Biological removal of heavy metals from wastewater

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One of the most promising areas of algal biotechnology lies in the field of wastewater treatment. Wastewater treatment by algae has particular potential since it represents one of the least expensive purification methods. Algae have the ability to accumulate the heavy metals and thereby remove toxic compounds from industrial wastewater. In this study, the Chlorella vulgaris was used for cadmium and lead removal. Results of the tests showed that 60% of the lead and 65% of the cadmium were removed at a retention time of 60 minutes at a pH value of 7. To study the combined effects of cadmium and lead on the performance of algal biosorption. Mixtures of the two metals with different ratios 1:1, 1:2, 2:1, were prepared and examined. The results of the tests showed that efficiency up to 93% of heavy metals removal can be achieved. Chock loading of heavy metals showed a negative effect on the biosorption process. Therefore biosorption of heavy metals by microbial biomass is strongly recommended as a powerful technique for the removal of heavy metals from polluted effluents.

توجد عدة طرق للتخلص من المعادن الثقيلة الموجودة في بعض المخلفات السائلة خصوصا المخلفات الصناعية و الناتجة عن طلاء المعادن و البطاريات و غيرها. و من هذه الطرق هناك طرق فيزيائية مثل الامتصاص و التبادل الأيوني و التأين الكهربي و التناضح العكسي و كذلك طرق كيميائية مثل الترسيب و البحث عن طريقة رخيصة للتخلص من هذه المواد هو الهدف الرئيسي من هذا البحث. و في هذا البحث استخدمت الطحالب كوسيلة بيولوجية لاميصاص الرصاص و الكادميوم كنموذج للمواد الثقيلة و تم اختبار قدرة الطحالب علي ازالة كل من الرصاص و الكادميوم كلا علي حدة ثم استخدام خليط من الرصاص و الكادميوم بنسب متغيرة و قد أبدي الطحالب قدرة عالية علي ازالة نسبة كبيرة من هذه التركيزات وصلت الي ٦٠ و ٦٥% من الكادميوم و الرصاص علي الترتيب في زمن لا يتجاوز الساعة الواحدة عندما كان الرقم الهيدروجيني يساوي سبعة. و لدراسة التأثير المشترك لوجود الكادميوم و الرصاص معا تم تحضير خليط بنسب متغيرة ما بين ١:٢و ١:١و ٢:١ و قد أوضحت النتائج امكانية ازالة حتي ٩٣% من هذه التركيزات في زمن بقاء قدره ٦٠ دقيقة عندما كان الرقم الهيدروجيني يساوي سبعة. كما تم دراسة تأثير لحمل الصدم المفاجئ علي نشاطية الطحالب و الذي بدا تأثيره سلبيا علي قدرة الطحالب علي الامتصاص مع زيادة تركيزات الأملاح و بناء علي ذلك نوصي باستخدام الطحالب كطريقة بيولوجية لازالة المعادن الثقيلة من المخلفات السائلة.

Keywords: Heavy metals, Lead, Cadmium, Chlorella vulgaris, Chock loading, Biosorption

1. Introduction

Trace quantities of many metals such as nickel (Ni), lead (Pb), chromium (Cr) and mercury (Hg) are important constituents of most wastewaters. Trace elements is a term that refers to those elements that occur at very low levels of few parts per million or less in a given system. Some of these metals are necessary for the growth of some microorganisms. The presence of any of these metals in excessive quantities however will interfere with many beneficial uses of water because of their toxicity; therefore it is frequently desirable to measure and control the concentration of these substances [1].

Numerous technologies exist for heavy metals removal from wastewater. These technologies range from simple clarification in a settling pond to a complex system of advanced technologies requiring sophisticated equipment and skilled operators. Physical and chemical methods including precipitation, dialysis, reverse osmosis and ion-exchange are the common methods in the removal of these heavy metals. The selection of the proper method depends on the type of wastewater and the molecular weight of the heavy metal. Finding the proper technology or combination of technologies to treat a particular wastewater samples that meet the environmental requirements and still be cost-effective can be challenging task [2].

