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Comparison between the Chromium (VI) and Cadmium (II) by absorption by marine algae Ulva.lactuca

H.ASNAOUI*
PhD student
Department of physics
Nuclear Physics Team,
and transport phenomena.
University Moulay Ismail

A.LAAZIRI
PhD student
Department of physcs
Nuclear Physics Team,
and transport phenomena.
University Moulay Ismail

M.KHALIS*
team leader
Department of physics
Nuclear Physics Team,
and transport phenomena.
University Moulay Ismail

Abstract-The present study concerns the test of marine algae as an absorbent for removing heavy metals from aqueous solutions. The elimination of the metal cations was carried by biological method (phytopurification) and the influence of physic and chemical parameters. In this study we are interested in the ability of the algae "ulva lactuca" to eliminate the chromium (Cr) and cadmium (Cd) from a previously prepared solution and the factors that may influence the absorption. The parameters studied were pH, mass, contact time between polluted water and algae (biomass and its impact on the absorption also other (physico-chemical parameters).The results show the absorption percentage R% = 72 % is observed at pH = 5 and m = 4g amount of living algae for Cr, and the elimination percentage of Cd is equal to R% = 96 % is observed at pH = 5 and m = 4g amount of living algae.

Keywords-algae, absorption, chromium, cadmium, ICP.

I. INTRODUCTION

The chromium and the cadmium are known to be highly toxic and are among the heavy metals which are potentially very dangerous for man and the environment. They issue from various industries such as tanneries, production of colorants, ink, paints, battery factories, etc., and are toxic even at low concentration and must imperatively be removed. The chromium toxicity is mainly induced from its hexavalent form, Cr(VI), comparatively to chromate and dichromate ions. It is toxic to humans, animals and even to plants. It can cause lung, kidney and liver cancers, as well as gastric damages. Its concentration should not exceed 0.05 mg/L in drinking water [1]. For cadmium, the upper limit level in drinking water should be 0.01 mg/L or less [2]. Toxicological studies have also shown that long-term effects of cadmium(II) poisoning include kidney damage and changes to the constitution of the bone, liver, and blood. Short-term effects include nausea, vomiting, diarrhoea, and cramps. So minimizing the production of hazardous waste and heavy metals is regarded as one of the most important environmental challenges that the world faces today[4].

To eliminate these heavy metals present in the industrial effluents, various processes can be applied, such as precipitation, adsorption, electrodepositing, electrocoagulation, membrane separation, liquid extraction, ion exchanges, etc [3-5].

The aim of this work is to evaluate the absorption capacity of ions (chromium and cadmium) in living marine algae (ulva lactuca). Our choice is at the same time, guided by ecological and economic considerations which impel us to look for natural sorbents, absorbent, these algae are abundant in nature and exploitable in the raw state or after a simple treatment. After saturation, residues of algae will be recovered and eventually incinerated or stored in appropriate places.

II. MÉTHODOLOGIE DES EXPÉRIENCES D'ADSORPTION :

A. Harvest and Preparation of algae

Marine green algae (ulva-lactuca) were collected with peaches to plankton net in October 2013 at room temperature 22 ° C (on) at the Moroccan Atlantic coast at the level of the beach of Rabat (34 ° 03' North latitude, and 6 ° 46' West longitude at an altitude of 79 m). These algae have been rinsed in sea water and placed in polyethylene plastic bags previously rinsed with distilled water acidified to pure nitric acid, upon arrival at the laboratory, the algae are again rinsed with distilled water.

Then they were crushed and the resulting particles serve for the remainder of our study.

B. Fourier transforms infrared analysis (FTIR)

The identification of functional groups on the surface of bio-sorbent was performed by infrared spectroscopy. The were ground and dried at 70°C for 48 h and analyzed by an infrared spectrometry (FTIR IR Affinity from Shimadzu) in the solid form, Spectra registered from 4000 to 500 cm-1.

