



The removal of metals (Cd, Cu and Zn) from the Tensift river using the diatom *Navicula subminuscula* Manguin: A laboratory study

Cherifi O.¹, Sbihi K., Bertrand M.² and Cherifi K.³

¹ Laboratory of Food, Environment and Health, Biology Department, Faculty of Sciences and Techniques, Marrakech, PO Box 549, 40000 Marrakech, Morocco

e-mail: cherifiouafa@gmail.com, agro_karim@yahoo.fr

² INTECHMER – Conservatoire National des Arts et Métiers, BP324, F-50103 Cherbourg Cedex, France.

e-mail: martine.bertrand@cnam.fr

³ Laboratory of Biotechnology and Valorization of Natural Resources, Faculty of sciences, Ibn Zohr University, P. O. Box 8106, 80000 Agadir, Morocco

e-mail: kcherifi@yahoo.com

Abstract

Various biomaterials have shown promise as sorbents to remove heavy metals from polluted waters at lower cost than conventional wastewater treatment technologies. The aim of this study is to characterize the ability of the freshwater diatom *Navicula subminuscula* Manguin to biosorb cadmium, copper and zinc from aqueous solutions. Our results indicate that the biosorption of metals by *N. subminuscula* increased as the initial concentration of metal ions increased in the medium until a concentration of 100-130 mg L⁻¹. Biosorption equilibrium was established in 30 minutes. The maximum metal ions biosorbed was found to be 42, 90 and 127 for 16 10⁸ diatoms per liter for Cd, Cu and Zn, respectively. The maximum uptake of metals was obtained at pH 6.0 for Cu and at pH 8.0 for Cd and Zn. An increase in the biosorption of *P. lanceolatum* was observed with an increase in temperature from 15 to 25°C. The biosorption of all three metal ions followed the Langmuir isotherm. Competitive biosorption of cadmium, copper and zinc ions was also achieved. The FTIR (Fourier Transformed Infra Red spectroscopy) results of algal biomass revealed the different functional groups at the diatom surface that are able to react with metals in the medium. The results all together suggest that *N. subminuscula* can be used as a biosorbent for an efficient removal of heavy metals from aqueous solutions which temperature and pH values could be close to the mean ones of the Tensifriver.

Keywords: Biosorption, FTIR, Heavy metal, *Navicula subminuscula*

1. Introduction

High concentrations metals, such as cadmium (Cd), copper (Cu) and zinc (Zn), cause toxic and harmful effects to living organisms in water and to its consumers [1, 2], even though Cu and Zn are vital elements. For these reasons, the development of systems for removing these metals from polluted areas is necessary. The search for new technologies to remove hazardous metals from wastewaters has

focused attention on the metal binding abilities of different biological materials instead of the existing conventional physicochemical methods [3, 4]. Among the biological material, microalgae have proved to be advantageous because they present several advantages, i.e. economic regeneration, metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed off, high efficiency in

dilute effluents and large surface area to volume ratio [5, 6, 7].

In Marrakech (Morocco), an important pollution is generated by the industry and mining which discharge of metals into the Tensift River, and mainly Cd, Cu and Zn [8]. Industrial wastewater and mining wastes flow directly into the environment without any treatment. In Morocco, there are only few studies on freshwater diatom ability to remove metals from the environment [9, 10, 11]. For these reasons, studies directed to this field are necessary. Thus, the purpose of this study is to evaluate the biosorption capacity of *N. subminuscula*. This diatom was chosen because it is dominant during all the year [12], and also because of the lack of information about its biosorption ability. In our work, the biosorption capacities of this diatom were evaluated using Langmuir isotherms. In order to characterize the process, the effects of variations of pH, temperature, algal biomass, and metal concentration were investigated; mixed metal systems were also studied. Moreover, information on the chemical composition of diatom surface was obtained using FT-IR. This was performed in order to reveal the molecular groups that could bind metals.

2. Materials and Methods

2.1. Isolation and cultivation of *N. subminuscula*

The microalga used was the benthic diatom *N. subminuscula* isolated from the Tensift River. This diatom was grown in sterilized modified WC medium at pH of 7.0 (Wright's Cryptophyta) [13]. Algal cultures were maintained in Erlenmeyer flasks of 2 liters-capacity in order to provide sufficient quantity of biomass for experiments. Cultures were incubated in a culture room illuminated at $72 \mu\text{E m}^{-2} \text{s}^{-1}$, they were shaken under a light/dark cycle of 16h/8h during 10 days at 25°C. Cultures were checked regularly microscopically in order to be sure of the absence of any contamination. These cultures were deemed axenic. Cells were removed from the culture medium by centrifugation (10,000 x g for 5min) and were washed three times with distilled water in order to remove the remaining culture medium.

