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# DOES THE BIOSORPTION PROCESS ABLE TO MITIGATE HEAVY METALS STRESS ?

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## ABSTRACT

There is a lack of information concerning the effect of biosorption process on plant growth under heavy metals stress. For this purpose, a hydroponic experiment was carried out to evaluate the ability of cotton stalks pretreated with sodium hydroxide as a biosorbent material on mitigating harmful effects of Cd, Pb and Ni on some vegetable crops. The experiment was consisted of three hydroponic treatments i.e., contaminated nutrient solution with or without the biosorbent material, and the control treatment (uncontaminated nutrient solution). The biosrbent material removed considerable amounts of heavy metals from the contaminated nutrient solution, especially $Pb^{2+}$ ions. Heavy metals contamination reduced fresh and dry weights of shoots and roots. Macro- and micronutrients concentration has been affected by heavy metals contamination. The accumulation of heavy metals increased extremely in roots as compared with shoots. Heavy metals concentration in roots reached the excessive levels, in particular, in the second treatment (without biosorbent material). The biosorbent material reduced the accumulation of Pb and Ni in shoots and roots. However, the concentration of Cd increased.

In conclusion, cotton stalks pretreated with sodium hydroxide could be a promising biosorbent material for the removal of heavy metals from wastewater prior to irrigation.

**Keywords**: Chemically modified cotton stalks; Biosorbent; Heavy metals uptake; Vegetable crops.

## INTRODUCTION

Heavy metals is the most widely recognized and used term for the large group of elements with an atomic density greater than 6 g $cm^{-3}$ (Phipps, 1981). Some heavy metals such as Fe, Mn, Zn, Mo and Cu are essential micronutrients, and play important roles in plant physiology. Although they could be phytotoxic if their concentrations exceed the essential limits. Other heavy metals like Cd, Pb and Ni, which have no identified physiological role, are non-essential. Furthermore, they could be phytotoxic even at low concentrations (Vázquez *et al.*, 1992). Nevertheless, there are some reports suggesting that Ni may have some functions in plant (Mishra and Kar, 1974). Plant exposure to heavy metals, especially by wastewater irrigation, will introduce various diseases and disorders. If excessive amounts are accumulated in plant tissues, heavy metals will adversely affect the physiological and biochemical characteristics of plant (Cheng, 2003).

Heavy metals could be released the soil surface and the groundwater as a result of different activities, such as industries, mining, and negative agricultural practices (Hawari and Mulligan, 2005). When heavy metals are discharged into water systems, they generally show a large tendency toward binding to aquatic sediments. Although this will lead to a temporary improvement of water quality, polluted aquatic sediments may still be seen as "time bombs" for future pollution of the overall ecosystem (Kelderman and Osman, 2007). Through a variety of micro-biological (e.g. activities of bottom-dwelling fish) and physico-chemical processes (e.g. pH changes, sediment oxidation and heavy metal complexation by anions like $Cl^-$), these heavy metals may effectively be recycled to the overlying water phase (Salomons and Förstner, 1984; Calmano *et al.*, 1993).

The use of reclaimed water in agriculture is an option that is increasingly being investigated and taken up in regions with water scarcity. In these circumstances, the use of reclaimed water in agriculture enables freshwater to be exchanged for more economically and socially valuable purposes (Winpenny *et al.*, 2010). In developing countries, wastewater reuse is conventionally carried out through direct application and/or mixed with fresh water. However, wastewater in these countries is actually a combination of agricultural drainage water, industrial effluents, and sewage water with different ratios, and without any system for separation. Undesirable constituents in wastewater can harm human health, and the environment. Hence, wastewater irrigation is an issue of concern to public agencies responsible for maintaining public health and environmental quality (Qadir *et al.*, 2010).