C. The Solutions

The chromium and cadmium solutions were prepared by dissolving the corresponding salts $K_2Cr_2O_7$ and $CdSO_4$, respectively, in demineralised water. The initial solution of concentration (C(Cd)=38,17 mg/l and C(Cr)=38,32 mg/l) was diluted to obtain other solutions of different concentrations. The solution pH was adjusted by means of HNO_3 and NaOH solutions (both of concentrations 0.1M and 1M), using a pH meter.

The percentage of biosorption is given by equation (1) [6]:

$$R\% = \frac{C_0 - C_t}{C_0} * 100 \quad (1)$$

With: C_0: the initial concentration of the metal in the aqueous solution.
C_t: Concentrations résiduelles du polluant à l'instant t ($mg.l^{-1}$).

D. Effect of pH

The batch experiment was carried out by contacting with the same amount of alga with (C(Cd)=38,17 mg/l and C(Cr)=38,32 mg/l) of metal solution in 50 ml stopper conical flask at different pH value, ranging from 2 to 7. The pH of the solutions was adjusted either by hydrochloric acid (HCl) or sodium hydroxide (NaOH). the mixture have been left 5 days at room temperature, filtered, and analysis by ICP.

III. RESULTATS ET DISCUSSION

A. *FTIR analysis*

Examination of the Infrared Spectra shows the presence of a wide band between 3000 and 3500 cm-1, this zone corresponds to the absorbance of the carboxyl groups (-COOH)alcohols (-C-OH), and amines (N-H) are capable of fixing heavy metals.

The allocation of the IR absorption bands observed on the Spectra was made by comparison with literature. Table 1 summarizes the overall results.

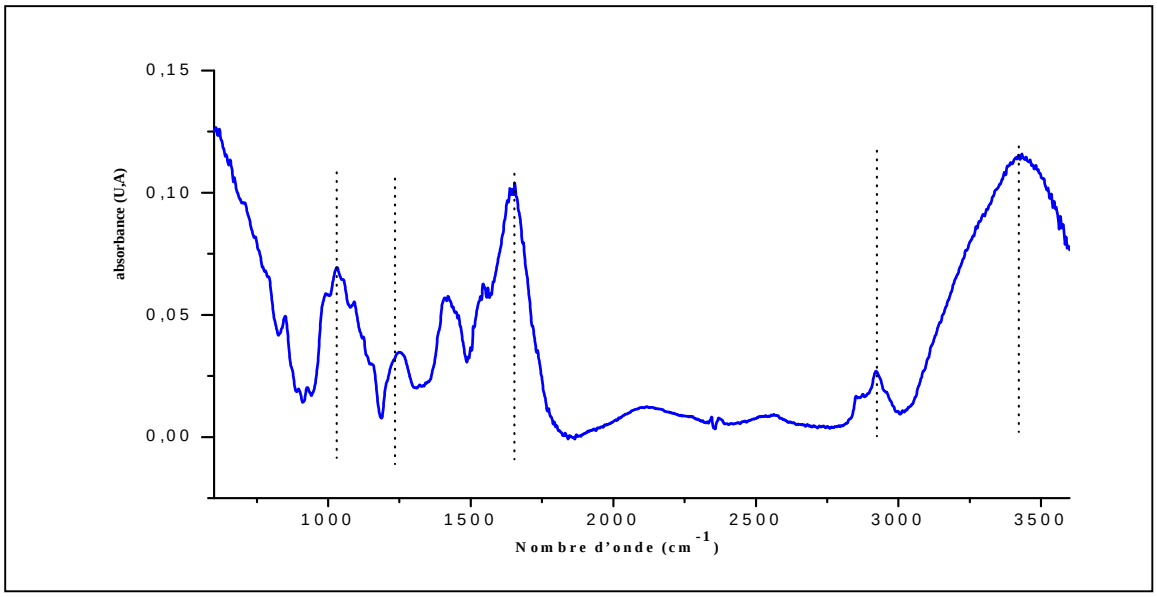

FIG. 1. FT-IR SPECTRA OF DIFFERENT FORMS OF ALGAE: PURE GREEN ALGA.

