

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

Moubarek Mébarki^{1,*}, Kadda Hachem^{1, 2, 3}, Meriem Kaid Harche¹

¹Laboratoire des Productions, Valorisations Végétales et Microbiennes, (LP2VM), Faculté des Sciences de la Nature et de la Vie, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf, BP 1505, El M'Naouar, 31000 Oran, Algeria

²Laboratoire de Biotoxicologie, Pharmacognosie et Valorisation Biologique des Plantes (LBPVBP), Faculté des sciences, Université Dr. Tahar Moulay de Saïda, BP 138 cité ENNASR, 20000 Saïda, Algeria

³Département de Biologie, Faculté des Sciences, Université Dr. Moulay Tahar de Saïda, BP 138 cité ENNASR, 20000 Saïda, Algeria

Corresponding author: e-mail: moubarek.mebarki@univ-usto.dz

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 $23.59\text{--}48.06\text{ mg}\cdot\text{g}^{-1}$ for *Q. Suber* and $22.56\text{--}38.19\text{ mg}\cdot\text{g}^{-1}$ for *Q. ilex* when [Cu(II)] was $100\text{--}500\text{ mg}\cdot\text{L}^{-1}$. 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 $53.76\text{ mg}\cdot\text{g}^{-1}$ and $36.06\text{ mg}\cdot\text{g}^{-1}$ and KF of $5.9\text{ mg}\cdot\text{g}^{-1}$ and $7.43\text{ mg}\cdot\text{g}^{-1}$, 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 adsorption¹, coagulation², advanced oxidation³, membrane separation^{4, 5}, foam flotation⁶, precipitation⁷, ozonation⁸, ion exchange⁹, filtration¹⁰, solvent extraction¹¹, electrolysis¹², synthetic oxidation¹³, liquid-fluid extraction¹⁴, and others. However, the main disadvantages of these methods are high operating costs and toxic waste production¹⁵. 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 sludge²¹ and have high binding capacities for metals²². 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 donation²⁸. 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 oligogalacturonans³². However, the practicality of these methods is limited by the use of reactive toxic substances and/or organic solvents, costly equipment, and long protocols³³. 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 $2.0\text{ mg}\cdot\text{L}^{-1}$ for copper³⁴. 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 body³⁵.

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 Bailey³⁶ and Carpita³⁷. 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 H₂O 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 (CuSO₄ · 5H₂O) 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 flask³⁸. Briefly, one volume of ammonium hydroxide (NH₄OH) 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, respectively³⁹.

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

$$\%RE = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where Q_e 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), C_i and C_e 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**
<i>Q. suber</i>	79.45 ± 1.0	36.47 ± 9.1
<i>Q. ilex</i>	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.

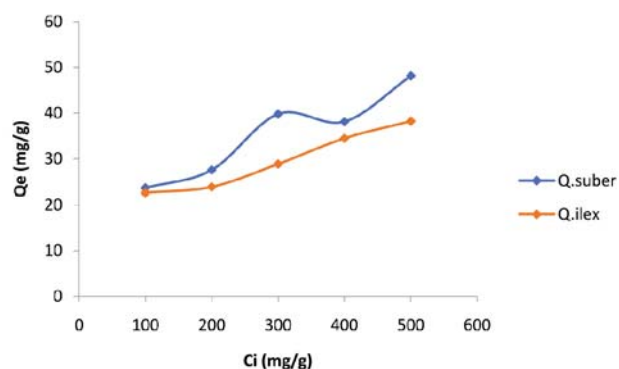
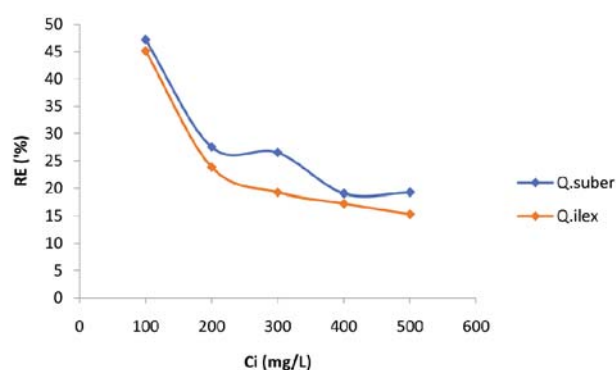
Figures 1 and 2 show that the quantity of Cu(II) adsorbed by the lignocellulosic fraction increased with initial Cu(II) concentration. From 100–400 mg·L⁻¹ Cu(II), the adsorption capacities Q_e increased from 23.59–48.06 mg·g⁻¹ and from 22.56–38.19 mg·g⁻¹ for *Q. suber* and *Q. ilex*, respectively.