Table 1
The estimated global metal discharge into wastewater in 1000 ton/year

Metal	Quantity
Cadmium	9.4
Chromium	142
Copper	112
Lead	138
Nickel	113
Zinc	226

The aim of this study was to investigate the ability of algae to eliminate a number of various heavy metals, particularly lead and cadmium in one metal solution system and to identify the limiting parameters for the metal removal process. As single metal ions rarely occur in nature, a study on the combined effect of two or more metals would be more realistic. The influence of the presence of a second metal on the uptake of a primary one was also examined. Moreover, the effect of chock load of heavy metals on the biosorption was tested.

1.1. The environmental impact of heavy metals

Global discharge of trace metals into wastewater effluent were estimated as illustrated in the following table 3.

Such discharges limit the multiple use of water in many regions of the world and potentially increase the frequency of chronic disease in human population.

1.1.1. Lead

Lead is the 36th most abundant element in the Earth crust with an average concentration of 15 mg/kg. Lead is used in storage batteries, metal products, pigments and chemicals. Also, lead arises from domestic wastewater and mining sources [4]. Acute lead poisoning in humans may cause severe damage of kidneys, liver, brain and control nervous system leading to sickness or death.

1.1.2. Cadmium

Cadmium is the 64th most abundant element in the Earth crust at an average concentration of 2.0 mg/kg. The major uses of cadmium are in electroplating and in the manufacture of storage batteries [4]. The effect of cadmium poisoning on human are very serious. They include high blood pressure, kidney damage, and destruction of red blood cells.

2. Materials and methods

2.1. Apparatus

As shown in fig. 1 the apparatus used in this research consists of two-1000 ml conical flasks. They were connected to each other by means of plastic hoses 1 cm in diameter. Both flasks were sealed by rubber stoppers and covered by aluminium foil to protect the media from any outside organisms.

Since algae need light and carbon dioxide to grow, a source of light has been installed day and night to provide a light intensity of 1000 Lux. To ensure a continuous source of CO_2 and to prevent settling of algae, the system was provided with a small air pump.

2.2. Methodology

2.2.1. Materials

Different concentrations of lead or cadmium were prepared in the range between 1.2 to 12 mg/l. To study the combined effects of cadmium and lead, mixtures of the two metals with different ratios 1:2, 1:1 and 2:1 were prepared and examined. Also, the effect of chock loads of heavy metals on the biosorption of algae was studied.

Synthetic wastes with concentration of 300 ppm of either lead or cadmium were used in this study as polluted effluents. 10 ml of such solution was mixed with 250 ml of algal solution, thus the resulting solution has a concentration of 11.54 ppm.

2.2.2. Microorganisms

Although numerous strains of algae were identified and isolated in the last five years, few of them showed capability to adsorb toxic heavy metals. The strain *Chlorella vulgaris* was chosen in this study for its high tendency to remove heavy metals in two successive steps, the first is the adsorption on its surface followed by fixation. It was obtained from the Botany Department, Faculty of Science, Alexandria University.

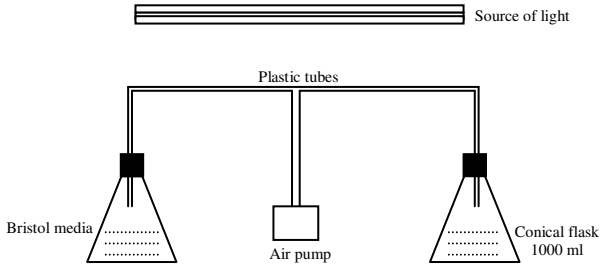

Fig. 1. Schematic diagram of the apparatus.