TABLE 1: BANDS IR OBSERVED FOR PURE GREEN ALGAE AND CADMIUM LOADED BIOMASS

Nombre d'onde de la bande observée (cm^{-1})	Attribution	Ref
3423	Vibrations OH, N-H.	**[7],[8],[9],**
2918	Vibration O-H	**[7],[8],[9],**
1650	vibrations C=O, N=O	**)[9],**
1550	vibrations C=C	**[8]**
1420	vibrations O-H	**[8]**
1250	vibrationsC-C-O	**[8]**
1030	vibrations -C-O	**[8]**
850	vibrations C-H	**[8]**

B. *pH Effect*

As known, the initial solution pH has a great influence on the elimination of metallic cations by absorption, due to its impact on the algae charge. Therefore its effect was considered for both cations (Cd and Cr) by varying its value as follows:

For c metallic cations (Cd and Cr), the pH values considered were 2, 3, 4, 5, 6, 7.

The obtained results are shown in Fig. (2), as follows:

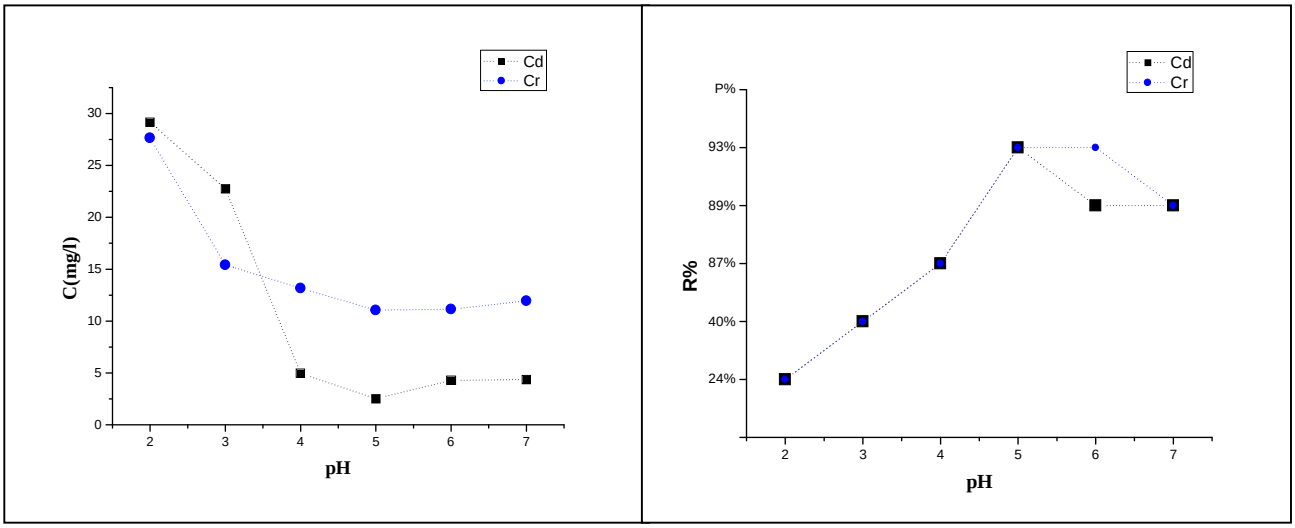

FIG. (2). EFFECT OF PH FOR THE RETENTION OF CR(VI) AND CD(II); CONDITIONS: C_0(Cr(VI)) =38,32 (mg/l), C_0(Cd (II) =38,17 (mg/l), m=4g.