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

Ci [mg/L]	<i>Q. suber</i>		<i>Q. ilex</i>	
	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).

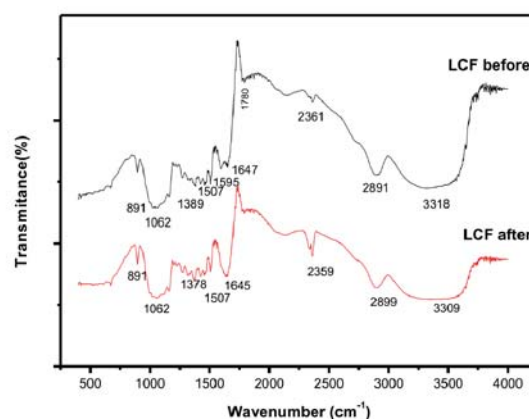
Table 3. Copper retention capacities of selected biosorbents

Biosorbent	Q _{max} [mg/g]	References
Tomato waste (<i>Solanum lycopersicum</i>)	34.48	43
Corn stalk	20.8	44
Sugar beet pulp	16.14	45
Single-celled green algae <i>Chlorella pyrenoidosa</i>	12.58	46
Fungus <i>Penicillium ochrochloron</i>	8.98	47
Sorghum stem <i>Sorghum bicolor</i>	7.93	48
Banana stem <i>Musa acuminata</i>	6.49	
Casuarinas fruit <i>Casuarina equisetifolia</i>	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 1062 cm⁻¹ represented a C-O stretch in polysaccharides⁵⁰. A band at ~1389 cm⁻¹ is associated with a C-H deformation in polysaccharides and a C_{aryl}-O vibration in syringyl derivatives⁵¹. Peaks at 1507 cm⁻¹ and 1595 cm⁻¹ were related to the aromatic skeleton of lignin. The band at ~1647 cm⁻¹ is characteristic of C=O stretching in carboxylates. The bands observed at 2891 cm⁻¹ correlate with symmetric C-H stretching and CH₂ group vibration. The bands at 3318 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 1389 cm⁻¹ to 1378 cm⁻¹, 1647 cm⁻¹ to 1645 cm⁻¹, 2361 cm⁻¹ to 2359 cm⁻¹, 2891 cm⁻¹ to 2899 cm⁻¹, and 3318 cm⁻¹ to 3309 cm⁻¹. The band at 1595 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, 1059, ~1375, 1594, 1645, 1783 and 3334 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 1.792 cm⁻¹, 2.901 cm⁻¹ to 2.891 cm⁻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.

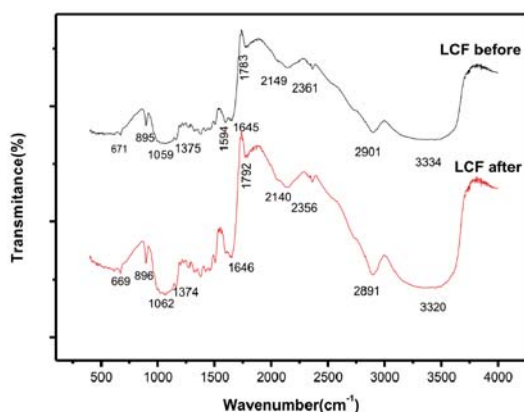


Figure 4. FTIR spectra of the lignocellulosic fraction (LCF) of *Q. ilex* before and after Cu(II) adsorption

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 cations⁵².

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 grew⁵². 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*, respectively⁵³.

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 model⁵⁴ 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:

$$Q_e = \frac{Q_{\max} K C_e}{1 + K C_e} \quad (3)$$

$$\frac{1}{Q_e} = \frac{1}{Q_{\max}} + \frac{1}{K Q_{\max}} \cdot \frac{1}{C_e} \quad (4)$$

where Q_e (mg·g⁻¹) is the quantity of Cu(II) adsorbed at equilibrium, Q_{\max} is the maximum adsorption capacity

