Full paper/Mémoire

Assessment of copper(II) biosorption from aqueous solution by agricultural and industrial residues

Étude du processus de biosorption des ions cuivriques(II) en solution aqueuse par deux résidus agricole et industriel

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A B S T R A C T

In this study, newspaper scraps (NS) and maize spatha (MS) treated in turn by HNO_3 and MeOH were evaluated for the biosorption of Cu^{2+} ions, on the basis of batch experiments. The effects of several parameters were investigated, including contact time, solution pH, shaking speed, biosorbent dosage and ionic strength. Under optimal conditions, the maximum sorption capacities (Q_{max}) were (60.386 ± 0.006) and (44.90 ± 0.02) μmol Cu^{2+} per g of sorbent, respectively, for NS and MS chemically treated with HNO_3. The optimal parameters were pH: 5, contact time: 40 min and shaking speed: 100 rpm for NS, while for MS the same parameters were pH 5, 20 min and 150 rpm, respectively. It was found that Cu^{2+} biosorption is disfavored by an increase in ionic strength and by the presence of some interfering cations. The experimental data obtained with NS best matched the Langmuir's sorption model ($R^2 = 0.994$) while the Temkin model best described biosorption on MS ($R^2 = 0.987$). The biosorption of Cu^{2+} on both materials followed pseudo-second order kinetics, and the desorption of Cu^{2+} ions was effective in 0.01 M HCl solution.

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R É S U M É

Les chutes de papiers journaux (CPJ) et les spathes de maïs (SM) tour à tour traitées par l'acide nitrique et le méthanol ont été évaluées pour l'élimination par biosorption en mode batch des ions Cu(II) en solution aqueuse. Plusieurs paramètres pouvant influencer la biosorption des ions Cu(II) ont été optimisés, incluant le temps de contact, le pH de la solution, la vitesse d'agitation, la dose du biosorbant et la force ionique. Dans les conditions optimales, les quantités maximales adsorbées (Q_{max}) sont de (60.386 ± 0.006) et (44.90 ± 0.02) μmol de Cu(II) par g de matériau, respectivement pour les CPJ et les MS traités par HNO_3 lorsque la solution initiale en ions Cu(II) est de 5×10^{-3} M. L'élimination des ions Cu(II) est meilleure à pH 5 après 40 min d'agitation à 100 tr/min pour les CPJ. Les mêmes paramètres sont pH 5, 20 min d'agitation et 150 tr/mn pour les MS. Il a été trouvé que la biosorption des ions Cu^{2+} est défavorisée par une diminution du pH et par une augmentation de la salinité de la solution. Par ailleurs, l'analyse de quelques ions poten- tiellement interférents a été effectuée. Les données expérimentales obtenues avec les CPJ

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sont bien décrites par le modèle de sorption de Langmuir ($R^2 = 0,994$) tandis que celles correspondant aux SM suivent plutôt le modèle de Temkin ($R^2 = 0,987$). La cinétique de biosorption des ions Cu^{2+} par les CPJ et les SM est du pseudo second ordre. La meilleure désorption des ions analysés est réalisée avec une solution de HCl 0,01 M.

1. Introduction

Copper is a very useful metal, because it finds many daily applications including, for example, manufacturing of electric cables and thermal pipes, coating materials for buildings, chemical catalysis and wood pulp production [1]. Copper is also an essential trace element that is vital to the health of living organisms (humans, plants and animals). However, at elevated concentration, it becomes detrimental to these organisms [2]. Yet, copper is known to be one of the most toxic heavy metals and one of the most widespread contaminants in the environment [3−7]. Several conventional methods are traditionally used to remove heavy metals from wastewater. However, the application of such technologies is restricted because of technical or economical limitations.

For a few years, efforts have been made for the improvement and the setting-up of new more effective, less expensive and especially ecological processes. Natural adsorbents such as clays and silica have been largely used for the elimination of pollutants [8,9].

In recent years, considerable attention has been focused on removal of heavy metal ions (or other pollutants) from aqueous solution using lignocellulosic materials (LCMs) [10−13] for several reasons: LCMs are naturally available in abundance, inexpensive, non-toxic and able to adsorb various pollutants at low concentration [12]. Moreover some of these materials can be regenerated and reused [14,15]. LCMs bear various functional groups such as hydroxyl, carboxyl, amine, amide, thiol, etc. that can easily form complexes or chelates with heavy metal ions [11−14].

The aim of this work was to study the biosorption of copper(II) from aqueous solutions using two LCMs: maize spatha (MS) and newspaper scraps (NS). MS are agricultural residues, defined as large foliaceous envelopes that protect the corncob. Paper is a material which was first manufactured from cellulose fibers contained in wood or other woody plants. Paper scraps are agro-industrial residues remaining after the cutting of coarse papers. The influence of several parameters (contact time, biosorbent dosage, shaking speed, pH of solution, initial concentration of the pollutant, and ionic strength) on the biosorption of Cu(II) in batch mode was studied. The involved process was described by using equilibrium and kinetic data of biosorption. The possibility to reuse the materials was also examined.

2. Materials and methods

2.1. Sample1

Newspaper scraps were collected from the printing workshops of the University of Dschang (Cameroon). Maize spatha were obtained from a local agricultural unit. They were sundried for 3 days under open atmosphere, cut up and crushed as finely as possible using a domestic mixer. The obtained powders were sieved into different fraction sizes (ranging from 0 to 200, 200 to 250 and 250−500 μm). Experiments were carried out with the smallest fraction size (0−200 μm) which exhibited the best results towards the adsorption of Cu(II) ions.