2.2. FT-IR spectroscopy

To give a qualitative and preliminary analysis of the main chemical groups present on the cell wall of biomass, an IR analysis in solid phase was carried out. For the FTIR study, 0.1 g of lyophilized biomass of *N. subminuscula* was encapsulated in 1 g of KBr

keeping the ratio 1:10, in order to prepare the translucent sample disks, by pressing the ground material with 8MT pressure bench press. Infrared spectra were obtained with a Perkin Elmer FTIR-2000 spectrophotometer [14].

2.3. Methods

2.3.1. Cultures of diatoms

Experiments were conducted in 250 ml Erlenmeyer flasks containing 100 ml of culture medium and 16×10^8 diatom cells. The temperature was maintained at 25°C and shaken at 150 rpm for 30 min using the LAB-LINE incubator-shaker (Orbit).

2.3.2. Metal solutions

The glassware was soaked in 10% (v/v) nitric acid overnight and rinsed thoroughly with ultrapure water. Stock solutions of Cd, Cu and Zn (1000 mg metal/l) were prepared from cadmium chloride (CdCl_2), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and zinc chloride (ZnCl_2) using ultrapure water. All working solutions were prepared by diluting the stock solution with ultrapure water. Sub-samples (5 ml) were taken from each flask at the beginning of biosorption tests and acidified for the determination of the total Cd, Cu and Zn contents.

2.3.3. Biosorption studies

The biosorption of Cd, Cu and Zn ions on the algal biomass was investigated in batch biosorption equilibrium experiments. The effect of the medium pH, contact time, initial metal concentration, initial biomass concentration, temperature and mixed metal ions on the biosorption rate and capacity were studied.

The effect of pH values (from 2 to 10) on the biosorption rate of Cd, Cu and Zn on *N. subminuscula* was investigated. The pH was adjusted with HCl or NaOH. The biomass was separated from the metal solution by centrifugation at 10,000 x g for 5min, and the samples were stored for further analysis. To observe the effect of contact time (from 0 to 180 min), similar incubation conditions were repeated until the equilibrium was reached. Medium samples (5ml) were drawn from every flask after a regular time interval to calculate the progress of biosorption.

In standard conditions, one metal is introduced in the culture medium at a concentration of 8 mg L^{-1} at the beginning of the experiment. When two or three metals were introduced, their individual concentration

was 4 mg L^{-1} and 2.66 mg L^{-1} , respectively, so that the total metal concentration was 8 mg L^{-1} . To study the effect of initial metal concentration on the biosorption capacity of *N. subminuscula*, the metal concentration was investigated in the range of $0\text{--}256 \text{ mg L}^{-1}$, and carried out at the optimal pH for each metal: 6.0 for Cu, and 8.0 for Cd and Zn.

The samples were analyzed for metal content by a flame atomic absorption spectrophotometer (UNICAM 929).

The analysis of the equilibrium data is essential to develop an equation which precisely represents the results and which can be used for design purposes. Various isotherm models have been used for the equilibrium modeling of biosorption systems. The Langmuir model is one of the most widely used ones to describe the biosorption process. The Langmuir isotherms assumes monolayer adsorption, and is presented by the following equation [15]:

$$q = \frac{q_{\max} b C_{\text{eq}}}{1 + b C_{\text{eq}}}$$

Where q is the amount in milligrams of metal biosorbed per gram of biosorbent material; C_{eq} is the metal residual concentration in solution; q_{\max} is the maximum specific uptake and b is the energy of biosorption.

2.4. Statistical analysis

All the experiments were repeated three times and average values were reported. Standard deviations were found to be $\pm 1.5\%$. Further, the error bars for the figures were so small as to be smaller than the symbols used to plot the graphs and, hence, not shown. The data were tested for normality and homogeneity of variance, and tests for significance between treatments were determined using a one-way analysis of variance (ANOVA). All analyses were carried out using the program SPSS 17.0 for Windows.

