Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, XXXX Volume 8, Issue 3, Page 884-893

http://www.jmaterenvironsci.com

ICMES2016. 1-3 Dec. 2016. Ouida

The siliceous microalga *Navicula subminuscula* (Manguin) as a biomaterial for removing metals from tannery effluents: a laboratory study

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

[1] *Laboratoire Aliments, Environnement et Santé, Département de Biologie, Faculty of Sciences and Techniques, Marrakech, Morocco. PO Box 549, 40000*

[2] *INTECHMER – CNAM-LUSAC, BP324, F-50103 Cherbourg Cedex, France*

[3] *Laboratoire de Biotechnologie et Valorisation des Ressources Naturelles, Faculy of Sciences, Agadir, Morocco. PO Box 28/s, 80000*

Received 28 Oct.2016,
Revised 28 Jan 2017,
Accepted 30 Jan 2017,

Keywords

- ✓ *Navicula subminuscula*,
- ✓ diatom,
- ✓ biosorption,
- ✓ hexavalent chromium,
- ✓ wastewater

cherifiouafa@gmail.com
Phone: (+212) 0667739621

Abstract

The ability of the diatom *Navicula subminuscula* (Manguin) to remove hexavalent chromium [Cr(VI)] was investigated in a batch system by the determination Cr(VI) toxic effects and biosorption by this species. The experiments have been performed under varying ranges of pH, contact time and initial ion concentrations. The results show a significant growth of *Navicula subminuscula* for Cr concentrations up to 10mg L^{-1}. The growth rate decreases as a function of increasing concentrations of Cr(VI). The IC50 is 9.2 mg L^{-1} for the artificial growth medium tested which is more than that calculated with river water (4.45mg L^{-1}) and tannery effluent water (0.088mg L^{-1}). The percentage of Cr(VI) biosorption increases with the decrease of pH: 50 % biosorption was measured at pH 7 whereas 92 % was reached at the extreme acid pH. The found linear plot of Ceq/q vs Ceq shows that biosorption follows the Langmuir biosorption model. The correlation coefficient was 0.993. At an initial concentration of 0.4g dried diatoms per liter with an initial Cr(VI) concentration of 20mg L^{-1}, the values for q_{max} and b were determined from the slope and intercept of the plot, and were found to be 94.97mg Cr(VI) per g of diatoms and 0.16L mg^{-1}, respectively. The wide ecological valence of this diatom to pollution parameters and the seasonal pattern of its life cycle are the main factors that make the biomonitoring of Cr(VI) by this species feasible.

1. Introduction

Metals ions are nowadays among the major pollutants in the environment. They are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders, as well as deleterious ecological effects at high concentrations. Chromium is one of the contaminants, which exists in hexavalent [Cr(VI)] and trivalent [Cr(III)] forms. Cr(VI) is more toxic than the Cr(III) one and requires more concern [1]. According to EPA (US Environmental Protection Agency), Cr concentrations range from 10 to 100mg L^{-1}. Cr(III) used in some tanneries and other manufacturing industries, is released and photo-oxidized in the more toxic Cr(VI) form. This oxidation has been reported by many other authors [2, 3].

Recently, heavy metal biosorption using biological material has emerged as a potential alternative instead of the existing conventional physicochemical methods [4, 5]. Among the biological material, microalgae have proved to be efficient because they present several advantages, i.e. economic regeneration, metal recovery potentiality, less amounts of chemical and / or biological sludge to be disposed off, high efficiency in dilute effluents and large surface area to volume ratio [6, 7, 8]. Moreover, diatoms are widely used to monitor river pollution because they are sensitive to water chemistry, especially ionic content, pH, dissolved organic matter, and nutrients [8].

In Marrakech (Morocco), an important pollution is generated by the tannery industry which discharges of metals into the Tensift River, and mainly chromium (≈ 40 tons/year) [9]. Tannery wastewater flows directly into the environment without any treatment. So, Cr(VI) was detected in the Tensift River with high values exceeding

International and National norms [10], specially at low river discharge and high activity of tanneries where the maximum of total chromium and Cr(VI) recorded were 1.28 and 0.1mg L^{-1}, respectively

The objective of this study was to investigate the ability of the diatom *Navicula subminuscula* Manguin (*N. subminuscula*) to tolerate chromium by the determination of a share of the toxic effect of Cr(VI) under laboratory and simulated environmental conditions and to evaluate the effect of various parameters including contact time and pH. Biosorption isotherm was applied to fit the experimental data. This species was chosen as biosorbent because it is one of the most abundant diatoms in the Tensift River and because of the relative lack of information about its biosorption ability. The main interest of this microalga lies in its ability to adapt easily to environmental factors and it is dominant during all the year [11].