All the chemical reagents were purchased and used as received: $CuSO_4.5H_2O$ from Acros organics; NaCl, $MgCl_2$, $CaCl_2$, $SnCl_2$, $FeCl_3$, NH_4OH, and NaOH from Fischer; CH_3OH and H_2SO_4 from BDH; KCl, $NaNO_3$, Na_3PO_4 and Na_2SO_4 from Prolabo; HNO_3 from Riedel-de-Häen. All the solutions were prepared with distilled water.

2.2. Pretreatment of biomass

Pretreatment with methanol was performed according to the procedure used by Nanseu-Njiki *et al.* [14]. Pretreatment with nitric acid was carried out as follows: into a bottle containing 5 g of biosorbent, a volume of 50 mL of 2 M HNO_3 was introduced. The mixture was kept under agitation at a speed of 200 rpm for 2 h, and then filtered. The obtained product was washed with distilled water to dilute and eliminate excess of nitric acid. Afterwards, the mixture was immersed in 0.1 M NaOH for 1 h in order to eliminate the rest of HNO_3 and to activate the functional groups found on the surface of biosorbents. The obtained products (NS_{HNO_3} and MS_{HNO_3}) were once more washed with distilled water to eliminate the rest of NaOH. They were sundried for two days, and then kept in an oven at 105 °C for 2 h.

2.3. Batch biosorption studies

The biosorption was carried out in the batch mode. Into a 100 mL flask, a given mass of biosorbent and 10 mL of Cu(II) solution at a given concentration were introduced. The pH was adjusted to desired values with solutions of NaOH or HCl. A series of flasks were prepared by varying the different parameters to be investigated. The flasks were placed in a mechanical platform shaker (Edmund Bühler, GmbH) and stirred for 40 min at a speed of 150 rpm.

The performance of biomaterials for the removal of Cu^{2+} ions from aqueous solutions was quantitatively evaluated using the amount of Cu^{2+} sorbed per unit mass of biosorbent (mol/g):

$$Q_{ads} = \frac{(C_i - C_e)}{m} V_s \tag{1}$$

The percent biosorption of metal ions (R, %) was calculated as follows:

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

where: C_i is the initial Cu^{2+} concentration (mol/L), C_e is the Cu^{2+} residual concentration (mol/L), V_s is the volume of Cu^{2+} solution (mL) and m is the mass of biosorbent used in the reaction mixture (g). Batch experiments were carried out at pHs ranging from 2 to 9 to determine the effect of pH on the sorption process. The effect of the initial metal concentration was investigated using Cu(II) concentrations varying from 10^{-5} to 10^{-2} mol/L. For experiments concerning the effect of sorbent mass, the dosage of each biosorbent was varied from 0 to 65 mg/L. For contact time experiments, the procedure was similar to that presented above, with the difference that the phases were separated after a determined period of contact time. All sorption experiments were performed at room temperature.

Cu(II) concentrations were spectrophotometrically measured: to 5 mL of Cu(II) solution, 2.5 mL of 10 M ammonia was added and the mixture was allowed to stand for about 5 min. The absorbance of the corresponding blue solution formed was measured at 610 nm using a Jenway UV–Vis spectrophotometer. For the determination of residual Cu(II) concentrations in filtrates where the concentration of this analyte was below 10^{-4} M, an organoclay modified electrode prepared by our group according to a previously published procedure [16] was used. Briefly, a carbon paste electrode chemically modified by a smectite clay bearing amine was used as the working electrode in a three electrode cell configuration comprising a tungsten wire counter electrode and a saturated calomel electrode (SCE) used as the reference electrode. Square wave anodic stripping voltammograms were recorded using a Palmsens potentiostat. The electrochemical analyzing procedure involved two successive steps: an open-circuit preconcentration of Cu(II) followed by voltammetric detection in 0.2 M HCl solution. The first step was achieved by dipping the working electrode in the filtrate containing Cu^{2+} ions, under stirring. After 4 min accumulation, the electrode was promptly removed, rapidly rinsed with water and then transferred into the electrochemical cell containing the detection solution. The previously accumulated species were then analyzed by square wave voltammetry after 60 s electrolysis at −0.8 V. The concentration of Cu(II) was finally determined using a calibration curve previously established (see Fig. S1 and S2, supporting information).

2.4. Desorption

Each LCM (20 mg) was contacted with 10 mL of a 5×10^{-3} mol/L Cu(II) solution. Upon agitation for a given period of time, the LCM was collected by filtration and washed three times with distilled water, to remove residual Cu(II) on the surface. It was then transferred into 10 mL desorbent solutions (0.001 M–0.1 M HCl). The mixtures were agitated for 1 h, then the filtrates were analyzed to determine the concentration of Cu(II) after desorption. The desorption ratio was calculated from the amount of metal ion uptake by the LCM and the percentage of desorption was obtained using Eq. (3):

$$\%D = \frac{\text{Amount of ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \qquad (3)$$

3. Results and discussions

3.1. Effect of chemical pretreatment on the biosorption of Cu(II)

Some researchers have reported that the biosorption capacity of LCMs can be improved upon chemical treatment [11]. Thus, MS and NS were pretreated using nitric acid and MeOH. Fig. 1 shows the amount of Cu^{2+} adsorbed by NS and MS, before and after pretreatment.

Regarding the raw materials, raw MS have a more important sorption capacity (1.06 mmol/g) than raw NS (0.865 mmol/g). Meanwhile, NS treated with methanol (NS_{MeOH}) or with nitric acid (NS_{HNO_3}) present better sorption capacities (1.255 and 2.154 mmol/g, respectively) than MS treated with methanol (MS_{MeOH}) and the nitric acid MS_{HNO_3} (1.125 and 1.380 mmol/g, respectively). These observations suggest that raw NS may contain more extractables than pristine MS. These extractables may congest NS pores, thereby diminishing their sorption capacity. Once NS are treated, their sorption capacity increases significantly compared to MS. Thus, the material containing more extractables has high sorption capacity upon chemical pretreatment that makes its pores more accessible. In this case, the diffusion of Cu(II) ions to the active sites on NS and MS is easy. Therefore, the study of other parameters was carried out with NS_{HNO_3} and MS_{HNO_3}.