Besides the classical wastewater treatments, which costs a lot, biosorption of heavy metal ions may represent a very promising technique. Primarily, because it is using biomaterials as adsorbents, which are generally abound in nature at low cost (Volesky, 2001; Vegliò *et al.*, 2003). This technique could be an ideal wastewater treatment method in developing countries, because of the low cost processing, and the high removal efficiency of heavy metals. On the other hand, chemical pretreatment with base solutions, mineral and organic acid solutions, organic compounds, oxidizing agents, dyes, etc. have been investigated for the purpose of increasing the efficiency of biosorbent materials (Wan Nagh and Hanafiah, 2008). Meanwhile, it was revealed that sodium hydroxide was the most efficient solution in this concern (Mosa *et al.*, 2011)

Despite intensive research of the biosorption process, little is known about how the biosorbent material could be able to alleviate the accumulation of heavy metals in plant tissues, and mitigate their harmful effect.

This study was aimed at assessing the ability of cotton stalks pretreated with sodium hydroxide on the removal of $Cd^{2+}$, $Pb^{2+}$ and $Ni^{2+}$ ions from a contaminated nutrient solution. This could be considered as a simulation experiment for future field irrigation trials.

## MATERIALS AND METHODS

### Location of the experiment, and setup of hydroponic treatments.

A hydroponic experiment was carried out in the Experimental Glasshouse of the Faculty of Agriculture, Mansoura University, Egypt (latitude of 31$^{O}$ 30 N and longitude of 30$^{O}$ 20 E) during the summer season of 2010/2011. Some meteorological data during the growing season of the experiment are listed in Table 1.

**Table 1: Averages of air temperature, relative humidity, pan evaporation and total precipitation during the growing season.**

| Month | Average temperature (C°) | Average relative humidity (%) | Average pan Evaporation (mm) |
|---|---|---|---|
| April | 21.4 | 63 | 4.0 |
| Mai | 24.5 | 61 | 4.8 |
| June | 27.3 | 65 | 5.5 |

The experiment was consisted of three hydroponic treatments i.e., contaminated nutrient solution with or without the biosorbent material, in addition to the control treatment (uncontaminated nutrient solution).

For each treatment, 6 plastic channels (4 m long, and 10 cm diameter) were installed. Each channel had 40 pores (6 cm diameter) in its upper side as a place for plastic pots. Every two channels were connected together by plastic tubes to represent a treatment. Each treatment was provided with a reservoir containing 10 L of Cooper nutrient solution (Cooper, 1979). In addition to an electrical pump for circulating the nutrients solution. The third treatment was provided with cotton stalks pretreated with sodium hydroxide as a biosorbent material. This biosorbent material was filled in cheese cloth filter bags, and connected to the end circulation tubes (Fig1).

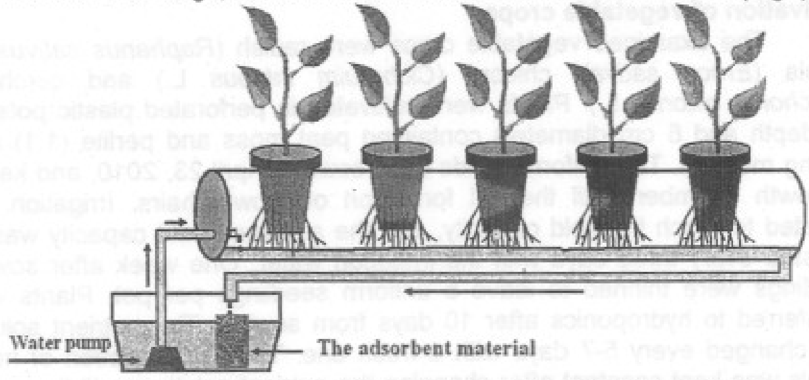

**Fig. 1: Schematic for the third hydroponic treatment.**

The nutrient solution of the second and the third treatment was contaminated with Cd, Ni and Pb in forms of $CdCl_2$, $NiSO_4$ and $Pb(CH_3COO)_2$ at concentrations of 50,100 and 200 µM, respectively.