2.2.3. Bristol media

To prepare stock solution of Bristol media [5], the following compounds with pre-specified quantities were used. Table 2 shows these compounds and the required weights. After preparation of the Bristol media, some species of *Chlorella vulgaris* was cultured for 36 hours in the media.

To prepare one liter of the media, the following quantities are mixed, 10 ml of solution A, 10 ml of solution B and 1 ml of solution μ and completed to 1000 ml with distilled water.

pH level was adjusted to the value of 7 with a solution of 1N NaOH. before sterilization.

2.2.4. Methods

To achieve the objectives of this work, the two conical flasks were simultaneously operated. Four runs were carried out according to the schedule shown in table 3.

Samples of each run were withdrawn by pipette and centrifuged at 6000 rpm for 3 minutes and the supernatants were filtered through filter paper 0.22 μm (cellulose acetate). Hydrochloric acid (1N) was added to the filtrate to lower the pH value to 2.5 at the same time to diminish the effect of the biomass presence on the accuracy of analysis. Heavy metals contents were determined by Atomic Absorption in accordance with the standard methods [6].

3. Results and discussion

As mentioned above, four runs were carried out and all of the experimental results were plotted. The first and the second runs studied the ability of algae to adsorb lead and cadmium from single metal wastewater. As shown in figs. (2, 3, 4 and 5)**,** the algae were able to remove 60% and 65% of lead and cadmium respectively at a pH value of 7.0 and a retention time of 60 minutes.

In general, the presence of different cations in the solution creates competition sites for the fixation step. That fact can be observed in the results obtained from the study of the combined effect of two metals [7].

Mixtures of lead and cadmium at different ratios 1:2, 1:1 and 2:1 were investigated. As seen in fig. 6, 53% only of both lead and cadmium could be removed. This can be attributed to the presence of lead with low concentration with respect to cadmium.

It is noted from figs. 7 and 8 that the efficiency of both metals removal is increasing up to 93%. It can be interpreted by the presence of equal concentrations of both metals or that high concentration of cadmium with respect to lead has a negative effect on the fixation of heavy metals.

Table 2
Composition and quantities of bristol media

Type	Compound	Quantity	Solution
A	$NaNO_3$	0.75 g	A x 100
	$CaCl_2.2H_2O$	25 mg	A x 100
	$MgSO_4.7H_2O$	75 mg	A x 100
	FeEDTA	20 mg	A x 100
B	K_2HPO_4	75 mg	B x 100
	KH_2PO_4	0.175 g	B x 100
	NaCl	20 mg	B x 100
μ	H_3BO_3	2.86 mg	μ x 1000
	$MnCl_2.4H_2O$	1.81 mg	μ x 1000
	$ZnSO_4.7H_2O$	0.22 mg	μ x 1000
	$CuSO_4.5H_2O$	80μg	μ x 1000
	MoO_3 85%	36μg	μ x 1000
	$CoSO_4.7H_2O$	90μg	μ x 1000

Table 3
Schedule of the experimental plan

Number of run	Concern
First run	Removal of lead only with initial concentration of 1.2 and 12 ppm
Second run	Removal of cadmium only with initial concentration of 1.2 and 12 ppm
Third run	Removal of mixture of lead and cadmium at different ratios 1:2, 1:1 and 2:1
Fourth run	Effect of chock loading on the biosorption of algae

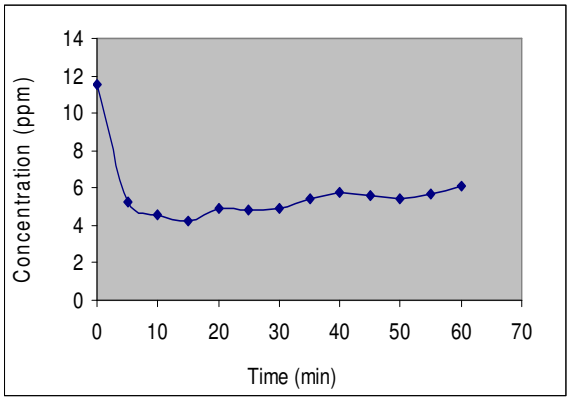

Fig. 2. Time course for removal of lead (initial concentration 11.54 ppm).