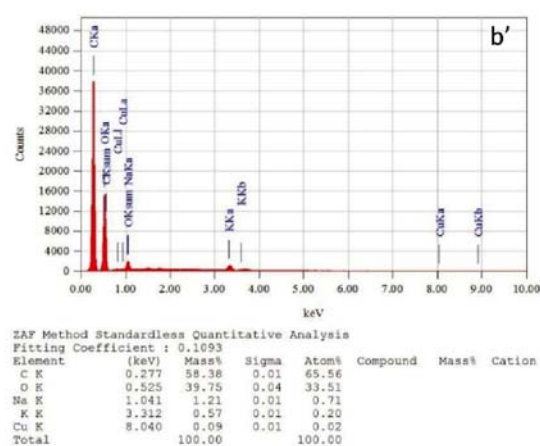
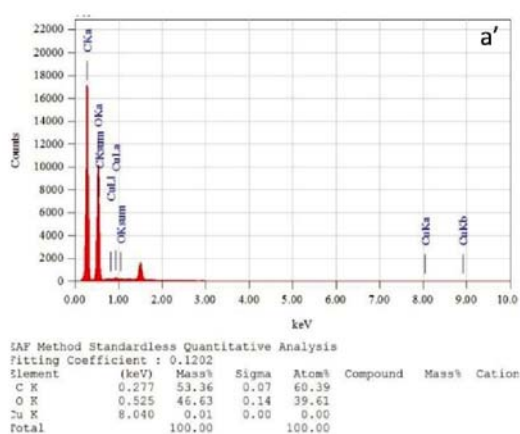
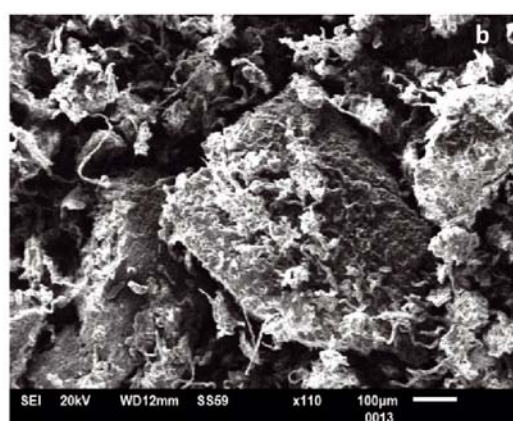
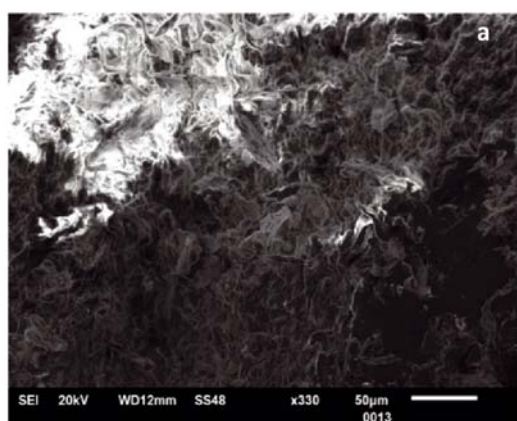


Figure 5. SEM and EDX of the lignocellulosic fraction of *Q. ilex* before (a, a') and after (b, b') copper adsorption

