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Lignocellulosic fraction of the pericarps of the acorns of *Quercus suber* and *Quercus ilex*: isolation, characterization, and biosorption studies in the removal of copper from aqueous solutions

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Pericarps of Algerian *Quercus ilex* (*Q. ilex*) and *Quercus suber* (*Q. suber*) were used as copper adsorbents in artificially contaminated solutions. Exposing accessible lignocellulosic binding sites enhanced adsorption. The lignocellulosic fractions of *Q. suber* and *Q. ilex* (36.47±9.1 and 47.66±9.3, respectively) were characterized by FTIR before and after adsorption. The aim was to identify the functional groups adsorbing Cu(II). SEM/EDX determined lignocellulose surface morphology and composition. The amount of adsorbent-bound Cu(II) increased with initial [Cu(II)]. Cu(II) adsorption range was 23.59–48.06 $mg \cdot g^{-1}$ for *Q. Suber* and 22.56–38.19 $mg \cdot g^{-1}$ for *Q. ilex* when [Cu(II)] was 100–500 $mg \cdot L^{-1}$. Adsorption isotherms and Langmuir and Freundlich models of the *Q. suber* and *Q. ilex* lignocellulosic fractions indicated natural Cu(II)adsorption capacities (Q_{max}) of 53.76 $mg \cdot g^{-1}$ and 36.06 $mg \cdot g^{-1}$ and KF of 5.9 $mg \cdot g^{-1}$ and 7.43 $mg \cdot g^{-1}$, respectively.

Keywords: adsorption, Cu(II), lignocellulosic fraction, pericarp, *Quercus* sp..

INTRODUCTION

Water pollution by heavy metal cations is a major concern in developing countries including Algeria. Various techniques have been used to remove heavy metals from wastewater. These include adsorption[1], coagulation[2], advanced oxidation[3], membrane separation[4, 5], foam flotation[6], precipitation[7], ozonation[8], ion exchange[9], filtration[10], solvent extraction[11], electrolysis[12], synthetic oxidation[13], liquid-fluid extraction[14], and others. However, the main disadvantages of these methods are high operating costs and toxic waste production[15].They also require expensive equipment and monitoring systems and are often energy demanding. Moreover, many of them are only marginal effective.

The utilization of agricultural and industrial waste products to purify wastewater has been extensively investigated[5, 16, 17, 18, 19, 20]. Biosorption is a cost-effective wastewater treatment tool. The materials are inexpensive, freely available and reusable. They produce minimal biological and chemical sludge[21] and have high binding capacities for metalsions[22]. Therefore, they could be applied in novel and practical which would increase the value and utility of agricultural or forestry by-products[23, 24]. Several economical and environmentally friendly waste materials have been considered as biosorbents. These include *Eucalyptus sheathiana* bark, Moringa or *Sophora japonica* residues, espresso coffee grounds, tea leaves, rice husks, tobacco stalks, white cedar stem, crab shells, mustard biomass, sawdust, corn silk, water lettuce dry biomass, herbaceous plants, pine bark, yeast, nutshells, citrus peels, and dead or living microorganisms[25, 26, 27, 28].

Successful metal ion uptake by agricultural wastes depends upon lignocellulosic biomass with acidic functional groups such as phenolics and carboxylates on its surface. Heavy metals may form complexes with these groups by hydrogen ion substitution or electron pair donation[28].Various unconventional, cost-effective adsorbents have been developed which are derived from natural materials and have high adsorption capacities. Adsorption has been improved by increasing the number of accessible carboxylate groups[29, 30, 31] via covalent grafting of aminated oligogalacturonans[32]. However, the practicality of these methods is limited by the use of reactive toxic substances and/or organic solvents, costly equipment, and long protocols[33]. Therefore, they have no real advantages over conventional methods.

Copper is used extensively in electroplating, metallurgy, mechanical assembly, plumbing, construction, electrical wiring, and other industries. Copper-containing wastewater effluents are generated by copper mining, the electronic and electrical industries, computer heat sink production, ceramic glazing, glass coloring, and copper-based fungicide application. The World Health Organisation (WHO) recommends a drinking water threshold of 2.0 $mg \cdot L^{-1}$ for copper[34]. Excessive copper may damage the liver and kidneys and cause anemia and reproductive/developmental toxicity. Therefore, the copper content in drinking water must be reduced to an acceptable level to ensure copper homeostasis in the human body[35].