**Preparation, and setup of the biosorbent material.**

Cotton stalks were obtained from El-Gimiza Agricultural Research Farm, Ministry of Agriculture, Egypt. Subsamples were ground using a stainless steel mill, digested with 5 mL of $HNO_3$ (65%) and 1 mL of $H_2O_2$ (30%) in a microwave digestion apparatus (model MLS GmbH, Germany; Tüzen, 2003). Heavy metals concentration was determined using an Inductivity Coupled Plasma Spectrophotometer (model ICP/CIROS CCD SOP, Germany). Elements concentration of cotton stalks before and after the chemical pretreatment is presented in Table 2.

**Table 2: Elements concentration of cotton stalks before and after the chemical pretreatment with sodium hydroxide.**

| Elements | P | K | Ca | Mg | Na | S | Fe | Mn | Zn | Co | Cu | Pb | Ni | Cd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (%) | | | | | | mgkg$^{-1}$)( | | | | | | | |
| Before pretreatment | 0.59 | 1.44 | 0.66 | 0.18 | 0.03 | 0.19 | 226.16 | 15.33 | 15.37 | 0.814 | 7.99 | 19.19 | 1.483 | 0.437 |
| After pretreatment | 0.12 | 0.25 | 0.49 | 0.13 | 0.69 | 0.04 | 72.24 | 7.3 | 10.11 | 0.783 | 7.55 | 17.55 | 0.85 | 0.275 |

To prepare the biosorbent material, cotton stalks were oven dried at 70°C over night, and ground using stainless steel equipment to pass through 1-mm sieve. The chemical pretreatment of cotton stalks were carried out by shaking 100 g of cotton stalks with 2 L of NaOH (0.1 M) at an agitation rate of 150 rpm for 4 h. After shaking, the chemically modified cotton stalks were filtered, washed with tap water, followed by double distilled water to remove the excess of NaOH until the pH was approximately 7. Then it was oven dried again at 70°C for 24 h. These procedures were carried out according to Mosa *et al.*, (2011). After preparing the biosorbent material, 100 g was filled in two cheesecloth bags to act as filters. These filters were connected to the end of circulation tubes. The nutrient solution, which contaminated with heavy metals was passed through the biosorbent material at the end of each circulation in order to remove heavy metals from the nutrient solution.

**Cultivation of vegetable crops.**

The examined vegetable crops were radish (*Raphanus sativus* L.), augula (*Eruca sativa*), chicory (*Cichoruim intybus* L.) and corchorus (*Corchorus olitorius* L.). Plants were cultivated in perforated plastic pots (10 cm depth and 6 cm diameter) containing peat moss and perlite (1:1) as a rooting medium. Ten uniform seeds were sown in April 23, 2010, and kept in a growth chamber until the full formation of growth hairs. Irrigation was adjusted to reach the field capacity, and the assumed field capacity was re-adjusted every three days with the irrigation water. One week after sowing, seedlings were thinned to leave 5 uniform seedlings per pot. Plants were transferred to hydroponics after 10 days from sowing. The nutrient solution was changed every 5-7 days with a fresh one. The concentration of heavy metals was kept constant after changing the nutrient solution until the end of the experiment. The biosorbent material was changed with changing the nutrient solution. Elements concentration of nutrient solutions were measured after every change using ICP. At harvest stage (45 days from sowing), fresh and dry weight values of shoots and roots were recorded.

**Plant analysis.**

Shoot and root samples were washed with distilled water, oven dried at 70°C over night and ground manually to avoid heavy metals contamination. The chemical analysis was carried out in the Institute of Soil Science and Forest Nutrition, Freiburg University Br., Germany. Nitrogen was determined using CNS analyzer (model Carlo Erba NA 1500 Series 2, Italy). To determine elements concentration of shoots and roots, 0.2 g was digested with 5 mL of $HNO_3$ (65%), and 1 mL of $H_2O_2$ (30%) in the microwave digestion apparatus. Elements concentration was determined using ICP.