3.2. Effect of the biosorbent dosage on Cu(II) biosorption

For a given volume and initial concentration of Cu(II) ions (precisely 10 mL of 5×10^{-3} M Cu(II)), the biosorbent dosage capacity defined by the biosorbent dosage on Cu(II) removal was examined by using the dosage in the range from 0.0 to 65 mg/10 mL as shown in Fig. 2.
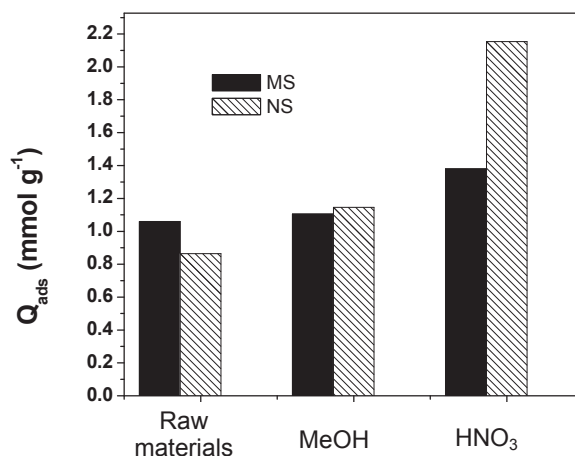

Fig. 1. Effect of pretreatment of biomass on the biosorption of Cu(II) ions. Experimental conditions: [Cu^{2+}]: 5×10^{-3} mol/L; biosorbent dosage: 2 g/L; contact time: 40 min; 150 rpm.
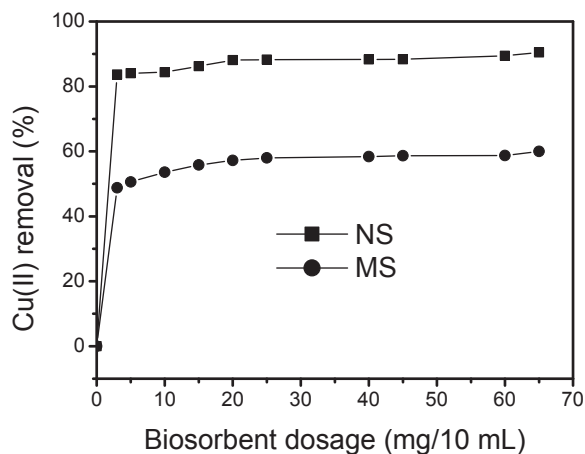
Fig. 2. Effect of biosorbent dosage on the biosorption of Cu(II) ions. Experimental conditions: [Cu^{2+}]: 5×10^{-3} mol/L; contact time: 40 min; 150 rpm. Volume of sorbate: 10 mL.

Fig. 3. Effect of shaking speed on the biosorption of Cu(II) ions. Experimental conditions: [Cu^{2+}]: 5×10^{-3} mol/L, Biosorbent dosage: 2 g/L, contact time: 40 min (NS_{HNO_3}) and 20 min (MS_{HNO_3}).

It was observed that an increase in the adsorbent dose from 0.25 to 2 g/L resulted in an increase in Cu(II) ion biosorption from 48 to 84% for MS_{HNO_3}, and from 84 to 90% for NS_{HNO_3}. A further increase in the adsorbent dosage (≥ 2 g/L) for both materials did not cause significant improvement in biosorption as a consequence of an equilibrium established between Cu(II) ions bound to the sorbents and those remaining in solution. Such a behavior was expected since an increase in adsorbent mass implies the availability of more adsorption sites since copper concentration is kept constant. Globally, one observes an increase in the sorption percentage of Cu(II) ions with the increase in the mass of biosorbents. Several authors obtained similar results during the biosorption of the same analyte on various types of lignocellulosic materials [17,18]. The results obtained indicated that a dosage of 2 g/L of biosorbent could be sufficient for the optimum removal of Cu(II) ions, a value which was used for further experiments.

3.3. Effect of shaking speed

The shaking speed is a parameter that can influence the kinetics of adsorption. Thus, keeping the biosorbent dosage of NS and MS at 2 g/L and the concentration of Cu(II) ions at 5×10^{-3} mol/L, the shaking speed was varied from 50 to 300 rpm (Fig. 3).

The results in Fig. 3 show that increasing agitation speed up to 100 rpm for NS_{HNO_3} and 150 rpm for MS_{HNO_3} increases the sorption capacity of the cupric ions. When the mixture is agitated, the solid particles move quickly in the solution, thus increasing the concentration of metal in the vicinity of their surface, probably towards a value close to the concentration within solution [19]. One can notice that the sorption capacity of copper (II) by the NS_{HNO_3} decreases more significantly from 2.45 mmol/g to 1.765 mmol/g beyond 100 rpm. This feature can be explained by a release of Cu(II) ions by the NS_{HNO_3} material at speed higher than 100 rpm. As a conclusion, one may consider that there is an optimal shaking speed, sufficient to support the contact
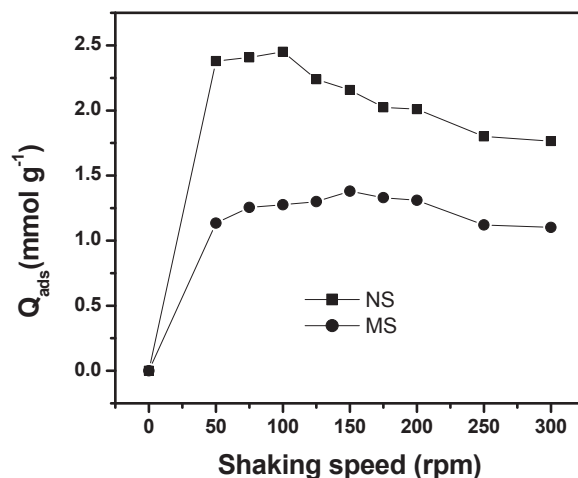
between biosorbent particles and Cu(II) ions, and sufficiently weak not to break the forces of sorption [20]. It is noted that at low agitation speed, the retention of Cu(II) ions is the highest.