2. Materials and methods

2.1. *Isolation and cultivation of the diatom*

The microalga used was the benthic *N. subminuscula* isolated from the Tensift River. *N. subminuscula* was grown in sterilized modified WC medium at pH - 7 (Wright's Cryptophyta) [12]. Algal cultures were grown in 1 liter media 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 µE m^{-2} s^{-1}; they were shaked under a light/dark cycle of 12/12 for 10 days at 20°C. Cultures were checked regularly microscopically. These cultures were deemed axenic.

2.2. *Analysis of Cr (VI) and total Cr*

The Cr (VI) concentrations of water and wastewater were determined by colorimetric technique (540 nm) with diphenylcarbazide (DPC) in acid solution as described in the standard method [13]. Total chromium amounts were determined by atomic absorption spectrophotometry (AAS) (UNICAM 929).

2.3. *Growth rate inhibition bioassays*

A batch method was used for growth-rate-inhibition bioassays using 250-mL borosilicate glass Erlenmeyer flasks, coated with Coatasil silanising solution to prevent adsorption of chromium to the glass. Test flasks were soaked in 10% (v/v) nitric acid overnight and rinsed thoroughly with distilled water. A stock solution (1000mg L^{-1}) of Cr (VI) was prepared from solid potassium dichromate $K_2Cr_2O_7$, generating Cr(VI). The stock solution was then appropriately diluted in the WC medium. The cells used in the experiments were transferred at an exponential phase to the WC medium.

Three culture media were tested. The WC culture medium, the tannery effluent water (collected at point N 31° 38' 4.64" W 7° 58' 44.76") and the Tensift River water (collected at point N 31° 41' 50.61" W 8° 3' 48.07").

2.3.1. Toxicity of Cr (VI) in the WC medium:

The tested concentrations ranged from 0 to 20mg L^{-1}. The higher concentrations were used to better simulate concentrations rejected in the tannery effluent (38mg L^{-1}). Preliminary tests, with concentrations higher than 20mg L^{-1}, do not allow *N. subminuscula* development.

2.3.2. Toxicity of Tensift River

The water samples taken from the Tensift River contained approximately 0.1mg L^{-1} of Cr(VI). And for the control [without Cr(VI)], we have used river water upstream of tannery effluents. For testing the Cr(VI) toxicity on *N. subminuscula* toxicity, Cr(VI) was inoculated at different concentrations ranging from 0.05 to 10 mg L^{-1} to test the ability of the diatom in removing high concentrations, if there are, in river water.

2.3.3. Toxicity of tannery effluent:

N. subminuscula was exposed to tannery effluent water at different Cr(VI) concentrations ranging from 0.038 to 0.76mg L^{-1}. The water of the Tensift River [without Cr(VI)] was employed as dilution water for preparing the simulated effluents.

For the three toxicity tests, each flask was inoculated with 10^4cells mL^{-1} of a prewashed *N. subminuscula* suspension according to OECD recommendation (1984). This low cell density was used to better simulate algal concentrations in the river. Flasks were incubated under the same conditions as mentioned above. Algal cell density was determined daily using a hemocytometer Malassez cell. Cell growth was considered as a parameter to monitor the toxic effect of Cr(VI) on *N. subminuscula*. Sub-samples (5mL) were taken from each flask at the beginning of each toxicity and biosorption test, prior for the determination of dissolved Cr(VI). In order to

determine the Cr(VI) biosorbed, 30 ml of culture were filtered on a 0.45 µm Millipore filter and the Cr(VI) in filtrate was determined.

2.4. *Biosorption studies*

Biosorption experiments were carried out in batch in 250 ml Erlenmeyer flasks (100 ml media) to determine the best conditions (pH and contact time) at which the maximum Cr(VI) biosorption was observed. These flasks were kept on a rotatory shaker at 150 rpm. After they were shaked for desired time periods, the cultures were filtered on a 0.45µm Millipore filter and then the filtrate was analyzed for Cr(VI) concentration.

The effect of pH on Cr(VI) biosorption by *N. subminuscula* was determined for pH values from 1 to 7 because the lower pH measured in the tannery effluents was 2.5 and the main pH value in the Tensift River was 6.9. The pH was adjusted using 0.1N HCl/NaOH. Dried *N. subminuscula* (0.4g) was added to 100 ml of culture medium with 10mg of Cr(VI) L^{-1}, in 250-ml Erlenmeyer flasks. The kinetic study for biosorption of Cr(VI) were conducted at varying initial Cr(VI) concentrations in the range of 1-20mg L^{-1}. Samples of 5ml were collected at definite time intervals from 15 to 1440 min for the Cr(VI) concentration determination.