3. Results and Discussion

3.1. Effect of biosorbent dosage on biosorption

The effect of algal biomass on the amount of Cd, Cu and Zn ions removed was studied by the exposure of different densities of diatom cells, between 8 and $40 \times 10^8 \text{ L}^{-1}$, to 8 mg L^{-1} Cd, Cu and Zn (these concentrations were determined after preliminary tests) (Fig. 1). The biosorption of Cd, Cu and Zn was dependent on the concentration of algal biomass in the medium; the higher the biomass, the higher the removal efficiency. Removal efficiency increased sharply up to $16 \times 10^8 \text{ cells L}^{-1}$. Beyond this cell abundance, there was no significant increase. Therefore, the optimum algal abundance selected for the other experiments was $16 \times 10^8 \text{ cells L}^{-1}$.

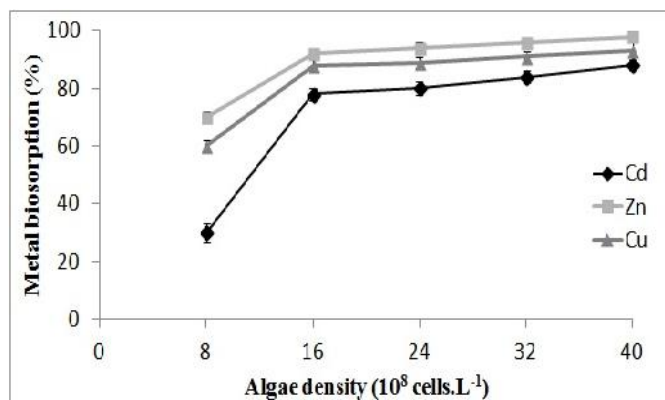


Figure 1. Effect of *N. subminuscula* cell abundance on the removal (%) of copper (Cu, triangle), cadmium (Cd, diamond) and zinc (Zn, square) ions. Initial ($T = 0$) metal ion concentration of 8 mg L^{-1} ; pH of 6.0 for Cu and 8.0 for Cd and Zn; temperature of 25°C ; contact time of 30 min.

3.2. Characterization of biosorbent systems

The IR absorption bands and corresponding possible groups able to interact with protons or metal ions are presented in Table 1. The results obtained give an idea on the presence of functional groups on the algal cell

surfaces and also on the mechanism of adsorption which is dependent on functional groups. The FTIR spectra bands revealed a wide diversity in functional groups reflecting the complex nature of the biomass composition. The table reveals slight changes in the absorption peak frequencies between non-contaminated algae and contaminated algae, especially

for amino, carbonyl, carboxylic and hydroxyl groups and silica, which suggested that there was a metal binding process taking place on the surface of the biomass [16, 17, 18]. For instance, in the presence of Zn, the carbon group shifted from 2932 to 2981 cm^{-1} which is significant. It indicates that this group is involved in Zn biosorption process. According to other studies, many functional groups interact with protons or metal ions, especially carboxylic groups [19, 20, 15, 21, 22].

3.3. Effect of pH on metal ion biosorption

The acidity of solutions is one of the most important factors affecting biosorption of metal ions. In the

medium, it affects the competition ability of hydrogen ions with metal ions to active sites on the biosorption surface [23, 24].

Different metal ions may have different pH optima, possibly due to the different solution chemistry of the species [21, 25]. The initial pH optimum for biosorption is also microorganism dependent because of different adsorptive sites of different species of microorganisms. The effect of initial pH on the equilibrium uptake of Cd, Cu and Zn ions was investigated between pH 2.0 and pH 10.0, on the equilibrium uptake of Cd, Cu and Zn ions, is presented in Fig. 2.

Table 1. Surface functional groups observed on diatom biosorbent *N. subminuscula* by FTIR spectroscopy

| Wavelength band (cm^{-1}) | | | | Functional groups |
|--------------------------------------|---------------------------|---------------------------|---------------------------|---|
| Native alga ¹ | alga with Cd ² | alga with Cu ³ | alga with Zn ⁴ | |
| 3428, 4215 | 3432, 4285 | 3436, 4377 | 3432, 3861 | Carboxylic/OH and N-H stretch |
| 2932 | 2935 | 2937 | 2981 | C-H ₂ stretching |
| 2857 | 2859 | 2858 | 2857 | C-H ₃ stretching |
| 1745 | 1748 | 1748 | 1746 | >C=O stretching of ester or fat acids |
| 1657 | 1658 | 1659 | 1659 | >C=O stretching for primary amids |
| 1545 | 1548 | 1548 | 1548 | N-H bending in amids |
| 1409 | 1412 | 1412 | 1414 | C-O stretching in carboxylates |
| 1376 | 1379 | 1379 | 1379 | N-H bending |
| 1242 | 1240 | 1239 | 1240 | Si-O-Si stretching, C-O stretch in the aromatic ring. |
| 1085 | 1081 | 1081 | 1081 | C-OH stretching vibrations |
| 798 | 780 | 780 | 780 | Si-O-Si stretching |
| 721 | 721 | 721 | 721 | Plane deformation |
| 597 | 599 | 599 | 598 | Plane deformation |
| 467 | 465 | 465 | 465 | C-N-C scissoring |