3.4. Effect of the ionic strength

The choice of NaCl as the salt was justified by the fact that most effluents contain in major part chloride and sodium ions. The concentration of NaCl was thus varied in order to evaluate the effect of ionic strength on the biosorption of Cu(II). The results obtained are represented in Fig. 4.

It can be seen that an increase in salinity decreases the sorption capacity of Cu(II) ions for both biosorbents. However, the sorption of Cu(II) decreases significantly when one passes from a solution free from NaCl to a 0.01 M. This sorption capacity decreases more significantly when the concentration of salt is varied from 0.01 to 0.1 M. This confirms that there is indeed a competition between the Cu^{2+} ions and Na^+ ions for the occupation of the same sorption sites, the sorption process proceeds thus by a cation exchange mechanism [21]. But, the presence of Na^+ ions in the studied concentration range does not influence notably the elimination of the Cu^{2+} ions. As for chloride ions, previous studies related to the sorption of Cu(II) ions showed that the type of anion present in the effluent to be treated affects very little the sorption capacity [22].

3.5. Effect of interfering ions

Effluents in general contain high concentrations of various ions, and it is well known that the sorption of ionic species on a solid can be influenced by the presence of other ions in solution. The study of the influence of several species was thus undertaken on Cu(II) biosorption by NS_{HNO_3} and MS_{HNO_3}. The investigated ions include Na^+, K^+, Mg^{2+}, Ca^{2+}, Sn^{2+} and Fe^{3+} as cations; and NO_3^-, SO_4^{2-} and
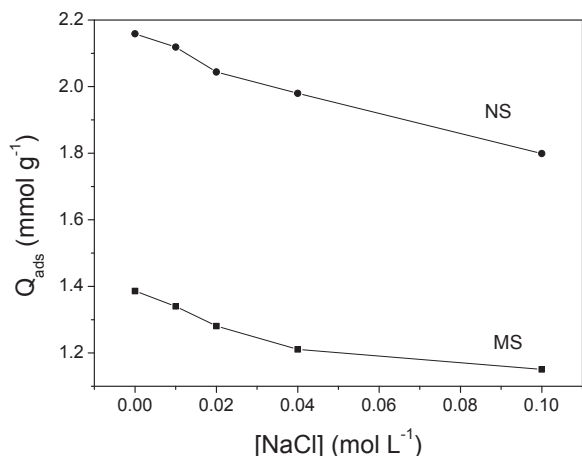
Fig. 4. Effect of ionic strength on the biosorption of Cu(II) ions. Experimental conditions: $[Cu^{2+}]$: 5×10^{-3} mol/L; m = 20 mg; granulometry: 0–200 μm, shaking speed: 150 rpm (MS_{HNO_3}) and 100 rpm (NS_{HNO_3}), V = 10 mL, contact time: 40 min (NS_{HNO_3}) and 20 min (MS_{HNO_3}).

PO_4^{3-} as anions. These species were introduced in turn in the solution containing Cu(II) ions, and their concentration was fixed at 0.01 M, a value sufficient to induce interferences with Cu(II) as revealed by the results obtained in the previous section during the analysis of the effect of ionic strength. The results obtained are shown in Fig. 5 for cations while the data relative to anions are provided as Supporting information (Fig. S3). As the main results, the presence of cations decreased the biosorption of Cu(II) by both biosorbents.

The inhibition of the uptake of Cu(II) follows the order $Fe^{3+} > Sn^{2+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$. The cations with a high charge density greatly compete for the occupation of the same sorption sites. A similar observation was made for anions, as the influence of PO_4^{3-} ions towards the biosorption of Cu(II) was more pronounced compared with SO_4^{2-} and NO_3^- (See Fig. S3, supporting information).

3.6. Effect of pH solution on Cu(II) biosorption

The pH is a remarkable parameter that can influence biosorption of metal ions. Yet, the competitive ability of H^+ species with other cations to the active sites on a sorbent surface is affected by the pH of the solution. The effect of solution pH on Cu(II) biosorption by NS_{HNO_3} and MS_{HNO_3} was investigated by using 2 g of each biosorbent per liter of 5×10^{-3} M Cu(II), and the results are shown in Fig. 6. For both materials, the biosorption of Cu(II) was relatively low for a strong acidic medium (pH 2), increasing slightly from pH 2 to pH 5. Between pH 5 and pH 6, the uptake of Cu(II) by biosorbent materials increased sharply, and then remained almost constant up to pH 9.

This could be explained by the fact that with low values of the initial pH, the surface of the sorbent is surrounded by H^+ ions that decrease the interactions between the cupric ions and the active sites of the sorbent. Thus, the reduction in the rate of sorption at low pH values can be due to the high concentration and the great mobility of the H^+ ions which are preferentially fixed by the sorbents [23]. With the increase in the pH, the total surface of the sorbent becomes negatively charged and consequently the adsorption of Cu(II) is favored. The results of the sorption of Cu(II) ions on NS_{HNO_3} and MS_{HNO_3} materials show that optimal elimination is obtained in the basic range of pH.