To the best of our knowledge, the present study is the first to test lignocellulosic fractions isolated from the acorn pericarps of *Q. ilex* and *Q. suber* as copper biosorbents. The pericarp is a waste product derived from acorn consumption and processing. Here, the Cu(II) ion adsorption capacities of the lignocellulosic fractions derived from the aforementioned oak tree species were compared. This paper proposes a new method of enhancing heavy metal adsorption using the accessible binding sites of the lignocellulosic fractions of plant cell walls.

EXPERIMENTAL

Plant material

Acorns were harvested from *Q. suber* and *Q. ilex*. These oak tree species are indigenous to north-western Algeria. *Q. ilex* acorns were collected from the Saida region (34°48'45.5"N, 0°09'43.5"E) and *Q. suber* acorns were sampled in the Oran region (35°38'20.3"N; 0°50'22.6"W) in December 2016. The acorns were cleaned and their pericarps were manually detached, dried in a ventilated oven at 40°C, milled (particle size < 200 μm), and stored in desiccators at room temperature.

Adsorbent isolation and preparation

The lignocellulosic fractions were isolated from the pericarps in triplicate according to the methods of Bailey[36] and Carpita[37]. The milled pericarp powder was continuously stirred in 80% v/v ethanol at 90°C for 20 min to extract the cell wall residues (cellulose, hemicelluloses, pectin, and lignin). The pectin was removed by mixing the extract with H_2O at 100°C for 20 min followed by 1% w/v ammonium oxalate at 85°C for 2 h. The hemicelluloses were removed from the depectinated residue with a mixture of sodium hydroxide (NaOH) and potassium hydroxide (KOH) (4.3 M) at 22°C for 24 h. The final remnant was the lignocellulosic fraction.

Batch adsorption experiments

Cu(II)solutions were prepared by dissolving cupric sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) in double-distilled water. In 100 mL flasks, 0.1 g lots of the lignocellulosic fraction were mixed with 50 mL copper sulphate solution ranging in initial concentration from 100–500 mg·L^{-1} (pH 5). The flasks were placed on a mechanical agitator and shaken at 250 rpm. After 2 h equilibration at room temperature, the Cu(II) ion concentrations were determined by colorimetry for each flask[38]. Briefly, one volume of ammonium hydroxide (NH_4OH) was mixed with four volumes of the adsorbed copper sulphate solutions, forming a blue complex. Absorbances of these solutions were measured at 620 nm in a 6715 UV/Visible Jenway spectrophotometer (Cole-Parmer, Staffordshire, UK).

Adsorption capacity and % copper removal were calculated using Eqs. 1 and 2, respectively[39].

$$Qe = \frac{(Ci - Ce)V}{W} \quad (1)$$

$$\%RE = \frac{Ci - Ce}{Ci} \times 100 \quad (2)$$

where Qe is the equilibrium adsorption capacity per gram dry weight of the lignocellulosic fraction (mg·g^{-1}), V is the volume of the Cu(II) solution (L), Ci and Ce are the initial and final Cu (II) concentrations after adsorption (mg·L^{-1}), respectively, and W is the dry weight in grams of the lignocellulosic fraction.

CHARACTERIZATION

The lignocellulosic fraction was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX).

The lignocellulosic fractions of the pericarps were pelletized with potassium bromide (KBr). One-milligram samples were diluted with 100 mg KBr before and after adsorption to identify the functional groups involved. The FTIR spectra were evaluated by FTIR spectrophotometry (400–4.000 cm^{-1}; 4 cm^{-1} resolution; 32 accumulations) (Cary 600; Agilent Technologies, Santa Clara, CA, USA).

Adsorbent surface morphology and elemental composition were determined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

The lignocellulosic fractions were examined at 250× and 10.000× under a JSM-6610 SEM (JEOL Ltd., Akishima, Tokyo, Japan). Images were photographed under the secondary electron detector at an acceleration voltage of 20 kV.

Adsorbents were subjected to EDX analysis (EX--9430054L1Q; JEOL Ltd., Akishima, Tokyo, Japan) before and after Cu(II) loading. Adsorption of copper cation onto the surfaces of the lignocellulosic fractions was verified.

RESULTS AND DISCUSSION

Yield of lignocellulosic fraction

The net lignocellulosic fraction yields are shown in Table 1. The cell wall residue constituted 79.45 ±1.0%and 86.09 ±1.4% of the dry mass of the *Q. suber* and *Q. ilex* pericarps, respectively. The lignocellulosic fraction constituted 36.47 ±9.1% and 47.66 ±9.3% of the cell wall residues from the pericarps of *Q. suber* and *Q. ilex*, respectively.