**Statistical analysis.**

Data was statistically analyzed according to the procedure outlined by Duncan (1955) using CoStat (Version 6.303, CoHort, USA, 1998-2004). Means of treatments were considered significantly when they were more than least significant differences (LSD) at the confidence level of 5% according to Gomez and Gomez (1984).

## RSULTS AND DISCUSSION

### Mean values of elements concentration after changing the nutrient solution.

The biosorbent material reduced the concentration of $Cd^{2+}$, $Pb^{2+}$ and $Ni^{2+}$ ions in the nutrient solution as shown in Table 3. The highest removal value was attributed with Pb. This is revealed to the high biosorption of $Pb^{2+}$ ions on organic matter compounds (Harrison and Lexen, 1984). Moreover, their biosorption is mainly occurred through the inner-sphere complexes with carboxyl and hydroxyl groups to be difficult for exchanging with other ions (Guo *et al.*, 2006).

**Table 3: Mean values of elements concentration ($mgL^{-1}$) after changing the nutrient solution.**

| Treatments | Metal ions concentration ($mgL^{-1}$) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | P | K | Ca | Mg | S | Fe | Mn | Zn | Co | Cu | Pb | Ni | Cd |
| First | 11.36 | 58.13 | 66.33 | 32.6 | 54.45 | 0.60 | 0.002 | 0.68 | 0.008 | 0.06 | 0.006 | 0.002 | 0.001 |
| Second | 14.80 | 47.59 | 62.97 | 29.03 | 60.60 | 0.39 | 0.005 | 0.48 | 0.009 | 0.02 | 1.235 | 0.402 | 0.34 |
| Third | 14.20 | 90.18 | 61.92 | 29.52 | 60.54 | 0.37 | 0.01 | 0.27 | 0.009 | 0.01 | 0.240 | 0.389 | 0.24 |

Macronutrients concentration (P, Ca, Mg and S) varied slightly among treatments. However, it was noticed that $K^{+}$ concentration recorded a high increase in the third treatment as compared with other treatments. Presumably due to the high influx of $K^{+}$ ions from the biosorbent material to the nutrient solution, as potassium is not immobilized in organic matter compounds (Marschner, 1995).

Micronutrients concentration (Fe, Mn, Zn and Cu) varied among treatments. Concentrations of Fe, Zn and Cu in the control treatment were higher than the second treatment. This could be attributed to the synergistic effect between $Cd^{+2}$ and metal ions of these micronutrients (Kabata-Pendias and Pendias, 2001), which increased their uptake by plants. The third treatment recorded the lowest values of these micronutrients. This is due to the biosorption of their metal ions. Meanwhile, $Mn^{+2}$ concentration in the control treatment was lower than other treatments. Presumably due to the antagonistic effect between $Ni^{+2}$ and $Mn^{+2}$ ions (Khalid and Tinsley, 1980). Therefore, decreased Mn uptake by plants, leaving $Mn^{2+}$ ions in the nutrient solution. Concentration of $Mn^{+2}$ ions in the third treatment was the highest. Perhaps because of Mn-complexes in different organic compounds are principally involved in electrostatic forces between the hydrated metal ion and oxygen-containing ligands, and these complexes are easily disrupted by proton or metal exchange (Senesi *et al.*, 1989). Accordingly, $Mn^{2+}$ ions were easily exchangable with other metal ions in the nutrient solution.

**Effect of different hydroponic treatments on the yield of vegetable crops.**

Heavy metals contamination led to a significant reduction ($p<0.05$) in fresh weight yield of both shoots and roots (Table 4). However, this reduction was not significant on corchorus shoots. On the other hand, the effect of heavy metals contamination on dry weight yield varied among vegetable crops. It was noticed that this effect was not significant on vegetable shoots. Although it was significant on chicory shoots. on the contrary, the effect on vegetable roots was significant. Although it was not significant on corchorus roots. Accordingly, it is clear that corchorus plants were more able to survive under heavy metals stress. Whereas, other vegetable crops were more sensitive, especially chicory plants.