In varying the initial solution pH from 2 to 7, it can be noticed that the elimination of Cr(VI) increase from 28 % to 71% , going through a maximum value of 71% ,at pH=5. For the increase of the pH, this can be explained as follows: at basis the protonation degree of the cell of algae is important. This induces an electrostatic attraction between the cell of algae which has acquired a positive charge and the $HCrO^{-4}$ anions and hence a maximal absorption achieved, comme l'a confirmé dans la littérature [10, 11].

The results of Fig. (2) show that the removal of cadmium increase from 24 % to 88%, going through a maximum value of 88% ,at pH=5. l'élimination Cd(II) is important at acid pH values. In fact, cadmium is in its free state as Cd^{2+} at a low pH where the protonation degree of the cell of algae is important, hence generating an electrostatic repulsion between the metallic cations and the positively charged of the cell of algae.

C. *.the mass effect on the absorption*

Different amount of living algae ranged from 1 to 8 g was applied to study the effect of algae dose on the absorption.

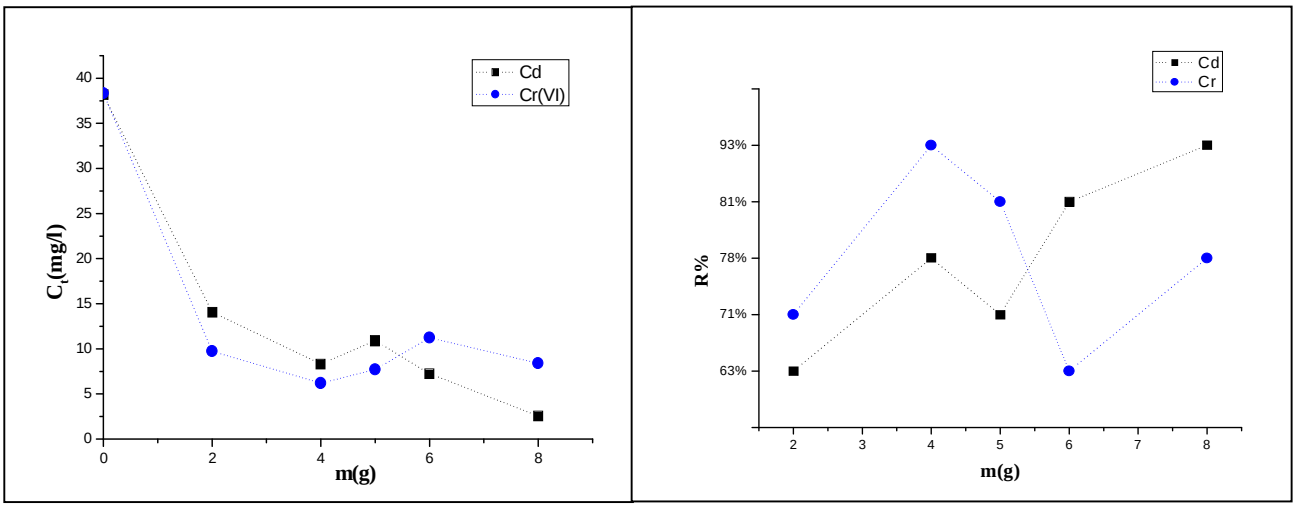

FIG. (3) EFFECT OF AMOUNT OF ALGAE FOR THE RETENTION OF CR(VI) AND CD(II); CONDITIONS: C0(Cr(VI)) =38,32 (mg/l), C0(Cd(II)) =38,17 (mg/l), pH=5.

of Cd(II) and Cr(VI) ions Fig. 3. The data revealed that the absorption efficiency of Cd(II) and Cr(VI) ions on ulva.lactuca was significantly affected by the amount of ulva.lactuca in the solution. In other words, the absorption of Cd(II) and Cr(VI) ions was increased with increasing the algae amount at higher amount than 5g (80%) and 8g (93%) for Cr and Cd, respectively. This behavior could be explained by the formation of cell of the algae at higher amount, which decreases the effective cell area for absorption [3]. Therefore; the amount 4g for the mixture of Cr(VI) and Cd(II) were selected as the optimum amount of the cell algae for the rest of the study.