Table 1. Lignocellulosic yields from pericarps of *Q. suber* and *Q. ilex*

	Cell wall residue*	Lignocellulosic fraction**
Q. suber	79.45 ± 1.0	36.47 ± 9.1
Q. ilex	86.09 ± 1.4	47.66 ± 9.3

*Percentage of the initial 15 g of acorn pericarp powder (dry weight);
**Weight % of cell wall residue

Q. ilex pericarps contained significantly more cell wall residue and lignocellulosic fraction than those of *Q. suber*. Genetic and environmental factors account for these differences. Saïda is a high plateau whereas Oran is a seacoast area. Moreover, geographic location, soil salinity, light intensity, hydration, plant species, harvest timing, and life cycle stage also influence the distribution and abundance of various compounds in plants[40, 41, 42].

Batch adsorption studies

The aim of this study was to determine the influence of the initial Cu(II) ion concentration on the adsorption capacities of lignocellulosic fractions derived from *Quercus ilex* and *Quercus suber* pericarps. Data are shown in Table 2 and in Figs. 1 and 2.

Figures 1 and 2 show that the quantity of Cu(II)adsorbed by the lignocellulosic fraction increased with initial Cu(II) concentration. From 100–400 mg·L^{-1} Cu(II), the adsorption capacities Qe increased from 23.59–48.06 mg·g^{-1} and from 22.56–38.19 mg·g^{-1}for *Q. suber* and *Q. ilex*, respectively.

The number of copper ions in solution and the copper absorption capacity increased with copper solution concentration. On the other hand, the % copper cation

Table 2. Copper adsorption by lignocellulosic fractions of *Q. suber* and *Q. ilex* pericarps

	Q. suber		*Q. ilex*	
Ci [mg/L]	Qe [mg/g]	%RE	Qe [mg/g]	%RE
100	23.59	47.18	22.56	45.13
200	27.50	27.50	23.81	23.81
300	39.72	26.48	28.81	19.21
400	38.06	19.03	34.44	17.22
500	48.06	19.22	38.19	15.27

Ci: initial concentrations of Cu(II)(mg/L); Qe: equilibrium adsorption capacity(mg/g); %RE: percentage removal

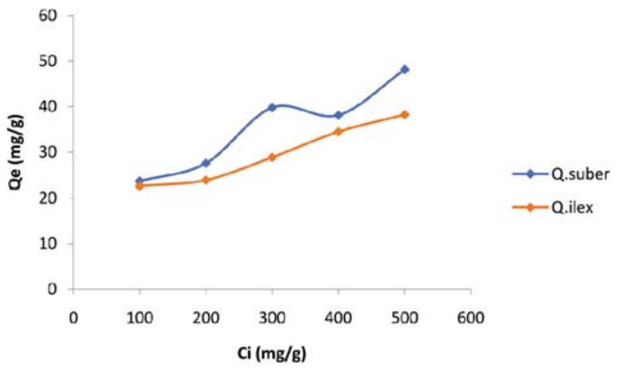

Figure 1. Effect of the initial Cu(II) concentration on lignocellulosic fraction adsorption capacities of *Q. suber* and *Q. ilex* pericarps

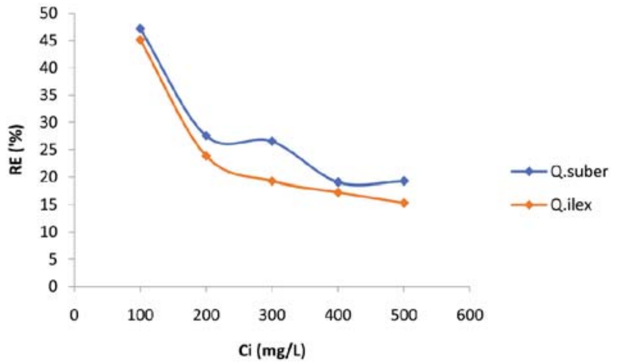

Figure 2. Effect of the initial Cu(II) concentration on the % adsorption removal by the lignocellulosic fractions of *Q. suber* and *Q. ilex* pericarps

removal by adsorption decreased with initial copper solution concentration from 47.18–19.22% and from 45.13–15.27% for *Q. suber* and *Q. ilex*, respectively.