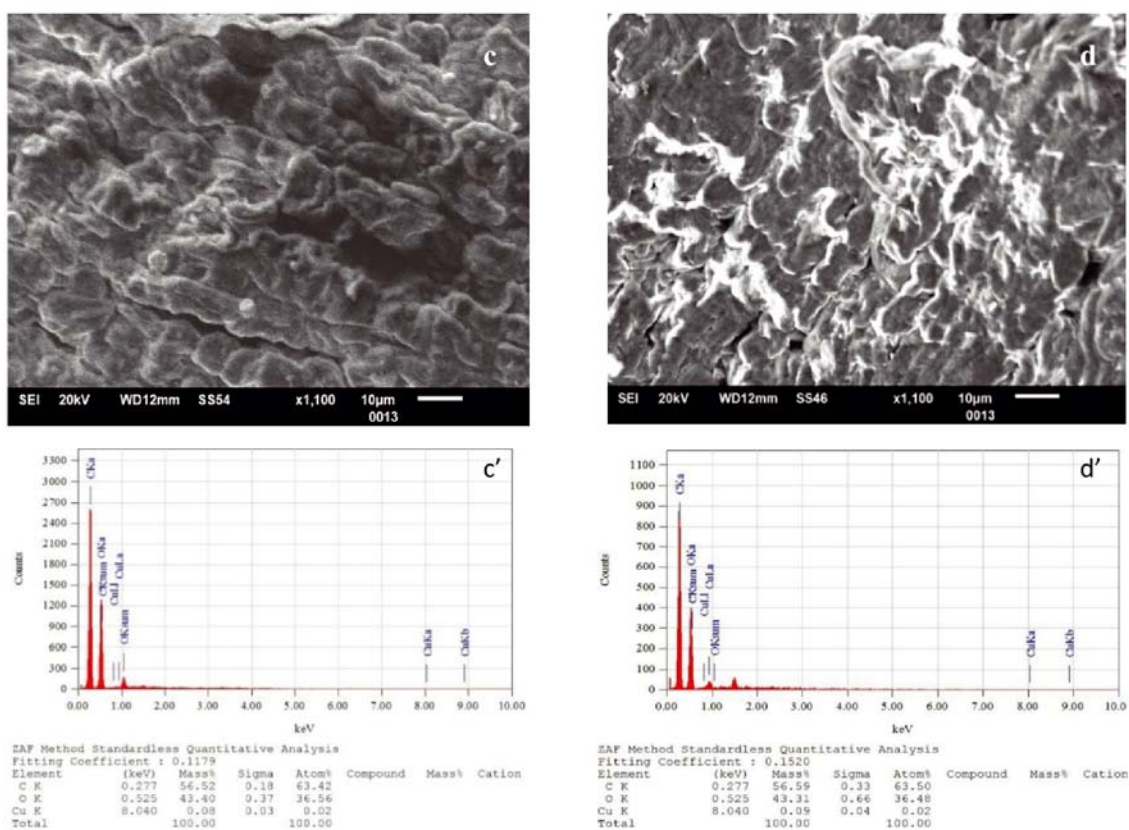


Figure 6. SEM and EDX of the lignocellulosic fraction of *Q. suber* before (c, c') and after (d, d') copper adsorption

of the adsorbent, $C_e(\text{mg}\cdot\text{L}^{-1})$ 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:

$$RL = \frac{1}{1 + (Q_{\max} \cdot K) \cdot C_0} \quad (5)$$

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 adsorption²⁸.

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 $53.76 \text{ mg}\cdot\text{g}^{-1}$ which surpasses the values recently reported for copper adsorption (Table 3).

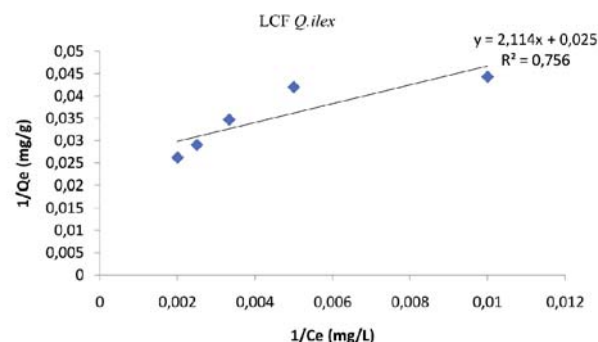


Figure 7. Langmuir isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. ilex*

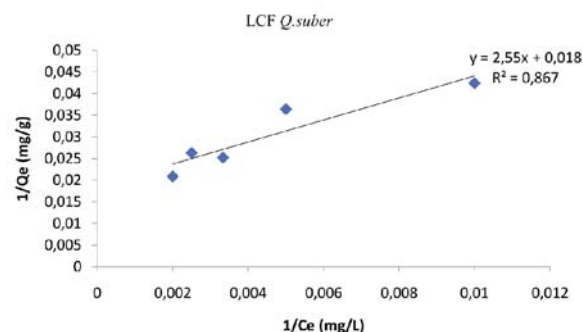


Figure 8. Langmuir isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber*

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

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

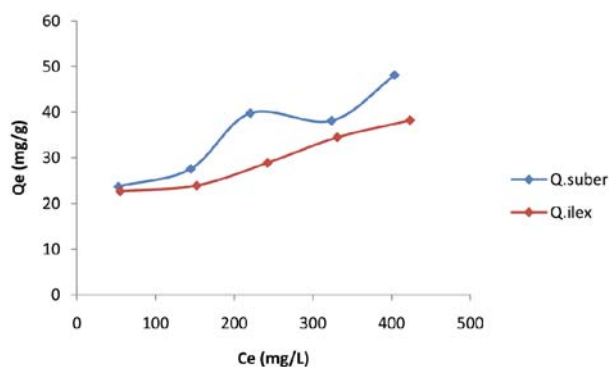


Figure 9. Adsorption isotherm of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber* and *Q. ilex*

Freundlich isotherm model

The Freundlich isotherm describes adsorption on heterogeneous surfaces⁵⁵ and is defined by the following equation:

$$Q_e = K_F \cdot C_e^{1/n} \quad (6)$$

where Q_e ($\text{mg}\cdot\text{g}^{-1}$) is the quantity of Cu(II) adsorbed at equilibrium, C_e ($\text{mg}\cdot\text{L}^{-1}$) is copper concentration in the solution at equilibrium and K_F ($\text{mg}\cdot\text{g}^{-1}$) and n ($\text{g}\cdot\text{L}^{-1}$) are indices of adsorption capacity and intensity, respectively⁵⁶. K_F and n can be interpolated from a linear plot of $\log Q_e$ vs. $\log C_e$, as follows:

$$\log Q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (7)$$

A high K_F is indicative of high adsorption capacity. The LCF of *Q. ilex* had $K_F = 7.43 \text{ mg}\cdot\text{g}^{-1}$ whilst that of *Q. suber* was only $5.9 \text{ mg}\cdot\text{g}^{-1}$ (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 adsorbent⁵⁷. 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.