- 1Native algae: *N. subminuscula* before biosorption test.
- 2Algae with Cd: *N. subminuscula* after biosorption test with Cd.
- 3Algae with Cu: *N. subminuscula* after biosorption test with Cu.
- 4Algae with Zn: *N. subminuscula* after biosorption test with Zn.

The lowest biosorption values were observed at pH 2.0 for all metal ions and could be attributed to the high concentration of protons competing with Cd, Cu and Zn cations for binding on the biomass. The increase in metal ions biosorption at higher pH values may be explained by the negative ionization of functional groups (such as -COO^-) on the cell surface which serve as binding sites. The optimal pH values were 6.0 for Cu and 8.0 for Cd and Zn. At high pH values, many negative charges are present on the cell surface; the ionic state of ligands such as carboxyl, phosphoryl, sulfhydryl, hydroxyl, and amino groups is such so as to promote reaction with the metal cations [26]. However, when the pH increases, the solubility of

metals decreases; above a limit value, metals are included in non-soluble hydroxylated complexes [14].

3.4. Effect of contact time on biosorption

Fig. 3 shows the results of kinetic experiments conducted to determine the equilibrium time required for the biosorption of Cd, Cu and Zn by *P. lanceolatum* biomass. For all the tested metal ions, the biosorption was firstly fast, then a plateau was gradually obtained within 30 min, accounting for ~ 19, 18 and 16 mg g^{-1} of sorption for Zn, Cu and Cd respectively. The initial first phase could be attributed to the fast adsorption of metal ions until saturation

of the sites on the surface of microalgae, whereas the following phase could correspond to a slower adsorption, which kinetic depends on the penetration

kinetic inside cells of previously adsorbed metal ions[27].

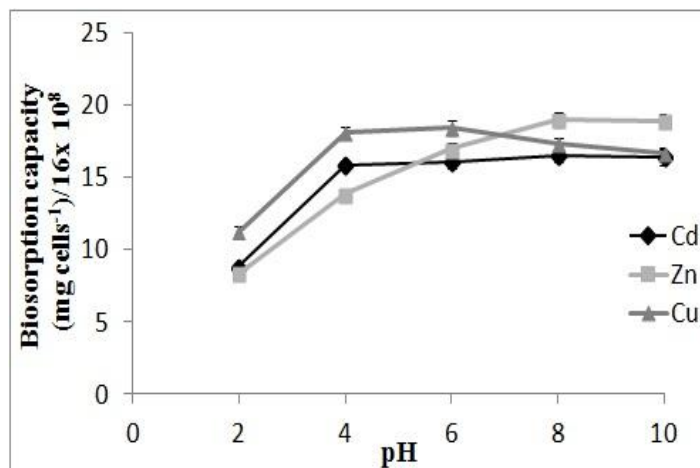


Figure 2. Effect of pH on the biosorption capacity of *N. subminuscula* cells for copper (Cu, triangle), zinc (Zn, square) and cadmium (Cd, diamond). Initial ($T = 0$) concentrations of metal ions of 8mgL^{-1} and diatom abundance of 1610^8 cells L^{-1} ; temperature of 25°C ; contact time of 30 min.

After this equilibrium period, the amount of biosorbed Cd, Cu and Zn ions on the algal biomass did not significantly change with time.

This trend in binding of Cd, Cu and Zn ions suggests that the binding may be through interactions with functional groups located on the surface of the biosorbents. The biosorption of heavy metal ions by microorganisms has often been observed to occur in two stages; an initial quick uptake due to surface adsorption on the cell wall components and subsequent slow uptake due to membrane transport of metal ions to the cytoplasm of the cells. The cell surfaces of many microorganisms consist of polysaccharides, proteins and lipids, and therefore offer several functional groups capable of binding to heavy metal ions [28]. Note that in such a biosorption process there are several parameters determining the biosorption rate, such as structural properties of both the sorbate and biosorbent (e.g. protein and carbohydrate composition and surface charge density,

topography and surface area). The amount of biosorbent, initial concentration of metal ions and the existence of other ions (which may compete with the ions of interest for the active biosorption sites) also affect the biosorption rate.