The data obtained in batch biosorption studies was used to calculate the equilibrium metal biosorption capacity. The Langmuir biosorption model was adopted for the estimation of maximum Cr(VI) uptake (q_{max}) where they could not be reached in the experiment [14].

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

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.

2.5. Data handling and statistical analysis

All the experiments were carried out in triplicate and the mean values with standard deviation are presented. The IC50, i.e. the inhibitory concentration to reduce the growth rate by 50%, was calculated during exponential growth phase, using linear interpolation method for sub-lethal toxicity using statistical software (ICp Ver.2.0) [15]. The data were tested for normality and homogeneity of variance. The confidence interval is 95 % for all parameters tested. Tests for significance between treatments were determined using a one-way analysis of variance (ANOVA), and the Duncan test ($p < 0.05$) was used for detection of differences between groups. All analyses were carried out using the program SPSS 17.0 for Windows.

3. Results

The choice of Cr(VI) concentrations in this study was done according to the total chromium (1.2 ± 0.12g L^{-1}) and Cr(VI) (38 ± 1.32 mg L^{-1}) concentrations found in tannery effluent water of Marrakech city.

3.1. *Toxicity test*

Figure (1) illustrates the growth of *N. subminuscula* cells exposed to different Cr(VI) concentrations. The maximum cell density reached in control cultures was $25.9x10^5$cells mL^{-1}. Duncan statistical analysis of this experiment shows that there is a significant difference between maximum cell densities achieved in all cultures from that obtained in control cultures ($P < 0.05$). But Cr(VI) concentrations of 2, 4 and 10mg L^{-1} triggered a same decrease in growth when compared with the other tested concentrations ($P < 0.05$) and suggests that this diatom has the same tolerance to these concentrations. The maximum cell density obtained in these cultures was nearly 2 times lower than those reached in control cultures. But the higher Cr(VI) concentration (20mg L^{-1}) affects more seriously the algal growth. The maximum cell density at the 10^{th} day of experiment did not exceed $4x10^5$cells mL^{-1}.

Growth rates decreased as Cr(VI) concentration in the medium increased ($r = -0.96$) and maximum growth rates were obtained in control cultures and in culture with 1mg L^{-1} of Cr(VI) (0.9 day^{-1}). The IC50 value calculated during the period of exposure to Cr(VI) was 9.2mg L^{-1}.

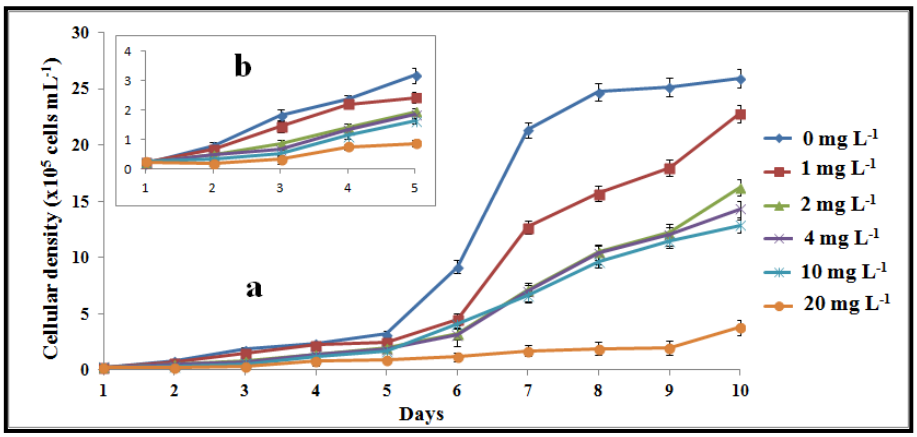

Figure 1: Growth curves of *N. subminuscula* cells exposed to different Cr(VI) concentrations during the long term exposure (a). The insert shows the growth curves during the first 4 days (b) (mean values ± SD; n=3).

Analogous tests using water from Tensift River where the alga thrives, and from tannery effluent instead of culture media, were performed. Figure (2) and (3) illustrate the growth curves of *N. subminuscula* cells exposed to different Cr(VI) concentrations of Tensift River and tannery effluents waters, respectively, during the period of study. Results show that this diatom tolerates concentrations of Cr(VI) until 4mg L^{-1} and 0.152mg L^{-1} for Tensift River and tannery effluents waters, respectively, which are less than that found with culture media. The IC50 values calculated during the period of exposure are just 4.45mg L^{-1} and 0.088mg L^{-1}, respectively, for river water and tannery wastewater.