The copper cation adsorption capacity of the lignocellulosic fraction prepared in the present study was higher than those reported for other biosorbents cited in the literature (Table 3).

Table 3. Copper retention capacities of selected biosorbents

Biosorbent	Q_{max} [mg/g]	References
Tomato waste (*Solanum lycopersicum)*	34.48	43
Corn stalk	20.8	44
Sugar beet pulp	16.14	45
Single-celled green algae *Chlorella pyrenoidosa*	12.58	46
Fungus *Penicillium ochrochloron*	8.98	47
Sorghum stem *Sorghum bicolor*	7.93	48
Banana stem *Musa acuminata*	6.49	
Casuarinas fruit *Casuarina equisetifolia*	4.54	
Pinion shell	4.29	49

FTIR analyses

The FTIR spectrum of the lignocellulosic fraction of *Q. suber* before Cu(II) adsorption showed a peak at 891 cm^{-1}which corresponds to a C-H deformation in cellulose. Another peak at 1.062 cm^{-1} represented a C-O stretch in polysaccharides[50]. A band at ~1.389 cm^{-1} is associated with a C-H deformation in polysaccharides and a C_{aryl}-O vibration in syringyl derivatives[51]. Peaks at 1.507 cm^{-1} and 1.595 cm^{-1} were related to the aromatic skeleton of lignin. The band at ~1.647 cm^{-1} is characteristic of C═O stretching in carboxylates. The bands observed at 2.891 cm^{-1} correlate with symmetric C–H stretching and CH_2 group vibration. The bands at 3.318 cm^{-1} are ascribed to the hydrogen-bonded O–H groups of cellulose and lignin.

After Cu(II) adsorption, the peaks in the FTIR spectrum of the lignocellulosic fraction shifted from 1.389 cm^{-1} to 1.378 cm^{-1}, 1.647 cm^{-1} to 1.645 cm^{-1}, 2.361 cm^{-1} to 2.359 cm^{-1}, 2.891 cm^{-1} to 2.899 cm^{-1}, and 3.318 cm^{-1} to 3.309 cm^{-1}. The band at 1.595 cm^{-1} disappeared (Figure 3). Therefore, the C-H, C=O, and O-H groups in the lignocellulosic fractions participated in Cu(II) adsorption.

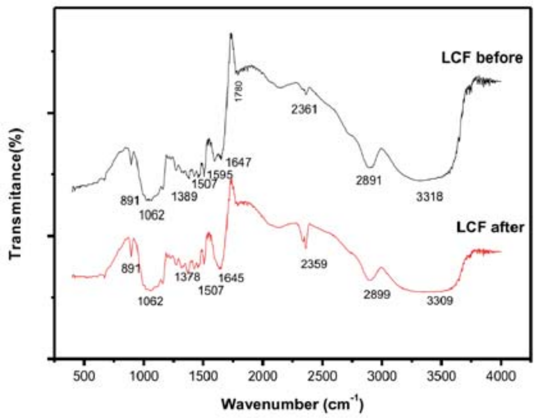

Figure 3. FTIR spectra of the lignocellulosic fraction (LCF) of *Q. suber* before and after Cu(II) adsorption

The lignocellulosic fraction of *Q. ilex* before copper adsorption produced spectral peaks at 671, 895, 1.059, ~1.375, 1.594, 1.645, 1.783 and 3.334 cm^{-1}.These peaks are associated with C-OH out-of-plane bending, C-H bending, C-O-C asymmetrical stretching, CH in--plane bending, C=C aromatic symmetrical stretching, C=O stretching vibration, and hydroxyl stretching, respectively.

Figure 4 shows the changes in the peaks from 1.783 cm^{-1} to 1.792cm^{-1}, 2.901 $cm^{-1}$to 2.891cm^{-1} and 3.334 cm^{-1} to 3.320 cm^{-1}. These shifts confirm that the C=O, C-H, and OH functional groups participate in Cu(II) adsorption.

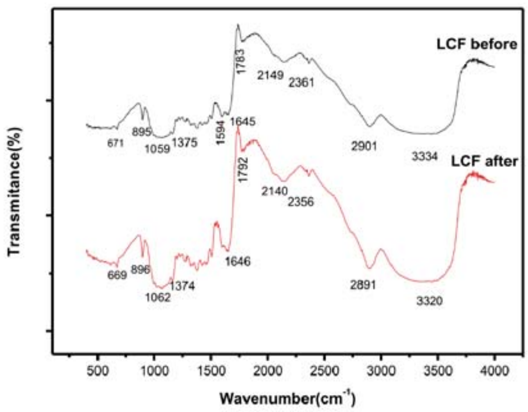

Figure 4. FTIR spectra of the lignocellulosic fraction (LCF) of Q. ilex before and after Cu(II) adsorption

SEM and EDX analyses

SEM and EDX confirmed that Cu(II) permeated the pores of the lignocellulosic fractions (LCF).