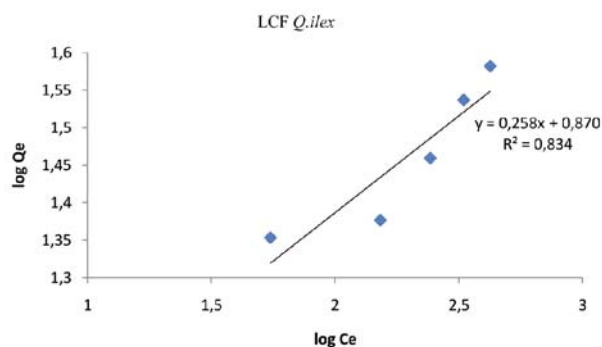


Figure 10. Freundlich isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. ilex*

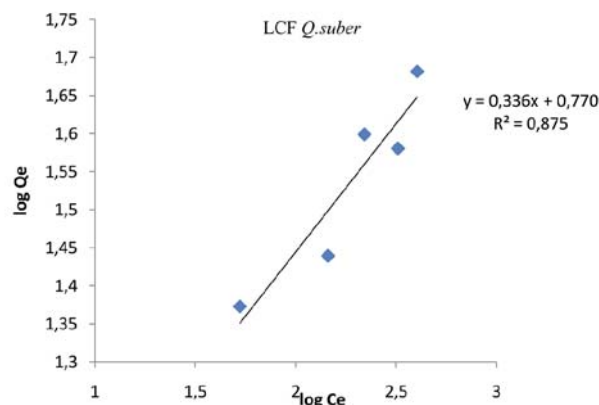


Figure 11. Freundlich isotherm model of copper (II) biosorption onto the lignocellulosic fraction of *Q. suber*

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.

ACKNOWLEDGMENTS

The authors thank Sahraoui Toufik of the *Laboratoire de Microscopie Electronique et des Sciences des Matériaux* (LMESM) USTO M-B for performing the SEM/EDX analyses. This study was funded by the University of Sciences and Technology Mohamed Boudiaf, Oran, Algeria.

LITERATURE CITED

1. Afroze, S. & Sen, T.K. (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water Air Soil Pollut.* 229, 225. DOI: 10.1007/s11270-018-3869-z.
2. Amuda, O.S., Amoo, I.A., Ipinmoroti, K.O. & Ajayi, O.O. (2006). Coagulation/flocculation process in the removal of trace metals present in industrial wastewater. *J. Appl. Sci. Environ. Manage.* 10(3), 159–162. DOI: 10.4314/jasem.v10i3.17339.
3. Wang, J.L. & Xu, L.J. (2012). Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application. *Crit. Rev. Environ. Sci. Technol.* 42, 251–325. DOI: 10.1080/10643389.2010.507698.
4. Rivas, B.L. & Palencia, M. (2011). Removal-concentration of pollutant metal-ions by water-soluble polymers in conjunction with double emulsion systems: A new hybrid method of membrane-based separation. *Sep. Purif. Technol.* 81(3), 435–443. DOI: 10.1016/j.seppur.2011.08.021.
5. Saleh, T.A. & Gupta, V.K. (2014). Processing methods, characteristics and adsorption behavior of tire derived car-

bons: A review. *Adv. Colloid. Interface Sci.* 211, 93–101. DOI: 10.1016/j.cis.2014.06.006.

6. Rubio, J., Souza, M.L. & Smith, R.W. (2002). Overview of flotation as a wastewater treatment technique. *Miner. Eng.* 15(3), 139–155. DOI: 10.1016/S0892-6875(01)00216-3.

7. Agwarambo, L., Magee, N., Nunez, S. & Mitt, K. (2013). Biosorption and chemical precipitation of lead using biomaterials, molecular sieves, and chlorides, carbonates, and sulfates of Na & Ca. *J. Environ. Prot.* 4(11), 1251–1257. DOI: 10.4236/jep.2013.411145.

8. Gähr, F., Hermanutz, F. & Oppermann, W. (1994). Ozonation-an important technique to comply with new German laws for textile wastewater treatment. *Water Sci. Technol.* 30(3), 255–263. DOI: 10.2166/wst.1994.0115.