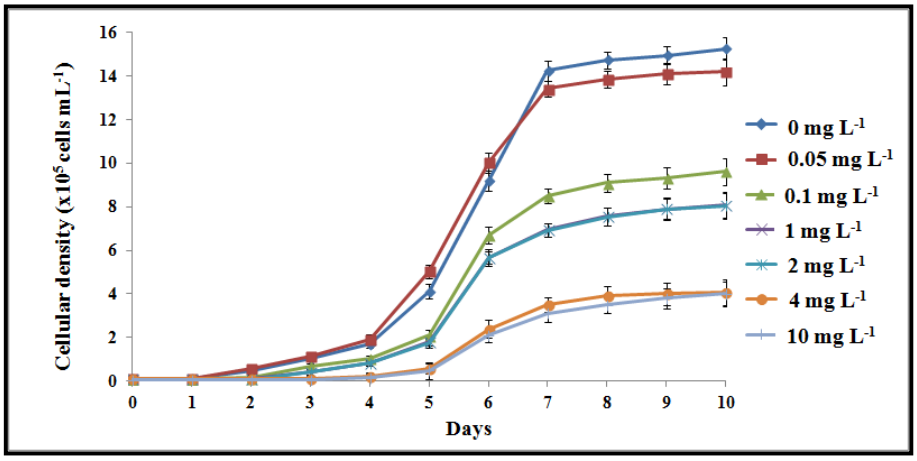

Figure 2: Growth curves of *N. subminuscula* cells exposed to different Cr(VI) concentrations of Tensift River water during the long term exposure (mean values ± SD; n=3).

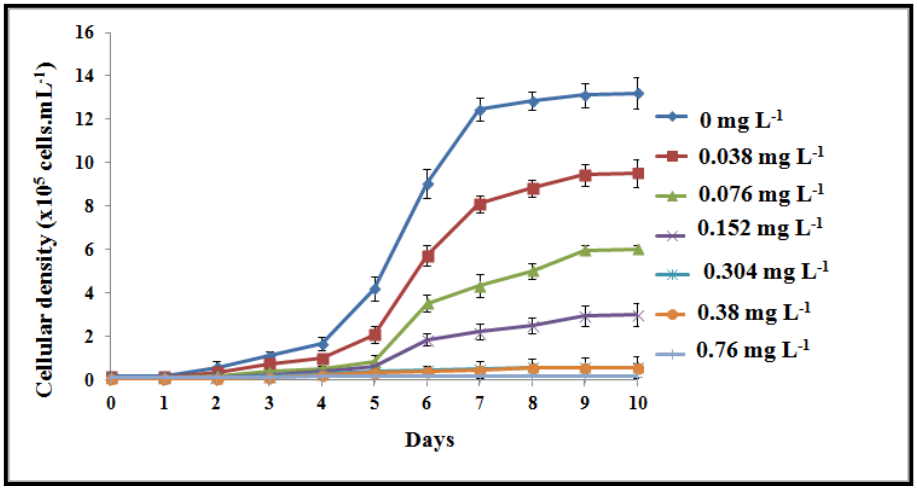

Figure 3: Growth curves of *N. subminuscula* cells exposed to different Cr(VI) concentrations of tannery effluent water during the long term exposure (mean values ± SD; n=3).

3.2. Biosorption of Cr(VI)

3.2.1. Effect of contact time

N. subminuscula cells are able to accumulate Cr(VI). Figure 4 shows the effect of contact time on the extent of biosorption of Cr(VI) by this microalga for different concentrations of Cr(VI). The results are given for the first 2 hours. It has been observed that the biosorption efficiency is maximum within the first 30 min. It reached 89% and 98% for the lower Cr(VI) concentrations (1 and 2mg L^{-1}). This increase was only 70% for higher concentrations (10 and 20mg L^{-1}).