Adsorbent surface morphology was examined by SEM. Figs. 5a and 6c show that the surfaces of the LCFs of *Q. ilex* and *Q. suber* before Cu(II) adsorption were porous and rough and consisted of lignin-coated cellulosic fibers. In contrast, the pores on the LCFs after Cu(II) adsorption appeared to be filled. Fig. 6d shows white dots on the surface of the lignocellulosic fraction of *Quercus ilex* following Cu(II) adsorption. These artefacts may have formed from reactions between lignocellulose and copper cations[52].

The EDX spectra revealed the surface atomic distribution and elemental composition of the lignocellulosic fraction (LCF). The Cu(II) peak appeared at 8 KeV. The copper identified in the pre-adsorption fractions probably originated from the soil in which the oak trees grew[52]. After adsorption, the relative % copper mass increased from 0.01–0.08%and from 0.08–0.09% in the LCFs of *Q. ilex* and *Q. suber*, respectively[53].

C, O, Na, and K were also detected on the adsorbent surfaces. The Na and K found in the lignocellulosic fraction (Fig. 5b')were derived from the sodium hydroxide (NaOH) and potassium hydroxide (KOH) used to remove the hemicelluloses from the pericarp.

Langmuir isotherm model

The Langmuir adsorption model[54] disclosed that monolayer adsorption occurs at dynamic homogeneous sites on the adsorbent surfaces. However, the particles adsorbed there did not interact.

No Cu(II) particle transmigration was detected on the adsorbent surface. The Langmuir isotherm equation(3) and its linearization (4) are as follows:

$$Qe = \frac{\mathrm{Qmax.K.Ce}}{\mathrm{1+K.Ce}} \quad (3)$$

$$\frac{1}{\mathrm{Qe}} = \frac{1}{Qmax} + \frac{1}{K.Qmax}.\frac{1}{\mathrm{Ce}} \quad (4)$$

where Qe ($mg \cdot g^{-1}$) is the quantity of Cu(II) adsorbed at equilibrium, Q_{max} is the maximum adsorption capacity