9. Abdel-Aziz, M.H., Nirdosh, I. & Sedahmed, G.H. (2013). Ion-exchange-assisted electrochemical removal of heavy metals from dilute solutions in a stirred-tank electrochemical reactor: a mass-transfer study. *Ind. Eng. Chem. Res.* 52(33), 11655–11662. DOI: 10.1021/ie400548w.

10. Dean, J.G., Bosqui, F.L. & Lanouette, K.H. (1972). Removing heavy metals from waste water. *Environ. Sci. Technol.* 6(6), 518–522. DOI: 10.1021/es60065a006.

11. Lin, S.H. & Juang, R.S. (2002). Removal of free and chelated Cu (II) ions from water by a nondispersive solvent extraction process. *Water Res.* 36, 3611–3619. DOI: 10.1016/S0043-1354(02)00074-X.

12. Tao, H.C., Lei, T., Shi, G., Sun, X.N., Wei, X.Y., Zhang, L.J. & Wu, W.M. (2014). Removal of heavy metals from fly ash leachate using combined bioelectrochemical systems and electrolysis. *J. Hazard. Mater.* 264, 1–7. DOI: 10.1016/j.jhazmat.2013.10.057.

13. Sreepasad, T.S., Maliyekkal, S. M., Lisha, K.P. & Pradeep, T. (2011). Reduced graphene oxide-metal/metal oxide composites: facile synthesis and application in water purification. *J. Hazard. Mater.* 186(1), 921–931. DOI: 10.1016/j.jhazmat.2010.11.100.

14. Nielsen, P.B., Christensen, T.C. & Vendrup, M. (1997). Continuous removal of heavy metals from FGD wastewater in a fluidised bed without sludge generation. *Water Sci. Technol.* 36(2–3), 391–397. DOI: 10.1016/S0273-1223(97)00413-7.

15. Ahluwalia, S.S. & Dinesh, G. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Biores. Technol.* 98(12), 2243–2257. DOI: 10.1016/j.biortech.2005.12.006.

16. Bailey, S.E., Olin, T.J., Bricka, R.M. & Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Res.* 33 (11), 2469–2479. DOI: 10.1016/S0043-1354(98)00475-8.

17. Mohan, D., Sarswat, A., Ok, Y.S., & Pittman, C.U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – a critical review. *Biores. Technol.* 160, 191–202. DOI: 10.1016/j.biortech.2014.01.120.

18. Vikrant, K., Giri, B.S., Raza, N., Roy, K., Kim, K.H., Rai, B.N., & Singh, R.S. (2018). Recent advancements in bioremediation of dye: current status and challenges. *Biores. Technol.* 253, 355–367. DOI: 10.1016/j.biortech.2018.01.029.

19. Robati, D., Mirza, B., Rajabi, M., Moradi, O., Tyagi, I., Agarwal, S. & Gupta, V.K., (2016). Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase. *Chem. Eng. J.* 284, 687–697. DOI: 10.1016/j.cej.2015.08.131.

20. Gupta, V.K., Nayak, A., Agarwal, S. & Tyagi, I. (2014). Potential of activated carbon from waste rubber tire for the adsorption of phenolics: effect of pre-treatment conditions. *J. Colloid. Interface Sci.* 417, 420–430. DOI: 10.1016/j.jcis.2013.11.067.

21. Barka, N., Abdennouri, M., El-Makhfouk, M. & Qoursal S. (2013). Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (*Opuntia ficus indica*) clado-

des. *J. Environ. Chem. Eng.* 1(3), 144–149. DOI: 10.1016/j.jece.2013.04.008.

22. Gupta, V.K. & Rastogi, A. (2008). Biosorption of lead from aqueous solutions by green algae *Spirogyraspecies*: kinetics and equilibrium studies. *J. Hazard. Mater.* 2008;152(1), 407–414. DOI: 10.1016/j.jhazmat.2007.07.028.

23. Afroze, S. & Sen, T.K. (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water Air Soil Pollut.* 229(7), 225. DOI: 10.1007/s11270-018-3869-z.

24. Gupta, V.K. & Saleh, T.A. (2013). Sorption of pollutants by porous carbon, carbon nanotubes and fullerene-an overview. *Environ. Sci. Pollut. Res.* 20(5), 2828–2843. DOI: 10.1007/s11356-013-1524-1.

25. Ahmaruzzaman, M. & Gupta, V. K. (2011). Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Ind. Eng. Chem. Res.* 50(24), 13589–13613. DOI: 10.1021/ie201477c.

26. Hao, X., Mohamad, O.A., Xie, P., Rensing, C. & Wei, G. (2014). Removal of zinc from aqueous solution by metal resistant symbiotic bacterium *Mesorhizobium amorphae*. *Separ. Sci. Technol.* 49(3), 376–387. DOI: 10.1080/01496395.2013.843195.