**Table 4: Fresh and dry weight yield (g/pot) of shoots and roots of different vegetable crops.**

| Vegetable crops | | Shoots | | Roots | |
|---|---|---|---|---|---|
| | | Fresh weight (g/pot) | Dry weight (g/pot) | Fresh weight (g/pot) | Dry weight (g/pot) |
| Radish | First | 27.95a | 3.33 | 4.02a | 1.01a |
| | Second | 23.22c | 3.25 | 2.89c | 0.81c |
| | Third | 25.46b | 3.29 | 3.24b | 0.87b |
| Arugula | First | 9.91a | 0.79 | 1.87a | 0.45a |
| | Second | 7.27c | 0.75 | 1.48c | 0.40c |
| | Third | 8.62b | 0.77 | 1.59b | 0.42b |
| Chicory | First | 24.78a | 2.02a | 4.65a | 1.07a |
| | Second | 17.06c | 1.89b | 2.58c | 0.67c |
| | Third | 20.18b | 1.94ab | 3.89b | 0.94b |
| Corchorus | First | 12.76 | 1.65 | 3.61a | 0.99 |
| | Second | 12.36 | 1.62 | 3.36b | 0.98 |
| | Third | 12.56 | 1.64 | 3.56a | 1.01 |

**Mean values followed by the same letter within treatments are not significantly different ( $p < 0.05$) according Duncan's multiple range test.**

The reduction of fresh and dry weight yield is revealed to the combined effect of Cd, Pb and Ni on the inhibition of the physiological and nutritional processes of plant (Ewais, 1997). The excessive concentration of Cd, beyond interfering with normal metabolism of some micronutrients, shows inhibitory effects on photosynthesis process. Also a disturbance in transpiration and $CO_2$ fixation (López-Millán *et al.*, 2009). The excess of Cd has an inhibitory effect on chloroplast development (Ghoshroy and Nadakavukaren, 1990), the Calvin cycle (Crupa *et al.*, 1993), and functions of plant enzymes (Chugh and Sawhney, 1999).

The adverse effects of Pb include its interference with other nutrients uptake, and translocation (Gopal and Rizvi, 2008 ). The excess of Pb caused an inhibition of photosynthesis process (Pinchasov *et al.*, 2006). As well as, changing the activity of several enzymes (Bansal *et al.*, 2002; Verma and Dubey, 2003; Cenkci *et al.*, 2010), and disturbance in the respiration rate (Romanowska *et al.*, 2002). Additionally, Excess of Pb has a pronounced effect on decreasing the nitrate-nitrogen absorption by plants. Otherwise, inhibiting the activities of nitrate reductase, glutamate dehydrogenase, glutamine synthase, and glutamic–pyruvic transaminase. Consequently, decreasing the synthesis of organic nitrogen compounds, such as protein and chlorophyll (Xiao *et al.*, 2008)

Concerning Ni effect, it was reported that it has an inhibitory effect on DNA, RNA and protein synthesis (Espen *et al.*, 1997). Excess of Ni uptake could also reduce relative water, and chlorophyll contents (Gajewska *et al.*, 2006). Beside an alteration in the uptake of essential nutrients and a reduction in $CO_2$ uptake, a possible disturbances in gas exchange, and generation of free radicals could be occurred. This may produce an oxidative stress (Ali *et al.*, 2009; Jozef *et al.*, 2009).

**Effect of different hydroponic treatments on Cd, Pb and Ni concentrations in shoots and roots.**

The contamination of Cd, Pb and Ni in the second and the third treatment led to a significant increase ($p<0.05$) in their concentration in shoots and roots as compared with the control treatment (Table 5). On the other hand, using the biosorbent material in the third treatment was attributed with a significant reduction in the concentration of Pb and Ni in shoots and roots. Nevertheless, the concentration of Cd in shoots and roots of the third treatment was higher than in the second treatment.