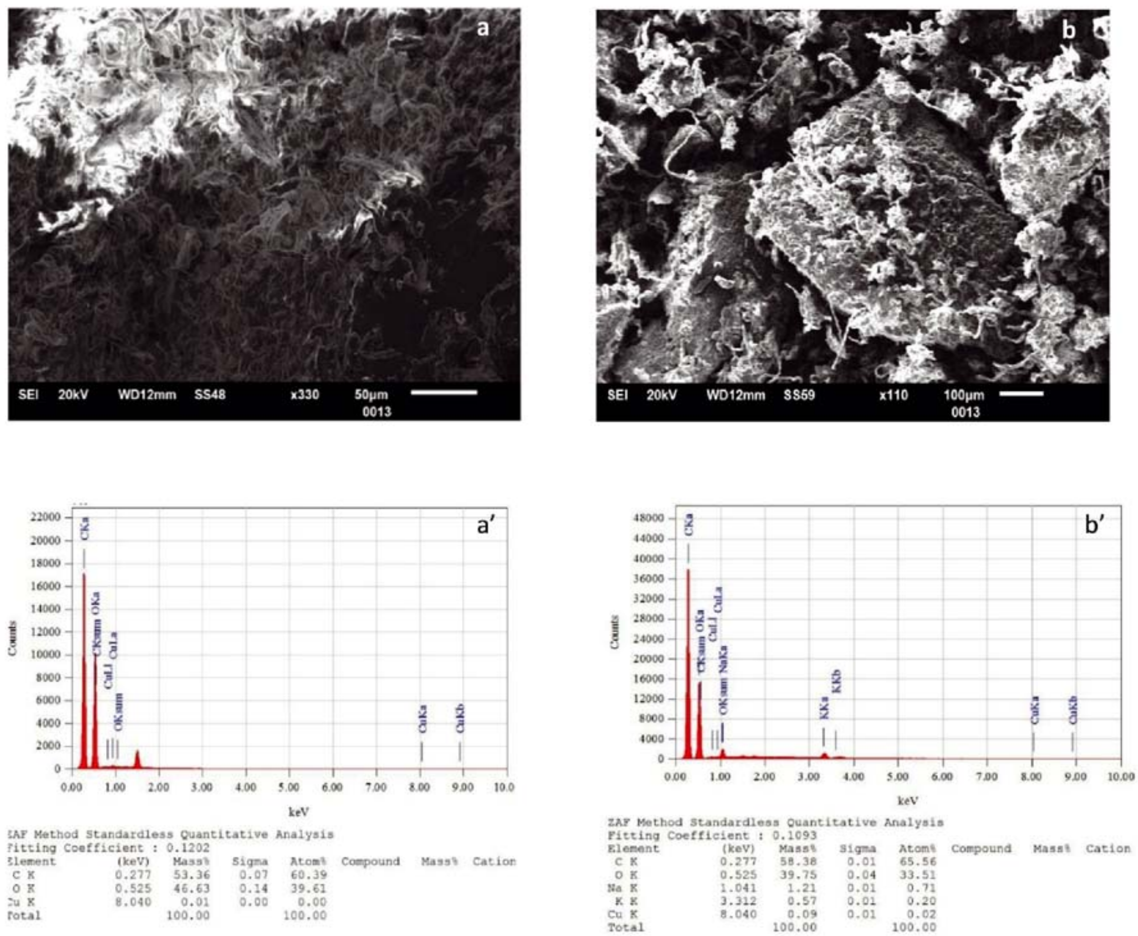

Figure 5. SEM and EDX of the lignocellulosic fraction of *Q. ilex* before (a, a') and after (b, b') copper adsorption

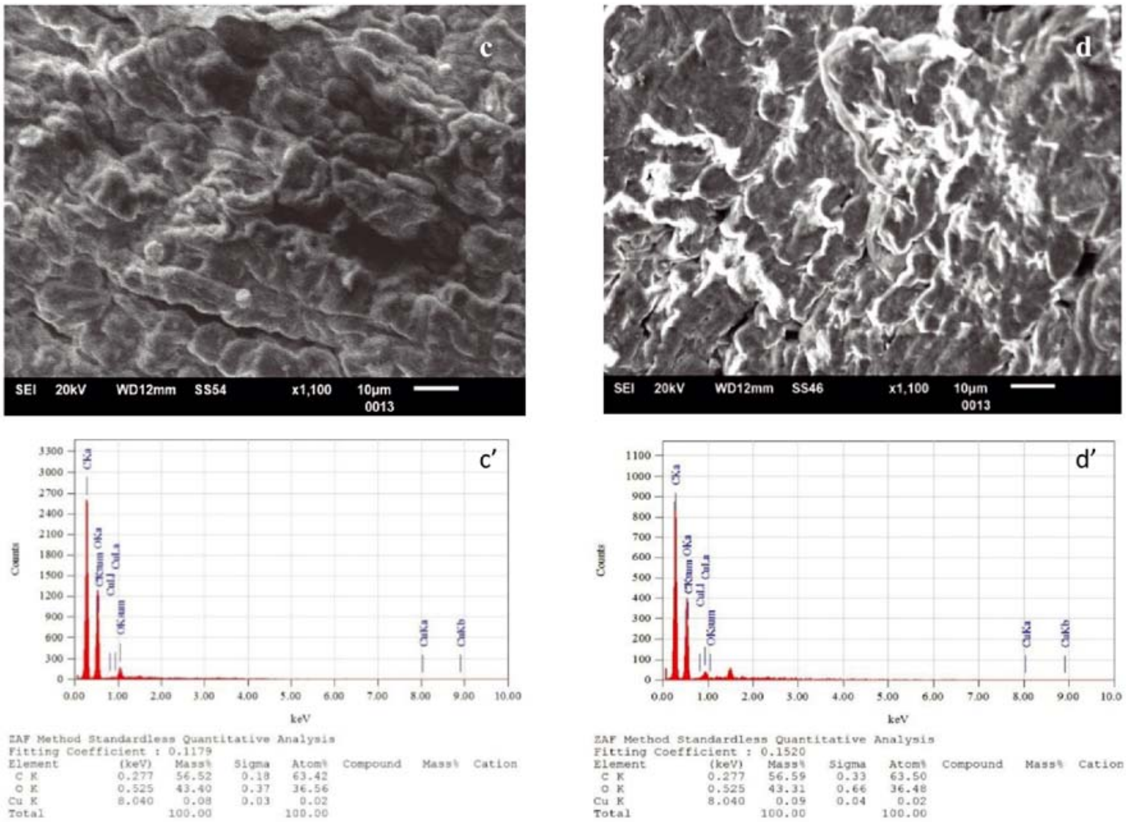

Figure 6. SEM and EDX of the lignocellulosic fraction of *Q. suber* before (c, c') and after (d, d') copper adsorption

of the adsorbent, Ce(mg·L^{-1}) is the concentration of the copper solution and K_L is the Langmuir constant.