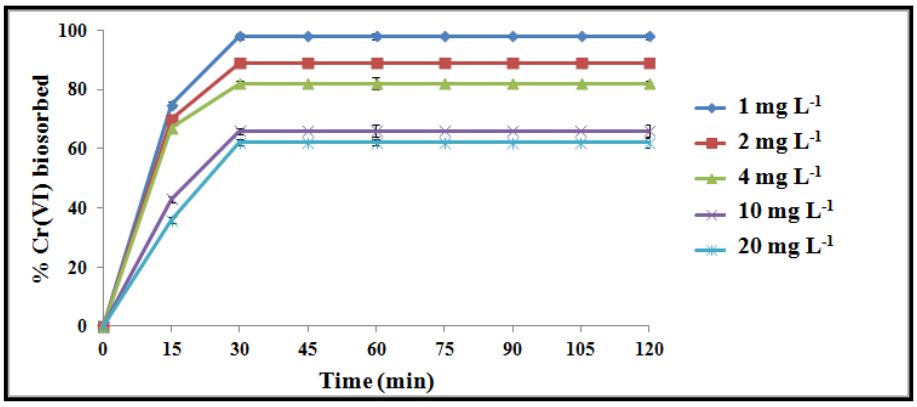

Figure 4: Effect of contact time on the biosorption of Cr(VI) by *N. subminuscula* at different concentrations in the artificial WC medium (Temperature: 20 °C, amount of diatoms: 0.4g.L^{-1}, pH 1.0, mean values ± SD; n=3).

Figure (5) shows the effect on contact time on the extent of biosorption of Cr(VI) by the diatom for the long term exposure during the toxicity test. Results show that the biosorption of Cr(VI) by the diatom was maintained during the 10 days of study. In culture with 20mg L^{-1} of Cr(VI), although the algal density and the growth were lower (Figure 1), Cr(VI) removal is almost complete (98%). For all Cr(VI) concentrations, the difference in biosorption between day 2 and day 10 is not significant (less than 3% of Cr(VI) biosorbed).

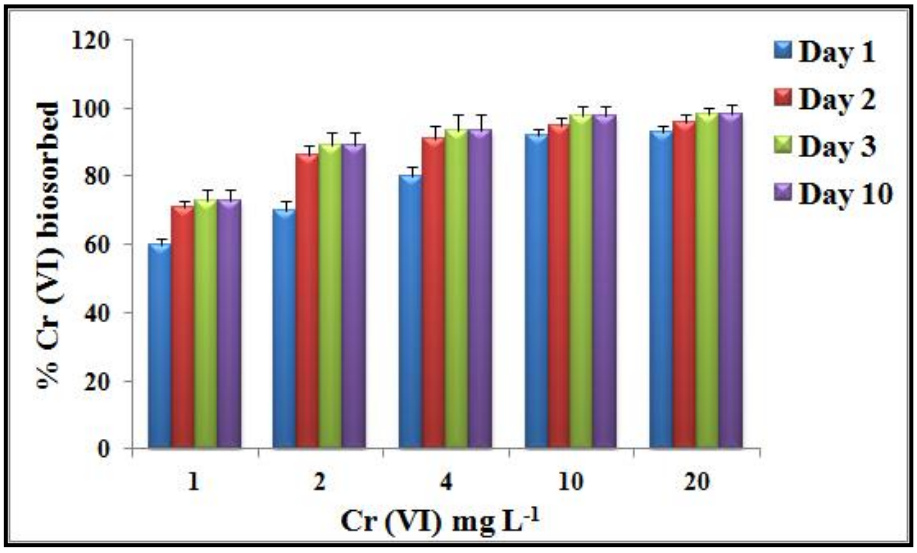

Figure 5: Percentage of Cr(VI) biosorption by *N. subminuscula* cells after 1, 2, 3 and 10 days of exposure to different Cr(VI) concentrations in the artificial WC medium (mean values ± SD; n=3).

To determine the effect of Tensift River water on the diatom biosorption, the amount of Cr(VI) at days 1, 2, 3 and 10 was measured. Results show that Cr(VI) removal increased with the increase of Cr(VI) concentrations. The minimum and the maximum Cr(VI) removed were 42% and 66%, respectively (Figure 6). In comparison with WC medium test, the amount of Cr(VI) removal decreased from 60% to 42% and from 98% to 61% for the lower and the higher Cr(VI) tested concentrations, respectively.