D. *Effect of Contact Time*

Fig. (4) shows that the absorption of the hexavalent chromium is very rapid during the first three days, indicating a great affinity between the algae for these cations. In fact the results show an elimination of R%(Cd) = 88% and R%(Cr)=85% for only 5 days. The retention capacity increases with time and reaches the equilibrium after 5 days with a removal of 88 %. For the case of cadmium, and 84% for chromium. which can be explained by a saturation of the functional group able to fix heavy metals.

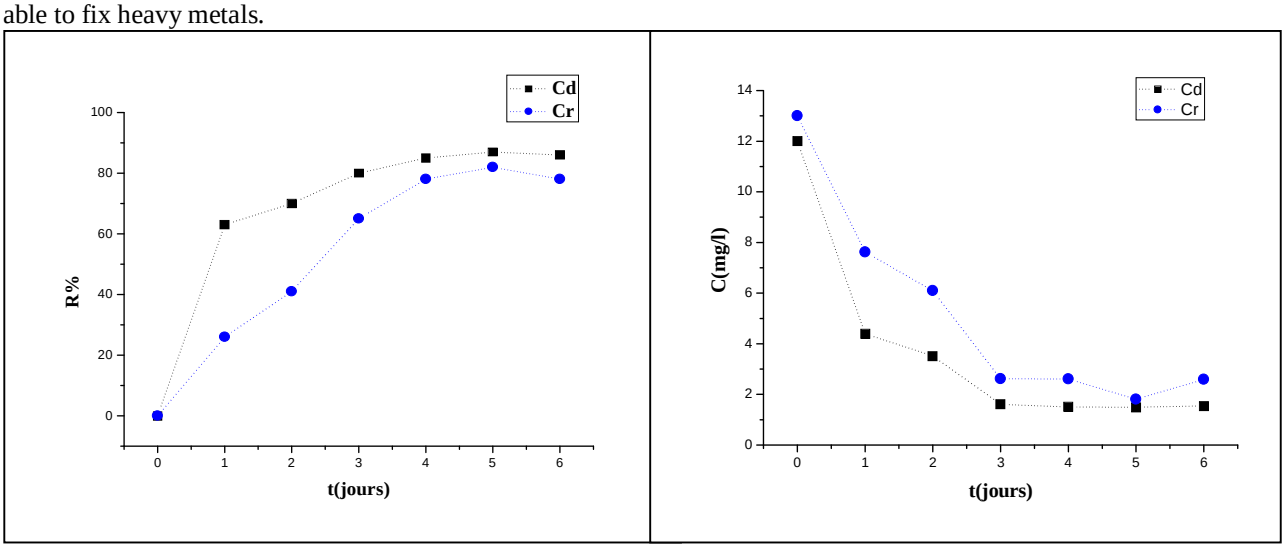

FIG. (4). EFFECT OF CONTACT TIME FOR THE RETENTION OF CR(VI) AND CD(II); CONDITIONS: C0(CR(VI)) =38,32 (mg/l), C0(CD(II)) =38,17 (mg/l), PH =5.

IV. CONCLUSION

The present work was designed to investigate the absorption behavior of Cr and Cd to the marines algae ulva lactuca. The maximum absorption capacities were 88% and 84% for Cd and Cr at optimum operating conditions (pH=5 t(days)=5 days m=4g), respectively. The experimental data revealed that Cd and Cr absorption were fitted to both phytopurification . The FTIR indicated that the amino, carboxyl, hydroxyl and carbonyl groups on the biomass algae are responsible for biosorption of Cd(II) and Cr(VI). Based on these results, ulva.lactuca algae can be used as an efficient low cost living plants for the removal of heavy metals from wastewater.

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