3.7. Sorption isotherms

In order to better describe the uptake of Cu(II) by NS_{HNO_3} and MS_{HNO_3} materials, three isotherm models (Langmuir, Freundlich and Temkin) were applied. In fact, interactions between the sorbate and adsorbents are indicated by sorption isotherms, and the initial metal concentration provides an important driving force to overcome all mass transfer resistances between the aqueous and solid phases. Isotherms are often exploited for the determination of the maximum sorption capacities of the pollutants and for the identification of the type of sorption. The nonlinear and linear formulae of Langmuir [24] are respectively represented by the following equations:
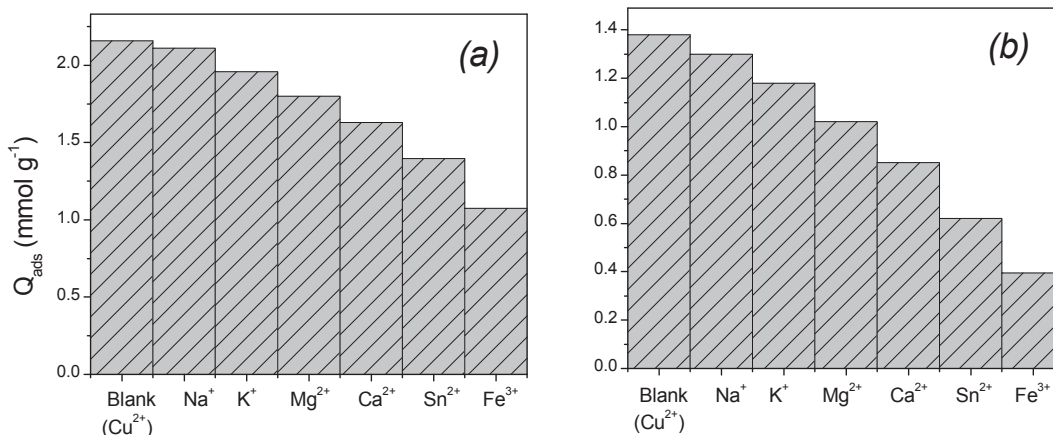

Fig. 5. Effect of interfering ions on the biosorption of Cu(II) ions. Experimental conditions: $[Cu^{2+}] = 5 \times 10^{-3}$ mol/L; m = 20 mg; shaking speed: 150 rpm (MS_{HNO_3}) and 100 rpm (NS_{HNO_3}), V = 10 mL; contact time: 40 min (NS_{HNO_3}) and 20 min (MS_{HNO_3}).
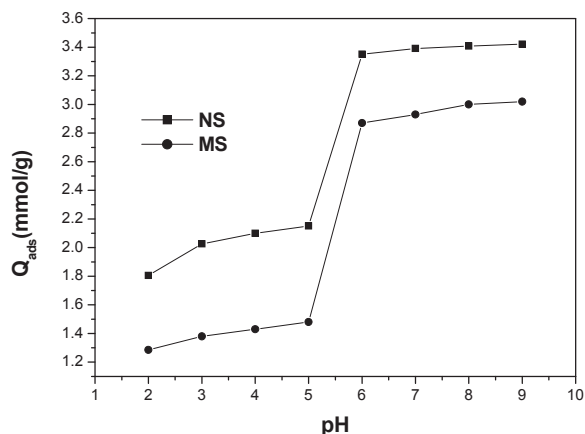
Fig. 6. Effect of pH on the biosorption of Cu(II) ions. Experimental conditions: $[Cu^{2+}]$: 5×10^{-3} mol/L; $m = 20$ mg; granulometry: 0–200 μm; shaking speed: 150 rpm (MS_{HNO_3}) and 100 rpm (NS_{HNO_3}), $V = 10$ mL, contact time: 40 min (NS_{HNO_3}) and 20 min (MS_{HNO_3}).

$$Q_e = \frac{k_L\, Q_{max}\, C_e}{1 + k_L C_e} \tag{4}$$

$$\frac{C_e}{Q_e} = \frac{1}{k_L\, Q_{max}} + \frac{C_e}{Q_{max}} \tag{5}$$

where Q_e (mmol/g) is the equilibrium copper(II) biosorption capacity of NS_{HNO_3} and MS_{HNO_3} and C_e (mmol/L) is the metal ion concentration in the solution at equilibrium. Also, Q_{max} (mmol/g) and K_L (L/mg) are Langmuir constants related to the maximum sorption capacity and rate of sorption which are obtained from the slope and intercept of the linear plot of C_e/Q_e versus C_e. The empirical Freundlich isotherm can be expressed as [25]:

$$Q_e = k_F\, C_e^{\frac{1}{n}} \tag{6}$$

$$\ln Q_e = \ln k_F + \frac{1}{n}\, \ln C_e \tag{7}$$

where k_F (mol/g) and $1/n$ are the Freundlich sorption constant and heterogeneity factor, respectively. k_F is related to the bonding energy and $1/n$ related to intensity of the sorption constant is related to the capacity of sorption and empirical parameter. $1/n$ and k_F are obtained by the slope and intercept linear plot of $\ln Q_e$ versus $\ln C_e$.

The Temkin isotherm is generally presented by the following equation:

$$Q_e = Q_{max} \frac{RT}{\Delta Q} \ln (k_T\, C_e) \tag{8}$$

Q_{max} (mmol g^{-1}) and K_T (L mmol^{-1}) are Temkin constants, R is the ideal gas constant (8.31 J mol^{-1} K^{-1}), C_e is concentration of ions with the metal equilibrium (mmol L^{-1}) and T is absolute temperature (K) [26,27].