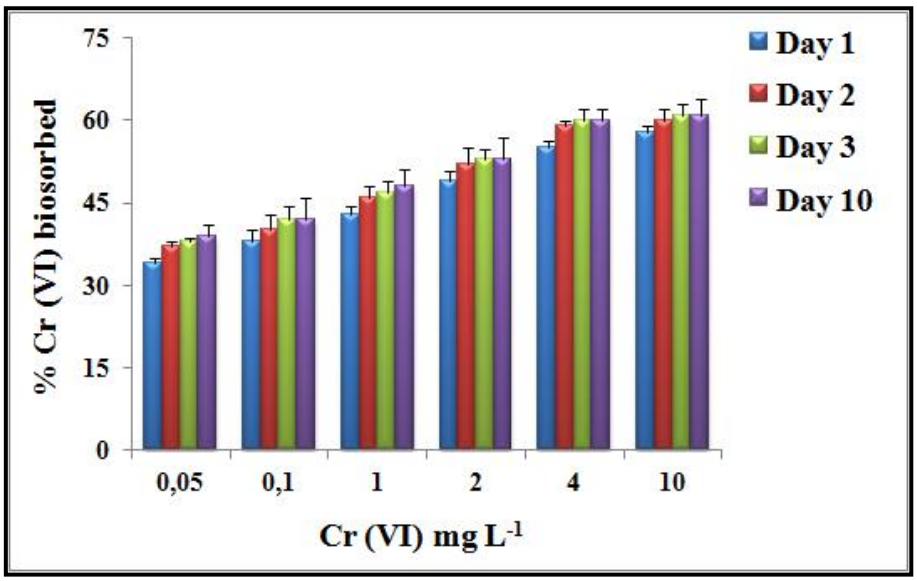

Figure 6: Percentage of Cr(VI) biosorption by *N. subminuscula* cells after 1, 2, 3 and 10 days of exposure to different Cr(VI) concentrations in Tensift River water (mean values ± SD; n=3).

3.2.2. Effect of pH

Earlier studies have indicated that the pH of a medium is an important parameter affecting biosorption of metals [15, 16]. Figure (7) illustrates the biosorption of Cr(VI) as a function of pH. From this figure, it is clear that the percentage of Cr(VI) biosorption increases with the decrease of pH: 53% biosorption was measured at pH 7 whereas 87% was reached at the extreme pH of 1.

3.2.3. Langmuir adsorption isotherm

The found linear plot of C_{eq}/q vs C_{eq} shows that biosorption follows the Langmuir biosorption model. The correlation coefficient was 0.995. q_{max}. The values for *b* were determined from the slope and intercept of the plot and were found to be 94.97mg Cr(VI).g diatoms^{-1} and 0.16L mg^{-1}, respectively.

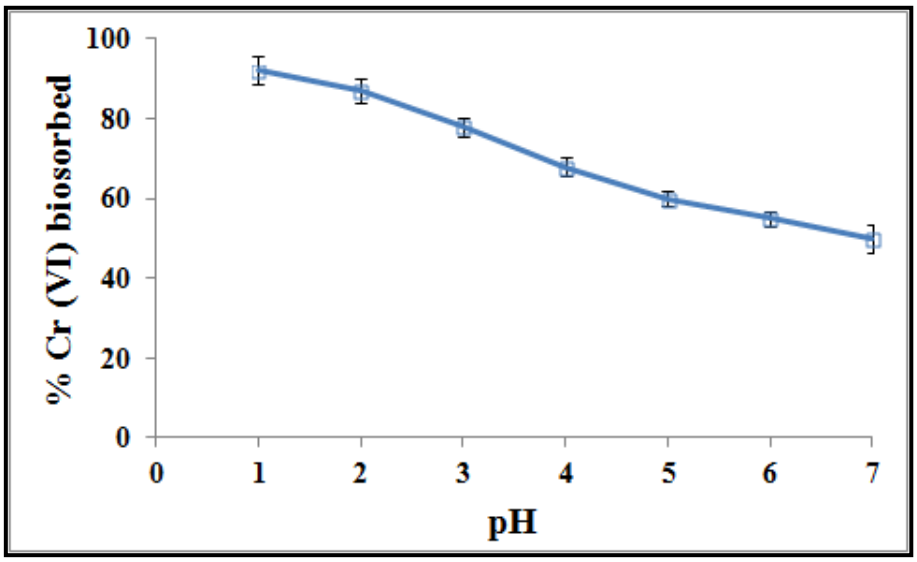

Figure 7: Effect of the pH of artificial WC medium on the biosorption of Cr(VI) by *N. subminuscula* (Temperature: 20°C, amount of diatoms: 0.4g.L^{-1}, Cr (VI) concentration: 10mg L^{-1}, contact time: 30 min, mean values ± SD; n=3).

4. Discussion

The effects of increased levels of metals on epiphytic or phytoplanktonic algal communities have been extensively studied under laboratory and natural conditions [17, 18, 19]. Generally in natural communities, investigations are performed on several days of exposure that simulates natural situations [20, 21]. This is the

reason why we study a long term exposure to Cr(VI) of *N. subminuscula* to test the ability of this diatom to remove Cr(VI) under laboratory conditions in a first step. Then, we substituted the culture medium with tannery effluent and river waters to have a simulation of the biomonitoring of this diatom.