27. Jakóbk-Kolon, A., Mitko, K. & Bok-Badura, J. (2017). Zinc sorption studies on pectin-based biosorbents. *Materials* 10(7), 844. DOI: 10.3390/ma10070844.

28. Haroon, H., Gardazi, S.M.H., Butt, T.A., Pervez, A., Mahmood, Q. & Bilal, M. (2017). Novel lignocellulosic wastes for comparative adsorption of Cr(VI): equilibrium kinetics and thermodynamic studies. *Pol. J. Chem. Technol.* 19(2), 6–15. DOI: 10.1515/pjct-2017-0021.

29. Marchetti, V., Clément, A., Gérardin, P. & Loubinoux, B. (2000). Synthesis and use of esterified sawdusts bearing carboxyl group for removal of cadmium(II) from water. *Wood Sci. Technol.* 34(2), 167–173. DOI: 10.1007/s002260000040.

30. Hachem, K., Astier, C., Chaleix, V., Faugeron, C., Krausz, P., Kaid-Harche, M. & Gloaguen, V. (2012). Optimization of lead and cadmium binding by oxidation of biosorbent polysaccharidic moieties. *Water Air Soil Pollut.* 223(7), 3877–3885. DOI: 10.1007/s11270-012-1156-y.

31. Genevois, N., Villandier, N., Chaleix, V., Poli, E., Jauberty, L. & Gloaguen, V. (2017). Removal of cesium ion from contaminated water: improvement of Douglas fir bark biosorption by a combination of nickel hexacyanoferrate impregnation and TEMPO oxidation. *Ecol. Eng.* 100, 186–193. DOI: 10.1016/j.ecoleng.2016.12.012.

32. Astier, C., Chaleix, V., Faugeron, C., Ropartz, D., Gloaguen, V. & Krausz, P. (2010). Grafting of aminated oligogalacturonans onto Douglas fir barks. a new route for the enhancement of their lead(II) binding capacities. *J. Hazard. Mater.* 182(1), 279–285. DOI: 10.1016/j.jhazmat.2010.06.027.

33. Yeo, T.H.C., Tan, I.A.W. & Abdullah, M.O. (2012). Development of adsorption air-conditioning technology using modified activated carbon – A review. *Renew. Sustain. Energy Rev.* 16(5), 3355–3363. DOI: 10.1016/j.rser.2012.02.073.

34. Nebagha, K.C., Ziat, K., Rghioui, L., Khayet, M., Saidi, M., Aboumaria, K., El Hourch, A. & Sebt, S. (2015). Adsorptive removal of copper (II) from aqueous solutions using low-cost Moroccan adsorbent. Part I: parameters influencing Cu (II) adsorption. *J. Mater. Environ. Sci.* 6(11), 3022–3033.

35. Li, Y., Xia, B., Zhao, Q., Liu, F., Zhang, P., Du, Q., Wang, D., Li, D., Wang, Z. & Xia, Y. (2011). Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin. *J. Environ. Sci.* 23(3), 404–411. DOI: 10.1016/S1001-0742(10)60442-1.

36. Bailey, R.W. (1967). Quantitative studies of ruminant digestion. *NZ J. Agric. Res.* 10(1):15–32. DOI: 10.1080/00288233.1967.10423074.

37. Carpita, N.C. (1984). Fractionation of hemicelluloses from maize cell walls with increasing concentrations of al-

kali. *Phytochemistry* 23(5), 1089–1093. DOI: 10.1016/s0031-9422(00)82615-1

38. Mehlig, J. (1941). Colorimetric determination of copper with ammonia. *Ind. Eng. Chem. Anal. Ed.* 13(8), 533–535. DOI: 10.1021/i560096a006.

39. Hameed, B.H., Mahmoud, D.K. & Ahmad, A.L. (2008). Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. *J. Hazard Mater.* 158(1), 65–72. DOI: 10.1016/j.jhazmat.2008.01.034.

40. Dawczynski, C., Schubert, R. & Jahreis, G. (2007). Amino acids, fatty acids, and dietary fibre in edible seaweed products. *Food Chem.* 103(3), 891–899. DOI: 10.1016/j.foodchem.2006.09.041.

41. El Gamal, A.A. (2010). Biological importance of marine algae. *Saudi Pharmaceut. J.* 18(1), 1–25. DOI: 10.1016/j.jsps.2009.12.001.

42. Proctor, M.C.F. (2000). The bryophyte paradox: tolerance of desiccation, evasion of drought. *Plant Ecol.* 151(1), 41–49. DOI: 10.1023/A:1026517920852.