For NS_{HNO_3} and MS_{HNO_3} materials, the Langmuir, Freundlich and Temkin isotherm models are illustrated in

Fig. 7 and Fig. 8, while the corresponding constants are gathered in Table 1.

A comparison of investigated models reveals that the Langmuir model presents a better correlation coefficient ($R^2 = 0.994$) for the NS_{HNO_3}. This implies that the NS_{HNO_3} sorption sites display an equivalent energy and are uniformly distributed so that cupric ion fixation proceeds by the monolayer type [16,28].

The maximum sorption capacities determined by the Langmuir model were 60.386 μmol/g for NS_{HNO_3} and 44.90 μmol/g for MS_{HNO_3} biosorbents. Although this model is rather common for biosorption of metal ions, it is difficult to compare the q_m values of various sorbents because the used experimental conditions have to be identical, what is not the case herein. Differences of metal uptake are due to the properties of each sorbent material such as the intrinsic structure, bearded functional groups and surface area. For comparison, copper(II) biosorption capacities obtained at NS_{HNO_3} and MS_{HNO_3} are higher than those of some other sorbent materials reported in the literature (Table 2).

In the case of MS_{HNO_3}, the Freundlich model seems to be more suitable ($R^2 = 0.970$) than the Langmuir model ($R^2 = 0.941$). Moreover, the sorption sites are heterogeneous and fixing energies are different [34,35]. The constant value $1/n$, determined by the Freundlich model (0.8 for MS_{HNO_3} and 0.56 for NS_{HNO_3}) between 0 and 1 is an indication of the affinity of the biosorbents for Cu(II) ions. These different values determined from this model show that the MS_{HNO_3} material has a better affinity with Cu(II) ions, compared to NS_{HNO_3}. This phenomenon could be explained by the fact that MS_{HNO_3} adsorption sites are more active than those of NS_{HNO_3}. This good ability of the pollutant to bind to the active sites present on the surface of MS_{HNO_3} is confirmed with regard to the adsorption equilibrium that was attained more quickly with MS_{HNO_3} (20 min) compared to NS_{HNO_3} (40 min).

Temkin's model was used to determine the different heats of adsorption involved during various adsorbate–adsorbent interactions. There is a large variation of heat with the
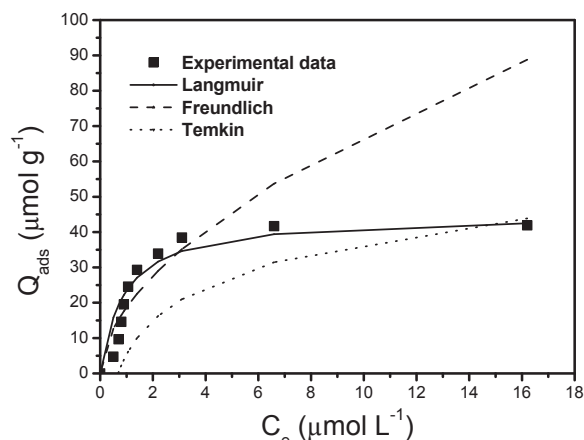

Fig. 7. Variation of the concentration of Cu(II) ions sorbed at the equilibrium in solution on NS_{HNO_3}. Simulation models of Langmuir, Freundlich et Temkin. Experimental conditions: $m = 20$ mg; granulometry: 0–200 μm; contact time: 40 min; shaking speed: 100 rpm; $V = 10$ mL.

Fig. 8. Variation of the concentration of Cu(II) ions sorbed at the equilibrium in solution on MS_{HNO_3}. Simulation models of Langmuir, Freundlich and Temkin. Experimental conditions: $m = 20$ mg; granulometry: 0–200 μm; contact time: 20 min; shaking speed: 150 rpm; $V = 10$ mL.
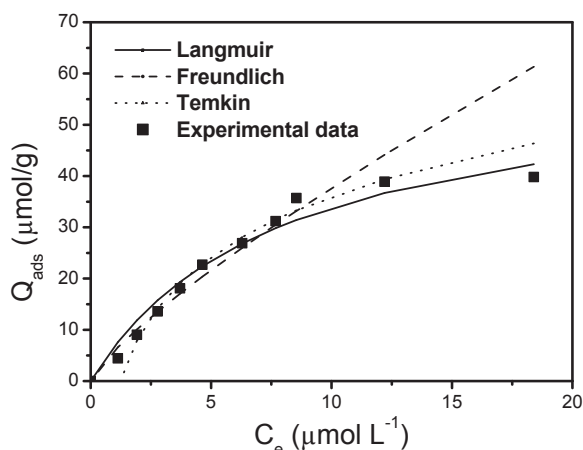
Table 1
Langmuir, Freundlich and Temkin constants for the adsorption of Cu(II) on NS_{HNO_3} and MS_{HNO_3}. Initial concentration.