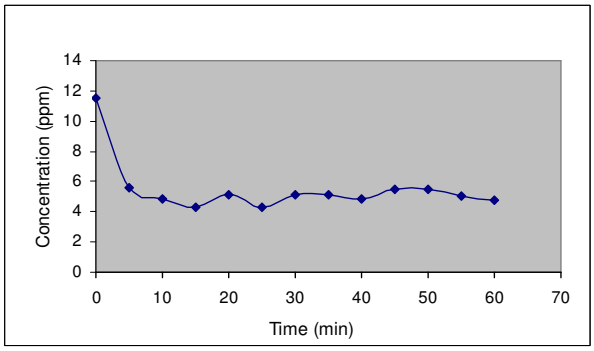

Fig. 3. Time course for removal of cadmium (initial concentration 11.54 ppm).

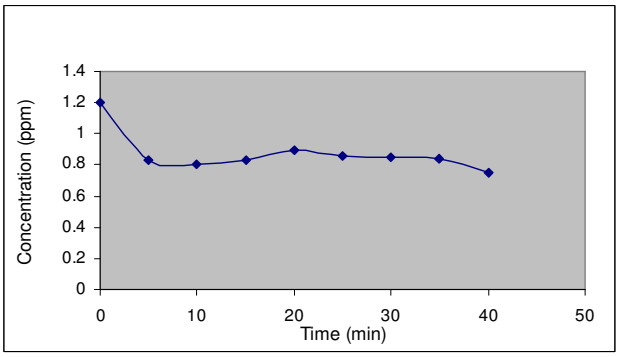

Fig. 4. Time course for removal of lead (initial concentration 1.2 ppm).

Also, the effect of heavy metals chock loads was examined, after 20 minutes and 40 minutes the concentration was increasing to the initial value. It is clear from figs. 9 and 10 that the efficiency of heavy metals removal is decreasing under heavy metal chock loads. Examination of figs. 9 and 10 reveals that the removal efficiency after the chock load was relatively low as before. This can be explained by the decrease of available fixation sites for more ions.

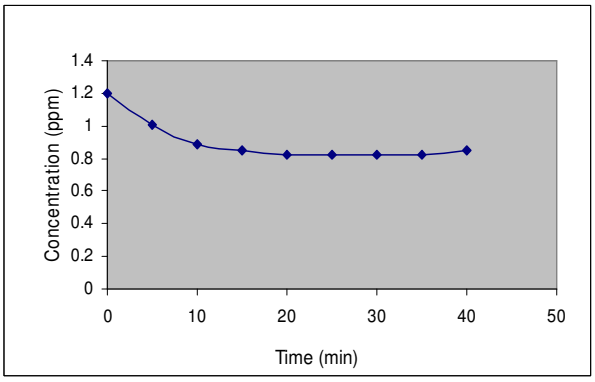

Fig. 5. Time course for removal of cadmium (initial concentration 1.2 ppm).

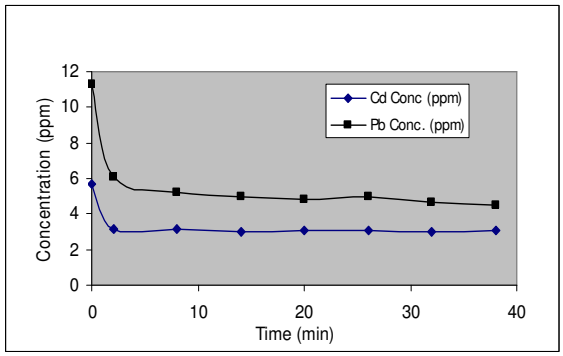

Fig. 6. Time course for removal of a mixture of Pb and Cd (ratio 2:1).