3.5. Effect of initial metal concentration on biosorption

The metal ion biosorption capacities of *N. subminuscula* are presented as a function of the initial concentration of Cd, Cu and Zn ions between 1 and 256 mg L^{-1} in the medium (Fig. 4). The biosorption capacities of the microalgae for Cd, Cu and Zn ions were studied as a function of the initial concentration these metals. The biosorption capacity of the biomass increased first with the increasing of initial concentration of metals and then reached a saturation value. The increase could be due to an increase in electrostatic interactions [29].

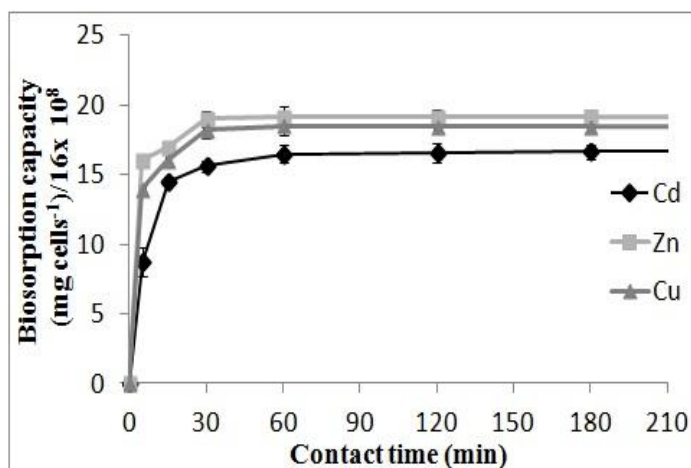


Figure 3.Effect of contact time on the biosorption capacity of *N. subminuscula* cells for copper (Cu, triangle), zinc(Zn, square) and cadmium (Cd, diamond). Initial ($T = 0$) concentrations of metal ions of 8mg L^{-1} and diatom abundance of $16 \times 10^8 \text{ cells L}^{-1}$; pH of 6.0 for Cu and 8.0 for Cd and Zn; temperature of 25°C .

The minimal initial metal concentrations for a maximal biosorption are around 128 mg L^{-1} for Zn and Cu and 64 mg L^{-1} for Cd (Fig. 4). The maximal

biosorptions of Cd, Cu and Zn ions were 42, 90 and 127 mg, respectively, by 16×10^8 diatoms in one liter.

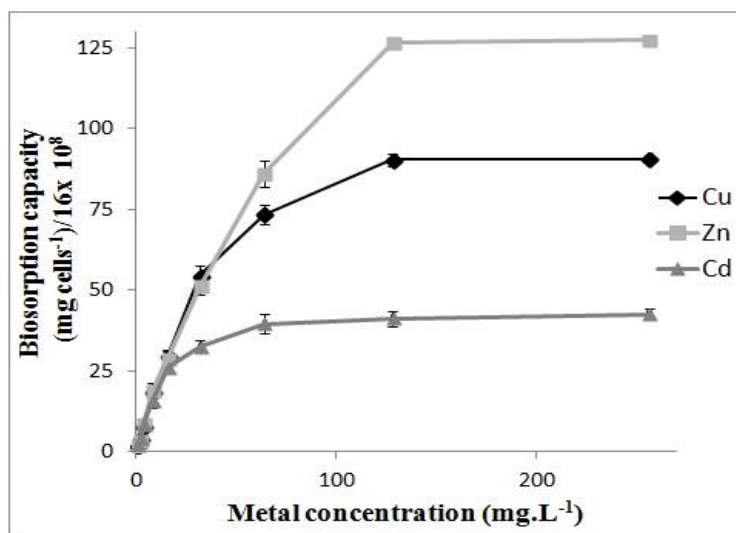


Figure 4.Effect of initial metal ion concentration on the biosorption capacity of *N. subminuscula* cells for copper (Cu, triangle), cadmium (Cd, diamond) and zinc (Zn, square). Initial ($T = 0$) diatom abundance of $16 \times 10^8 \text{ cells L}^{-1}$; pH of 6.0 for Cu and 8.0 for Cd and Zn; temperature of 25°C ; contact time of 30 min.