The Langmuir isotherm may be characterized by a dimensionless constant separation factor (RL) defined as:

$$RL = \frac{1}{1+(Qmax.K).C0} \quad (5)$$

where (R_L = 1) is a linear isotherm, (0 <R_L<1) is a favorable isotherm, (R_L> 1) is an unfavorable isotherm and (R_L = 0) is irreversible adsorption[28].

The R_L shown in Table 4 (0.004 and 0.005 for the LCFs of *Q. ilex* and *Q. suber*, respectively) indicate that these materials are suitable for Cu(II) adsorption. Nevertheless, the model presented in Figs. 7 and 8 shows a low degree of linearization with the adsorption data (R^2 = 0.756 for *Q. ilex*; R^2 = 0.8675 for *Q. suber*).Therefore, Cu(II) adsorption does not reach saturation on either LCF. This finding aligned with the adsorption isotherms presented in Fig. 9. Moreover, K_L was comparatively high for the *Q. ilex* adsorbent. Thus, it can retain Cu(II) even when the residual Cu(II) concentration is low. The lignocellulosic fraction of *Q. suber* had a Q_{max} of 53.76 mg·g^{-1} which surpasses the values recently reported for copper adsorption (Table 3).

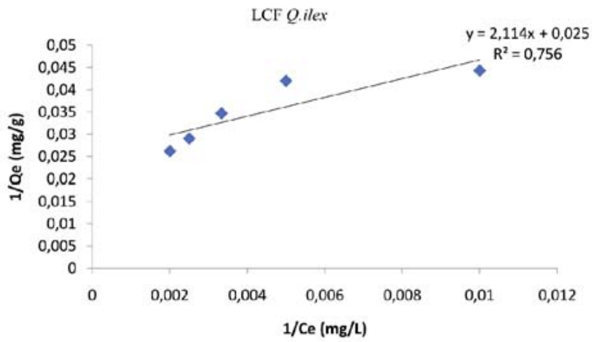

Figure 7. Langmuir isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. ilex*

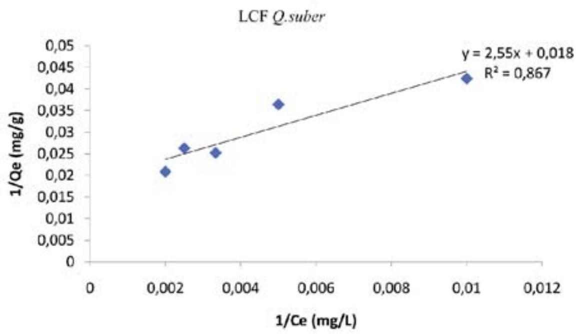

Figure 8. Langmuir isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber*

Table 4. Langmuir and Freundlich parameters for copper adsorption by lignocellulosic fractions (LCF) of *Q. ilex* and *Q. suber* pericarps

	Langmuir isotherm				Freundlich isotherm			
LCF Pericarp acorn	Q_{max} [mg/g]	K_L [L/mg]	R^2	RL	K_F [mg/g]	1/n	n [L/mg]	R^2
Q.suber	53.76	0.007	0.8675	0.005	5.9	0.3368	2.96	0.87
Q.ilex	39.06	0.012	0.756	0.004	7.43	0.258	3.87	0.834

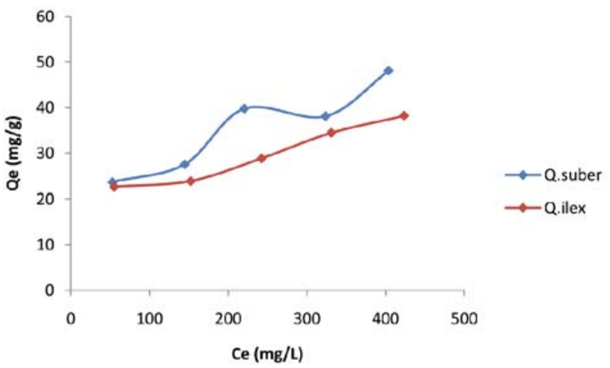

Figure 9. Adsorption isotherm of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber* and *Q. ilex*