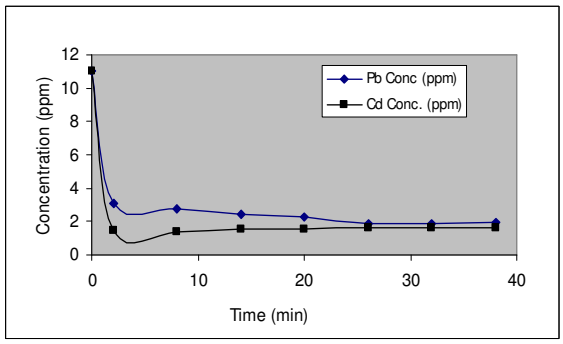

Fig. 7. Time course for removal of a mixture of Pb and Cd (ratio 1:1).

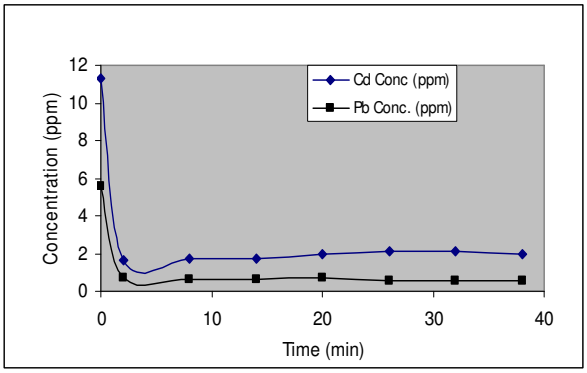

Fig. 8. Time course for removal of a mixture of Pb and Cd (ratio 1:2).

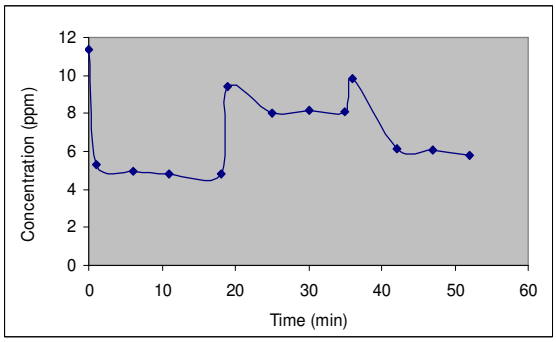

Fig. 9. Effect of chock load on lead removal.

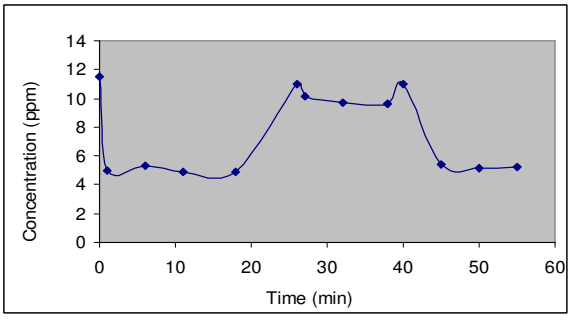

Fig. 10. Effect of chock load on cadmium removal.

4. Conclusions

Based on the observations and the results obtained from this study, the following points can be concluded:

1) Microorganisms play an important role in the removal of heavy metals from wastewater specifically algae. They have the ability to uptake and accumulate the heavy metals such as cadmium and lead from the wastewater to level far exceeding the metal level in the water.
2) Chlorella vulgaris can remove 65% of cadmium and 60% of lead at a pH value of 7.0 and a retention time of 60 minutes.
3) Up to 93% removal efficiency of a mixture of lead and cadmium with 1:1 and 1:2 ratios can be achieved at pH value of 7.0 and a retention time of 60 minutes.
4) Chock loads have a negative effect on the biosorption of heavy metals by *Chlorella vulgaris*
5) Algae provide a useful tool for minimizing of heavy metals in polluted effluents.

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