^{-1}$ for lead. This indicates a high adsorption capacity. Also, the values of $1/n$ lie between 0.57 and 0.8 which are close to zero. According to (Haroon et al. 2017) such values indicate a heterogeneity of the adsorption sites. These results should be related to the chemical compositions characteristic of the crude residue compared with the other fractions studied.

Conclusion

This study shows that acorn pericarps can be used as an efficient sorbent to remove metal cations from synthetic aqueous solutions. The results obtained by modeling the experimental isotherms of adsorption by the Langmuir and Freundlich models show that the latter (Freundlich) is adequate for modeling the adsorption process of copper, nickel and lead on the different residues of the pericarps. Indeed, the correlation coefficients R^2 lie between 0.90 and 0.99, while the Langmuir is adequate for modeling the isotherms of adsorption of cadmium. Adsorption capacities of crude acorn pericarps or parietal residues were higher than those of other previously described biosorbents. Furthermore, the results of the adsorption studies allow us to conclude that the selectivity of the pericarps with respect to metal cations can be optimized by diversifying the chemical composition of the residues to be tested. Comparatively to previous studies, this work has shown that it is possible to generate such functions directly on the structure by sequential extraction of

the constituent polysaccharides of the materials without scratching. Since acorn pericarps is freely abundant, cheap, locally available, and has a high adsorption capacity, it can be considered as economically viable for the elimination of trace metal elements in polluted water.

Acknowledgements This article is dedicated in memoriam to Professor Meriem Kaïd Harche, who initiated this work and who devoted her career to valorizing the Algerian plants. The authors also acknowledge Dr. M. Guillon for his help in manuscript editing.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by M. Mébarki, K. Hachem and C. Faugeron-Girard. The first draft of the manuscript was written by M. Mébarki and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding M.M. received a grant from Université des Sciences et de la Technologie d'Oran-Mohamed Boudiaf (Algeria).

Declarations

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

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