Freundlich isotherm model

The Freundlich isotherm describes adsorption on heterogeneous surfaces[55] and is defined by the following equation:

$$Qe = K_F . Ce^{1/n} \quad (6)$$

where Qe ($mg{\cdot}g^{-1}$) is the quantity of Cu(II) adsorbed at equilibrium, Ce ($mg{\cdot}L^{-1}$) is copper concentration in the solution at equilibrium and K_F ($mg{\cdot}g^{-1}$) and n ($g{\cdot}L^{-1}$) are indices of adsorption capacity and intensity, respectively[56]. K_F and n can be interpolated form a linear plot of log Qe vs. log Ce. as follows:

$$\log Qe = \log K_F + \frac{1}{n} . \log Ce \quad (7)$$

A high K_F is indicative of high adsorption capacity. The LCF of *Q. ilex* had K_F = 7.43 $mg{\cdot}g^{-1}$ whilst that of *Q. suber* was only 5.9 $mg{\cdot}g^{-1}$ (Table 4; Figs. 10 and 11). The factor 1/n estimates the adsorption intensity or surface heterogeneity. A value of 1/n approaching zero indicates heterogeneity of the adsorbent[57]. The LCF of *Q. ilex* was more heterogeneous than that of *Q. suber*. The adsorption capacity is favorable when $0 < 1/n < 1$. Based on this criterion, the adsorption capacities of both *Q. ilex* and *Q. suber* LCF were favorable. Linearization with the adsorption data (R^2 = 0.834 for *Q. ilex* and (R^2 = 0.87 for *Q. suber*) suggested that the Freundlich isotherm model more accurately described the copper (II) ion biosorption kinetics than the Langmuir model.

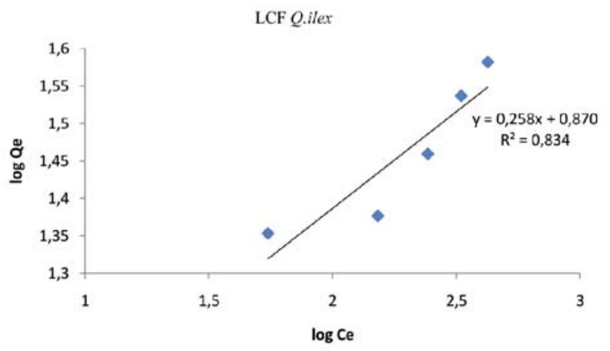

Figure 10. Freundlich isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. ilex*

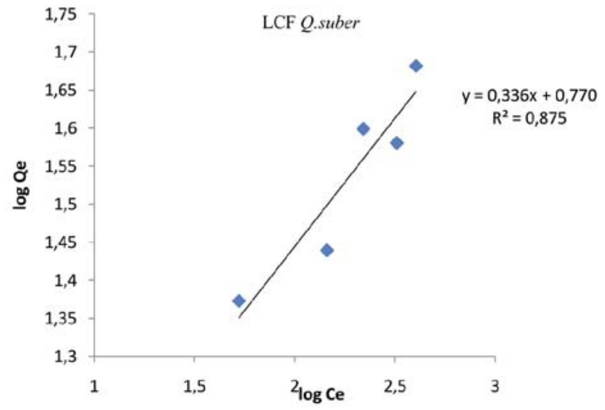

Figure 11. Freundlich isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber*

CONCLUSION

The identification of new adsorbents and the evaluation of their functional properties have become research priorities. Here, we studied the copper adsorption capacity of the lignocellulosic fractions of the pericarps from the acorns of the oak tree species *Quercus suber* and *Quercus ilex*. These species are widely distributed across the Mediterranean coast, particularly in north-western Algeria. The equilibrium adsorption capacity of the lignocellulosic fraction could be optimized by increasing the initial copper concentration. A Langmuir isothermal model adequately described the adsorption process. FTIR and SEM/EDX analyses indicated that adsorption occurs specifically through physicochemical interactions between the lignocellulosic fraction and the metal cations. The lignocellulosic fraction of acorn pericarps may be very promising as an adsorbent effectively removing copper cations from wastewater.

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