43. Yargıç, A. Ş., Yarbay Şahin, R. Z., Özbay, N., & Önal, E. (2015). Assessment of toxic copper(II) biosorption from aqueous solution by chemically-treated tomato waste (*Solanum lycopersicum*). *J. Clean. Prod.* 88, 152–159. DOI: 10.1016/j.jclepro.2014.05.087.

44. Vafakhah, S., Bahrololoom, M. & Saeedikhani, M. (2016). Adsorption kinetics of cupric ions on mixture of modified corn stalk and modified tomato waste. *J. Water Res. Prot.* 8(13), 1238–1250. DOI: 10.4236/jwarp.2016.813095.

45. Reddad, Z., Gerente, C., Andres, Y. & Le Cloirec, P. (2002). Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* 36(9), 2067–2073. DOI: 10.1021/es0102989.

46. Moreira, V.R., Lebron, Y.A.R., Freire, S.J., Santos, L.V.S., Palladino, F., Jacob, R.S. (2019). Biosorption of copper ions from aqueous solution using *Chlorella pyrenoidosa*: Optimization, equilibrium and kinetics studies. *Microchem. J.* 145, 119–129. DOI: 10.1016/j.microc.2018.10.027.

47. Lacerda, E.C.M., dos Passos Galluzzi Baltazar, M., dos Reis, T.A., do Nascimento, C.A.O., Côrrea, B., Gimenes, L.J. (2019). Copper biosorption from an aqueous solution by the dead biomass of *Penicillium ochrochloron*. *Environ. Monit. Assess.* 191, 247. DOI: 10.1007/s10661-019-7399-y.

48. Mokkapati, R.P., Mokkapati, J. & Ratnakaram, V.N. (2016). Kinetic, isotherm and thermodynamics investigation on adsorption of divalent copper using agro-waste biomaterials, *Musa acuminata*, *Casuarina equisetifolia* L. and *Sorghum bicolor*. *Pol. J. Chem. Technol.* 18, 68–77. DOI: 10.1515/pjct-2016-0031.

49. Calero, M., Blázquez, G., Dionisio-Ruiz, E., Ronda, A. & Martín-Lara, M.A. (2013). Evaluation of biosorption of copper ions onto pinion shell. *Desalination Water Treat.* 51, 2411–2422. DOI: 10.1080/19443994.2012.747472.

50. Faix, O. (1992). Fourier transform infrared spectroscopy. In S.Y. Lin & C.W. Dence (eds.), *Methods in lignin chemistry* (pp. 233–241). Berlin, Heidelberg: Springer Berlin Heidelberg. DOI: 10.1007/978-3-642-74065-7_16.

51. Collier, W.E., Schultz, T.P. & Kalasinsky, V.F. (1992). Infrared study of lignin: reexamination of aryl-alkyl ether C—O stretching peak assignments. *Holzforschung* 46(6), 523–528. DOI: 10.1515/hfsg.1992.46.6.523.

52. Ramavandi, B. & Asgari, G. (2018). Comparative study of sun-dried and oven-dried *Malva sylvestris* biomass for high-rate Cu(II) removal from waste water. *Proc. Saf. Environ. Prot.* 116, 61–73. DOI: 10.1016/j.psep.2018.01.012.

53. Sinha, A., Singh, V.N., Mehta, B.R. & Khare, S.K. (2011). Synthesis and characterization of monodispersed orthorhombic manganese oxide nanoparticles produced by *Bacillus* cells simultaneous to its bioremediation. *J. Hazard. Mater.* 192(2), 620–627. DOI: 10.1016/j.jhazmat.2011.05.103.

54. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40(9), 1361–1403. DOI: 10.1021/ja02242a004.

55. Freundlich, H. (1907). Über die adsorption in lösungen. *Z. Für Phys. Chem.* 57, 385–470. DOI: 10.1515/zpch-1907-5723.

56. Yargıç, A.Ş., Yarbay Şahin, R.Z., Özbay, N. & Önal, E. (2015). Assessment of toxic copper(II) biosorption from aqueous solution by chemically-treated tomato waste. *J. Clean. Prod.* 88, 152–159. DOI: 10.1016/j.jclepro.2014.05.087.

57. Haroon, H., Gardazi, S.M.H., Butt, T.A., Pervez, A., Mahmood, Q. & Bilal, M. (2017). Novel lignocellulosic wastes for comparative adsorption of Cr(VI): equilibrium kinetics and thermodynamic studies. *Pol. J. Chem. Technol.* 19(2), 6–15. DOI: 10.1515/pjct-2017-0021.