Biosorbents	Isothermes types	Constants	
NS_{HNO_3}	Langmuir	Q_m (μmol/g)	60.386 ± 0.006
		K_L (L/μmol)	1.088 ± 0.004
		R^2	0.994 ± 0.009
	Freundlich	$1/n$	0.56 ± 0.02
		K_F (μmol^{1-n}.L^n. g^{-1})	18.67 ± 0.02
		R^2	0.68 ± 0.03
	Temkin	ΔQ (kJ/μmol)	8.04 ± 0.02
		K_T (L/μmol)	1.47 ± 0.03
		R^2	0.88 ± 0.04
MS_{HNO_3}	Langmuir	Q_m (μmol/g)	44.90 ± 0.02
		K_L (L/μmol)	0.13 ± 0.02
		R^2	0.94 ± 0.03
	Freundlich	$1/n$	0.8 ± 0.05
		K_F (μmol^{1-n}.L^n. g^{-1})	5.97 ± 0.09
		R^2	0.97 ± 0.09
	Temkin	ΔQ (kJ/μmol)	8.78 ± 0.08
		K_T (L/μmol)	0.83 ± 0.02
		R^2	0.99 ± 0.02

MS_{HNO_3} (8.779 kJ/mol) compared to NS_{HNO_3} (8.044 kJ/mol). This may reflect the fact that interactions between Cu(II) ions and MS_{HNO_3} are more energetic than interactions between Cu(II) ions and NS_{HNO_3} [14].

Table 2
Comparison of maximum capacities of some adsorbent materials for Cu(II) ion sorption, from the literature.

Adsorbent material	Q_m (mg/g)	References
Cellulose	7.06	[29]
Peanut hull carbon	65.57	[30]
Dried activated sludge	62.50	[31]
Olive leaves powder	71.43	[32]
Phanerochaete chrysosporium	248.15	[33]
Pinussylvestris	28.83	[16]
Globosum leaves powder	12.45	[11]
Newspaper scraps	286.83	This work
Maize spatha	176.96	This work

3.8. Sorption kinetics

Contact time is a fundamental parameter in all transfer phenomena of biosorption. Experiments were carried out to determine the time of equilibrium for biosorption. Both materials showed a fast rate of sorption during the first 10 min of the metal-biosorbent contact. This observation agrees with the previous other work on sorption of copper on biosorbents [13,16,36]. The equilibrium occurred within 20 min for MS and 40 min for NS. After this equilibrium period, the amount of adsorbed metal ions did not significantly change with time. The sorption kinetics was examined for better understanding of the dynamics of biosorption of Cu^{2+} on the biosorbents. With the number of the kinetic models which appear in the literature, the pseudo-second order and the intra-particle diffusion were applied to the experimental data obtained (Fig. 9). The modeling of the experimental kinetic data allows a description of the mechanisms of fixation, in particular by the calculation of the rate of sorption, the coefficients of mass transfer and intra-particle diffusion [37,38]. The linear and nonlinear formulae of the kinetic model of the pseudo-second order are given respectively by the following equations:

$$q_t = \frac{q_e^2 k_2 t}{1 + (q_e k_2 t)} \tag{12}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \tag{13}$$

where k_2 (g/mol/min) is the rate constant of second-order sorption, t (min) is the contact time, q_e (mmol/g) is the amount of cupric ions sorbed at equilibrium and q_t (mmol/g) is the amount of cupric ions sorbed at any given time t. This model is used to determine the reaction half time ($t_{1/2}$ (min)) [26,37].

$$t_{\frac{1}{2}} = \frac{1}{q_e k_2} \tag{14}$$

The intra-particle diffusion model evaluates the contribution at the diffusion of copper within biosorbents in the whole biosorption process. The model is defined by the following relationship:

$$\ln R = \ln k_{id} - \alpha \ln t \tag{15}$$

where R is the percentage of the adsorbed biosorbents, K_{id} is the rate constant of intra-particle diffusion, A is a gradient whose value depends on the sorption mechanism [37,39]. The constants related to these models are given in Table 3.

The high correlation coefficient values show that the sorption data match pseudo-second order kinetics. This is generally the case for the biosorption of heavy metals or the organic compounds [17,26,32]. This is also confirmed by the values of the sorption capacity evaluated from the pseudo-second order (2.155 ± 0.002) mmol/g NS_{HNO_3} and (1.400 ± 0.007) mmol/g MS_{HNO_3} that are close to the experimental average values (2.157 mmol per g NS_{HNO_3} and 1.44 mmol per g MS_{HNO_3}) obtained during the variation of contact time. This implies that the limiting step of the
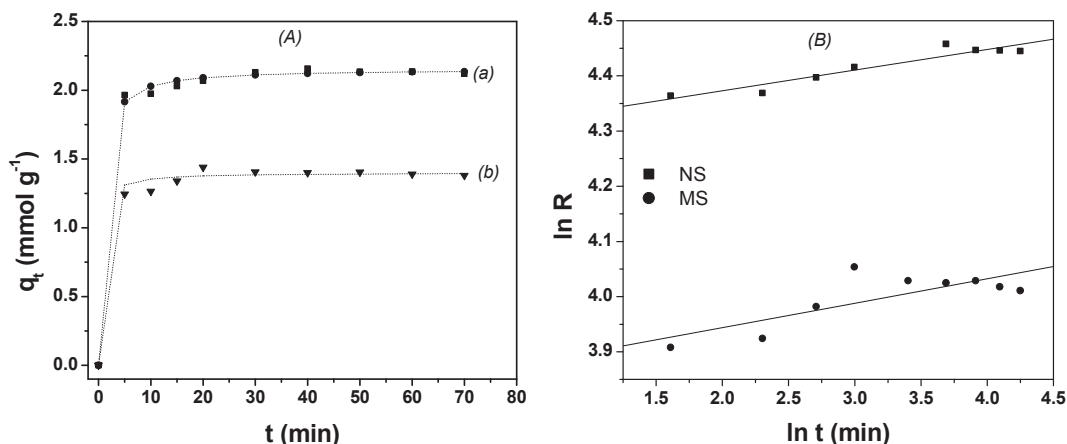
Fig. 9. Effect of contact time on Cu(II) biosorption. (A) Pseudo second order (a) NS_{HNO_3} and (b) MS_{HNO_3} and (B) intra-particle diffusion kinetic models. Experimental conditions: $m = 20$ mg; granulometry: 0–200 μm; $t_{MS} = 20$ min; $t_{NS} = 40$ min $v_{MS} = 150$ rpm; $v_{NS} = 100$ rpm; $V = 10$ mL.

copper biosorption on the biosorbents is governed by chemisorption [39,40]. The reaction half time confirms that the biosorption process is very fast in the first moments on MS (0.337 min) compared with those of the NS (0.620 min).This observation shows that the sorption sites of MS although less significant seem to be more available for the uptake of cupric ions.