From the linear transformation of the data, values of Langmuir and Freundlich parameters for Cd, Cu and Zn were calculated (Table 2). High correlation coefficient (r^2) values (>0.99) obtained with all three metal ions show clearly that the Langmuir isotherm model is suitable to describe the biosorption equilibrium of these metals by *N. subminuscula* over

the studied initial concentration range. RL values for biosorption of these metal ions were between zero and one, indicating favorable biosorption [30]. Higher q_{max} and K_f values for Zn, compared with Cu and Cd, confirmed the stronger binding affinity of *N. subminuscula* for Zn compared with Cu and Cd (Table 2).

Table 2. Biosorption equilibrium constant obtained from Langmuir and Freundlich isotherms for the biosorption of Cd, Cu and Zn ions onto *N. subminuscula* cells.

| Metal ions | Langmuir | | | Freundlich | | |
|------------|---------------------------------|---------------------------|-------|------------|------|-------|
| | q_{max} (mg g ⁻¹) | b (L mg ⁻¹) | r^2 | K_f | n | r^2 |
| Zn | 127 | 0.113 | 0.998 | 9.27 | 1.93 | 0.892 |
| Cu | 90 | 0.141 | 0.997 | 8.41 | 1.89 | 0.901 |
| Cd | 42 | 0.453 | 0.998 | 8.89 | 2.85 | 0.899 |

Notes: q_{max} : maximum specific uptake (mg g⁻¹); b : equilibrium constant (L mg⁻¹); K_f and n : Freundlich constants of adsorption capacity and adsorption intensity, respectively; r^2 : correlation coefficient.

3.6. Effect of temperature on biosorption

The temperature of the medium might be important for energy-dependent mechanisms in metal biosorption by microalgal cells [31]. The temperature range used in the experiments for metal biosorption was between 15 and 40°C (Fig. 5). There was a sharp increase in Cd biosorption with a 15-25°C increase in temperature.

However, no significant difference with temperature was measured for Cu and Zn. The increase in biosorption indicates the endothermic nature of the biosorption process, as previously reported for other adsorbent systems [32, 10].

The increase in biosorption might be due to the increase in diffusion rate of the adsorbed molecules across the diatom external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing the temperature modifies the equilibrium capacity of the adsorbent for a particular adsorbate [33]. This author suggested also that the increase in

adsorption with increasing temperature might be due to an increase in the total pore volume: surface of the adsorbent, an increase in the number of active sites, and an increase in the mobility of molecules. It has been reported that the increase in sorption with temperature could be attributed to either an increase in the number of active surface sites available for sorption or to a decrease in boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of the adsorbate in the boundary layer decreases [34].

3.7. Biosorption in mixed-metal systems

For the determination of synergistic/antagonistic effect of cations present in the effluent metal solution, the biosorption of metal ions by *N. subminuscula* in a mixed-metal system was investigated. To test the binding of each metal ion in the presence of others, metal solutions containing either one metal alone (8 mg L⁻¹) or mixed with another (4 mg L⁻¹ for each metal) or two others (2.66 mg L⁻¹ for each metal) were tested.

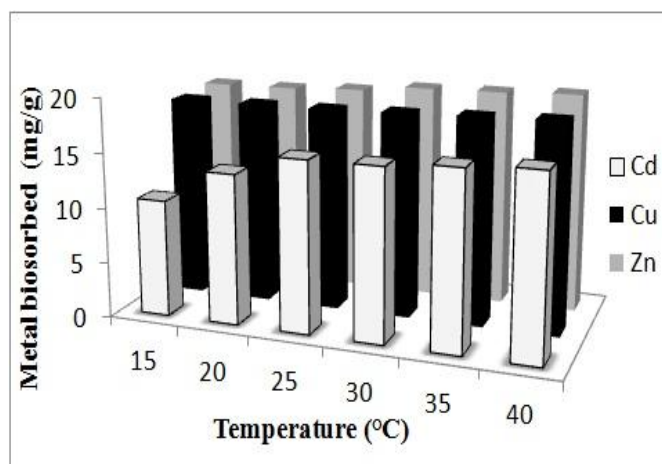


Figure 5. Effect of the temperature on the biosorption of Cd, Cu and Zn by the algal biomass. Initial conditions: diatom density: 16 10⁸ cells L⁻¹; concentration of Cd, Cu and Zn: 8mg/l; pH 6.0 for Cu; pH 8.0 for Cd and Zn; contact time: 30 min.