According to Figure 1, as the Cr(VI) concentration increased in the medium, total *N. subminuscula* growth decreased. Despite the use of a low initial cell density, the culture grew in different conditions during the long-term exposure time, except in the highest concentration (20mg L^{-1}). The difference between the cellular density at 2, 4 and 1mg L^{-1} ranges within 20% which is not significant according to Duncan statistical analysis. It suggests that this specie has a large tolerance to Cr(VI) concentrations up to 1mg L^{-1}. For Cr(VI) concentration of 20mg L^{-1}, diatoms seem to recover from day 9 that could mean that Cr(VI) may have an algistatic rather than an algicide effect. Previous studies showed that the Cr(VI) concentrations that affect growth in microalgae are largely variable and depend on different test conditions such as cell densities and test media used [22, 23].

The same test was done with tannery effluent and river waters (Figure 2 and 3) and it demonstrates the influence of the environmental conditions on algal growth. The cultures with Tensift River water grew in Cr(VI) concentrations lower than 10mg L^{-1} (Figure 2). The culture with tannery effluent water grew with concentrations not higher than 0.152mg L^{-1} (Figure 3). Tensift river water and tannery effluent are surely complex matrices containing a large number of contaminants which can be responsible for part of the observed toxicity and for the higher sensitivity of *N. subminuscula* to Cr(VI) in this medium. Indeed, the BOD_5 (45±0.45) and the COD (2500±13.08) of the tannery effluent are sharply higher [24]. Thus, the suitability of a given species for Cr(VI) remediation must be verified in the actual matrix to treat. Many authors had reported that organisms show an integrating response to their environment, as well as to fluctuations in water quality [25, 26]. This is the reason why the growth of *N. subminuscula* was affected. But in general, this diatom tolerates Cr(VI) concentrations up to 4 mg L^{-1} in Tensift river water which is much higher in comparison with other works. In fact, it has been reported that 7 species of algae could tolerate no more than 6.4 (chlorophyceae) and 0.32 (diatoms) mg L^{-1} of chromium. Also, *N. subminuscula* is considered to be an eurytopic species, able to tolerate a wide range of environmental changes, with a wide cosmopolitan distribution [27, 28, 29].

The IC50 value during the 10 days of the study was 9.2mg L^{-1} and it is much higher in comparison with other species. For instance, [30] studied the IC50-72h of chromium on the growth of the green microalga *Scenedesmus incrassatulus* in a batch culture, which was 2.09mg L^{-1}. Similarly with respect to the Chlorophyceae, *Chlorella vulgaris* tolerates concentrations not exceeding 1mg L^{-1} [31]. *N. subminuscula* appears again, more tolerant to this metal like *Planothidium lanceolatum* whose IC50 was 8.7mg L^{-1} [32]. According to some authors, collection of metals using diatoms seems very promising [33].

As shown in Figure (4), the Cr(VI) removal by *N. subminuscula* differed between the various concentrations of Cr(VI) in the medium. However, the maximum Cr(VI) sorption rate was observed during the first 30 min. According to some authors some microalgal species such as *Nannochloropsis gaditana* are able to remove 100% of metals in less than 2 days [34]. Also, it has been found that within the first few minutes of exposure to cadmium, most of it was removed thanks to biosorption by the diatom *Phaeodactylum tricornutum* which metabolism can be disturbed some minutes later [4, 33]. In contrast, the Cr(VI) removed during the toxicity test is maintained until the 10^{th} day with a slow uptake (Figure 5). It has been reported that the biosorption of heavy metal ions by microorganisms has often been observed to occur in two phases; (i) the initial phase is very rapid occurring immediately after exposure to metal and probably passive and due to surface adsorption on the cell wall components (ii) the second phase is extended and slow down with duration of more than one month due to membrane transport of metal ions to the cytoplasm of the cells [34, 18]. It suggests that *N. subminuscula* removes Cr(VI) by adsorption and absorption. For the high Cr(VI) concentrations where the percentage of dead cells exceeded 50%, better performance of biosorption was noted in comparison with living ones (low Cr(VI) concentrations). Dead cells do not require a nutrient supply [35]. Therefore, the use of dead algal cells is more advantageous for water treatment as they do not cope with toxic metals [36, 34].

The results of the effect of pH (Figure 7) show the pH-dependence biosorption and the suitability of biosorbent for treatment of acid water like tannery effluent water where the pH is acid (2.5). Many authors found that the maximum biosorption for algal species is at very acid pH values [5, 39, 40, 41].