The intra-particle diffusion model enabled us to study the diffusion of copper within the biosorbents throughout the process. The diffusion constants show that the diffusion is very fast for NS_{HNO_3} ($K_{id} = 73.553$ mmol/g.min$^{1/2}$) compared to MS ($K_{id} = 47.229$ mmol/g.min$^{1/2}$).

3.9. Desorption of copper (II) ions adsorbed

The performance or the effectiveness of a biosorbent can also be determined by its possibility to be reused. The desorption results are given in Fig. 10 where the variation of desorption percentage is plotted against concentration of the desorption solution.

The desorption percentage obtained for the various concentrations of HCl (0.001–0.1 M) lies between 84.38

and 95.88% for NS and 78.84 and 90.34% for the MS_{HNO_3}. Therefore, the NS_{HNO_3} have a capacity more significant to release the copper ions compared to the MS_{HNO_3}. The undesorbed fraction of copper may be bound to the NS and MS through a different mechanism other than physical sorption. The desorption percentage of NS_{HNO_3} and MS_{HNO_3} is 84.38 and 78.84%, when the concentration of HCl is 0.001 M and 95.88 and 90.34% when the concentration of HCl is 0.01 M, respectively. Then, it is clear that the desorption results from cation exchange between the protons in solution and the sorbed cupric ions. The action of the protons only starts effectively from a certain concentration of HCl. The desorption process even slows down for higher concentrations of HCl (0.1 M), in the order of 89.78%–84.24% for the NS and MS, respectively. This can be explained by the fact that for such concentrations, the hydrochloric acid could modify the structure of the materials,

Table 3
Pseudo-second order kinetic and intra-particle diffusion parameters for biosorption of copper on NS and MS.

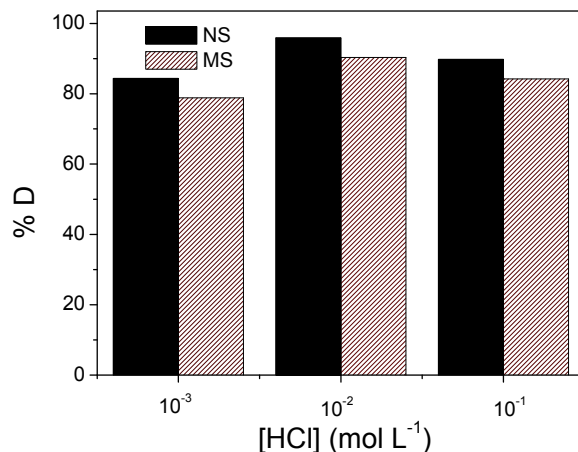| Biosorbents	Kinetic model	Constants	
NS_{HNO_3}	Pseudo-second order	K_2	0.75 ± 0.09
		q_e	2.155 ± 0.002
		R^2	0.99 ± 0.02
		$t_{1/2}$	0.620 ± 0.001
	Intraparticle diffusion	K_{id}	73.55 ± 0.02
		α	-0.037 ± 0.005
		R^2	0.874 ± 0.001
MS_{HNO_3}	Pseudo-second order	K_2	2.1 ± 0.3
		q_e	1.400 ± 0.007
		R^2	0.99 ± 0.02
		$t_{1/2}$	0.337 ± 0.002
	Intraparticle diffusion	K_{id}	47.229 ± 0.044
		α	-0.05 ± 0.02
		R^2	0.612 ± 0.001

Fig. 10. Effect of the desorption solution HCl (0.001, 0.01 and 0.1 M) on the recovery of sorbed Cu(II) ions on NS_{HNO_3} and MS_{HNO_3}. Experimental conditions: $m = 20$ mg (containing copper), Contact time: 60 min, shaking speed: 200 rpm, $V = 10$ mL of HCl.

increasing the affinity between the cupric ions and the biosorbent [14,22,37].

4. Conclusion

The ability of two natural biosorbents (newspaper scraps (NS) and maize spatha (MS)) for the removal of copper(II) ions from aqueous solution was evaluated. An optimization of the parameters affecting the rate of removal and the mechanisms that take place during the biosorption of copper ions were investigated. It was noticed that to achieve sorption capacities, optimal conditions should be as follows: Cu(II) ion concentration: 5×10^{-3} M, contact time: 40 min for NS_{HNO_3} and 20 min for MS_{HNO_3}, pH 5, shaking speed: 100 rpm for NS_{HNO_3} and 150 rpm for MS_{HNO_3}, and biosorbent dosage: 2 g/L. The sorption isotherms showed that the distribution of the sorption sites on the surface of NS_{HNO_3} is homogeneous and heterogeneous for MS_{HNO_3}. The sorption kinetics of both materials is best described by the pseudo-second order model. The interfering ions in solution decreased significantly the sorption capacity of the cupric ions. Furthermore, the stripping medium (0.01 M HCl) used allows to consider the reuse of the investigated biosorbents (a desorption rate of 95.8% for NS_{HNO_3} and 90.34% for MS_{HNO_3}). The promising results obtained throughout this work showed that both materials are important sorbents useful for the treatment of water polluted by Cu(II) ions.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.crci.2016.01.017

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