Fig. 6 shows the biosorbed metal percentage obtained with *N. subminuscula* in mixed-metal solutions. It appears clearly that in the multi-metal systems, the biosorption capacity of the algal cells for each metal was lower than in the single metal systems. It reduces the biosorption of Cu, Zn and Cd by 3.75%, 13.88% and 15.95%, respectively compared to the single metal systems, indicating that complex interactions of

several factors such as ionic charge, ionic radii, and electrode potential affect the biosorption of metals on the algal cells. Indeed, different cations compete for the same binding sites. It has been reported that metal biosorption is increased as the ionic radii of metal cations affect the ion exchange and adsorption process [28].

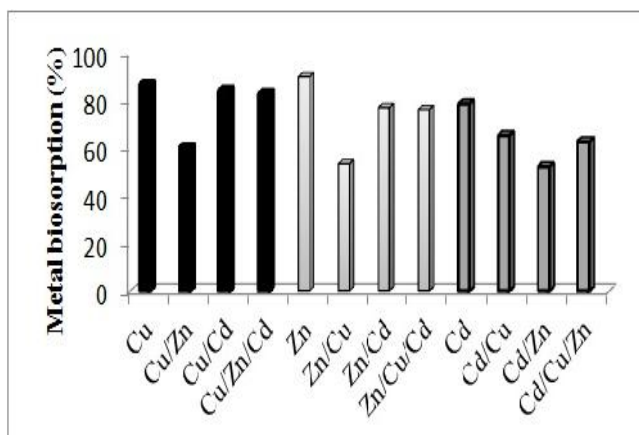


Figure 6. Biosorption (%) of copper (Cu), zinc (Zn) and cadmium (Cd) by *N. subminuscula* cells in cultures with one, two or three metal ions. In each case, total metal concentration = 8mg L^{-1} , i.e., 4mg L^{-1} each for two metals and 2.66mg L^{-1} of each for three metals. Diatom abundance of $16 \times 10^8\text{ cells L}^{-1}$; pH of 6.0 for Cu and 8.0 for Cd and Zn; contact time of 30 min.

The same result has been observed on *P. lanceolatum*, another diatom dominant in Tensift River [10]. In culture media with two metals, Zn seemed to efficiently prevent the sorption of the other metal. This could be explained by Zn ions reacting quickly to their binding sites and/or that these sites are more numerous. In culture media with three metals, the sorption of each metal was hardly lower than in the control, probably because each metal was present at a relatively low concentration, allowing easy sorption on all potential binding sites. It should also be noted that the differences in metal biosorption during the mixed-metal experiments were in accordance with the class specifications of each metal ion. Cd and Zn, which are in the same group of elements (group IIB of the periodic table), have adsorption capacities that are very close to each other, compared with Cu, which is in a different group (IB) [35]. However, Zn and Cu share very similar ionic radii (0.74 \AA and 0.73 \AA , respectively), contrasting with Cd (0.97 \AA).

4. Conclusion

The described batch studies provide significant information on the biosorption of Cd, Cu and Zn on the diatom *N. subminuscula* with respect to the

optimum pH, cell concentration and temperature for the maximum removal of metals from aqueous solutions. The results indicate that *N. subminuscula* is an effective biosorbent of Cd, Cu and Zn under the environmental conditions characterizing the Tensift River. The maximum Cd, Cu and Zn biosorption capacity was found to be 42, 90 and $127\text{ mg per } 16 \times 10^8\text{ diatom cells L}^{-1}$, occurring within 30 min of contact, at 25°C , an initial metal concentration of 8mg L^{-1} and an optimum pH of 6.0 for Cu, and 8.0 for Zn and Cd. These results are similar to those obtained with *P. lanceolatum*, another diatom dominant in the Tensift River who has the ability to remove also the hexavalent chromium Cr(VI)[10, 11]. Therefore, the widely available biomasses of *N. subminuscula* and *P. lanceolatum* in the Tensift River indeed have the potential to be used as an effective and economic materials for the removal of heavy metals from wastewater streams and tannery effluents, as found for other freshwater diatoms in different environments [36, 37, 19, 38]. Further studies are necessary to ascertain performance with industrial wastewaters at a larger scale. The performance of immobilized diatoms for the removal of pollutants should also be investigated [39].

5. References

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