The linearized biosorption isotherm of Cr(VI) ions obtained shows a very high regression correlation coefficient (> 0.99). This value strongly supports the fact that the Cr(VI) algal biosorption data closely follows the Langmuir model of sorption model and is very suitable for describing the equilibrium isotherm of Cr(VI) by the algal cells in the studied concentration range. The value of q_{max} appears to be significantly higher for the Cr(VI). A large value of "*b*" also implied strong bonding to Cr(VI) to the *N. subminuscula* cells. Table 1 shows a comparison between the results of this work and others found in the literature. The value of Cr(VI) specific

uptake found in this work was generally higher than those reported elsewhere. But it is lower than that reported for the cyanobacterias *Synechocystis* sp. and *Oscillatoria laete-virens*.

Table 1: A comparison of the Langmuir biosorption constants obtained from the Langmuir biosorption isotherms for Cr (VI) ions and algal species.

Biosorbant	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	Reference
Chlorella vulgaris	79.3	0.003	0.937	[42]
Scenedesmus obliquus	58.8	0.005	0.868	[42]
Chlamydomonas reinhardetii	24.9	n.a[1]	0.998	[43]
Synechocystis sp.	153.6	0.002	0.921	[42]
Oscillatoria laete-virens	103.09	0.06919	0.9886	[44]
Nitzschia closterium	81.73	n.a[1]	n.a[1]	[45]
Planothidium lanceolatum	93.4	0.13	0.995	[32]
Navicula subminuscula	94.97	0.16	0.997	Present study

n.a[1]: not available

Thus, *N. subminuscula* is a diatom very tolerant to Cr(VI). Its growth is only inhibited by more than 4mg L^{-1} in Tensift River. In addition, the wider ecological valence of this diatom to pollution parameters and the seasonal pattern of the life cycle are the main factors that make the biomonitoring of Cr(VI) based on this species feasible. This performance encourages us to test the capacity of other toxic metal phytoextraction by this alga and by other eurytopic diatoms in Tensift River because the diatoms are present in all river systems and can easily be introduced onto natural stones [26]. Indeed, previous studies have reported that *P. lanceolathum*, another diatom dominant in the same River, has a high potential to remove Cr(VI) [31]. Other authors have reported that periphyton, especially diatoms, have been preferred for river biomonitoring [46, 47].

The studied water samples are suitable for irrigation according to its physicochemical characterisitics. As well as these water samples fallen in the good irrigation water classes (class C2-S1 and C3-S1) of the US salinity diagram. On the other hand, this water was polluted with organic residuals and bacteria from waste effluents. The application of photocatalytic treatment technique using fluorine as photocatalyst has shown good activity toward the removal of pollutants in presence of UV-visible light irradiation. The removal efficiencies were found to be 86.9% and 100% for the removal of dissolved organics and bacteria, respectively. Accordingly, it is considered environmentally safe, cheap and effective technique for water treatment.

5. Conclusion

This study investigated the potential use of *N. subminuscula* algal cells for the removal Cr(VI) from wastewaters. It indicates that this diatom which is widely available can be used as biosorbent material for removal of Cr(VI) from tannery effluents and from Tensift River waters. The adsorption process is fast enough, as a high removal rate takes place within half an hour of contact time. In comparison with other studied algae, *N. subminuscula* is more resistant to high levels of Cr(VI) and can accumulate high amounts of this element. The IC50 calculated is 9.2mg L^{-1} under laboratory conditions; it is higher than that calculated with tannery effluent and river waters which is an integrating response to its environment. Thus, the suitability of a given species for Cr(VI) remediation must be verified in the actual matrix to treat. The maximum Cr(VI) biosorption capacity for *N. subminuscula* was found to be 94.97mg Cr(VI).g $diatoms^{-1}$ at an initial concentration of 0.4g dried diatoms per liter with initial Cr(VI) concentration of 20mg L^{-1}. The equilibrium data fitted well in the Langmuir isotherm. Biosorption experiments showed that the microalgae *N. subminuscula* possesses a very high

maximum biosorption capacity that depends on biomass growth conditions. Further studies are necessary to ascertain results with other initial algal densities and higher efficiencies in the adsorption process of the microalgae. Later on, practical applications of such techniques at larger scales would be useful for bioremediation of heavy metal polluted wastewaters since there is a lack of industrial wastewater treatment. Therefore, *N. subminuscula*, *Planothidium lanceolatum*; two diatoms from Tensift River - and possibly other microalgae - may have the potential to be used as an ecofriendly and economic biosorbent cheap material for the removal of toxic metals in polluted waters.

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(2017) ; http://www.jmaterenvironsci.com