Cotton stalks are mainly composed of cellulose, hemicelluloses, and lignin, which contain methyl esters that do not bind metal ions significantly in its untreated form. However, methyl esters modified to carboxylate ligands after the pretreatment with sodium hydroxide (Rehman *et al.*, 2006). Therefore, increased the ability of cotton stalks for the removal of heavy metal ions, and reduced the uptake of $Pb^{2+}$ and $Ni^{2+}$ ions by vegetable crops. Although the biosorbent material led to remove considerable amounts of $Cd^{2+}$ ions, cadmium concentration in shoots and roots in the third treatment was higher than in the second treatment. This could be attributed to the antagonistic effect between $Pb^{2+}$ and $Cd^{2+}$, which decreased the uptake of $Cd^{2+}$ ions by vegetable crops (Devi Prasad and Devi Prasad, 1982; Teresa *et al.*, 2002). As mentioned before, the biosorbent material in the third treatment removed most of $Pb^{2+}$ ions from the nutrient solution, leaving $Cd^{2+}$ ions readily for absorption by plants.

The accumulation of Cd, Pb and Ni in vegetable roots was higher than shoots. This finding was reported by several researchers (Jian *et al.*, 2000; Van der Vliet *et al.*, 2007; Shentu *et al.*, 2008). The concentration of Cd, Pb and Ni in roots reached the excessive levels in the second and the third treatment (Kabata-Pendias and Pendias, 2001). Therefore, it is recommended to avoid the consumption of vegetable roots, as it is considered as a pool for heavy metals accumulation. Cadmium concentration in shoots reached the excessive levels in both treatments. Nickel reached the excessive levels in the second treatment. However, the biosorbent material reduced the uptake of Ni by plants, and it did not reach the excessive levels. Meanwhile, Pb concentration in shoots did not reach the excessive levels in both treatments.

**Table 5: Effect of hydroponic treatments on Cd, Pb and Ni concentration (mg kg$^{-1}$) in shoots and roots of different vegetable crops.**

| Vegetable crops | | Heavy metals concentration (mgkg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Shoots | | | Roots | | |
| | | Cd | Pb | Ni | Cd | Pb | Ni |
| Radish | First | 0.33c | 1.12c | 2.72c | 0.58c | 5.06c | 3.38c |
| | Second | 52.54b | 14.84a | 10.97a | 247.38b | 160.32a | 198.30a |
| | Third | 88.19a | 4.93b | 7.36b | 322.38a | 109.10b | 112.69b |
| Arugula | First | 0.51c | 0.35c | 1.12c | 0.45c | 0.84c | 1.51c |
| | Second | 90.20b | 6.53a | 11.55a | 271.71b | 167.89a | 180.75a |
| | Third | 122.74a | 2.83b | 6.24b | 297.93a | 115.05b | 119.10b |
| Chicory | First | 0.28c | 1.81c | 0.53c | 0.70c | 4.89c | 3.27c |
| | Second | 102.02b | 14.00a | 8.15a | 390.97b | 566.51a | 160.25a |
| | Third | 140.83a | 5.31b | 4.42b | 431.97a | 110.99b | 80.92b |
| Corchorus | First | 0.21c | 0.54c | 1.61c | 0.40c | 6.32c | 3.49c |
| | Second | 36.46b | 1.94a | 7.52a | 144.04b | 71.96a | 62.21a |
| | Third | 40.12a | 0.97b | 6.12b | 184.68a | 46.73b | 47.51b |

**Mean values followed by the same letter within treatments are not significantly different ( $p < 0.05$) according Duncan's multiple range test.**

## Effect of different hydroponic treatments on macronutrients concentration in shoots and roots.

Data in Table 6 indicated that heavy metals contamination reduced significantly ($p<0.05$) nitrogen concentrations in shoots and roots of vegetable crops. Although the reduction in shoots was not significant in some cases. Nitrate uptake is mediated by transporters in the plasma membrane of root cells (Henriksen and Spanswick, 1993). Therefore, heavy metals contamination may caused a reduction in the potential of plasma membrane to absorb $NO_3$ ions (Hernández *et al.*, 1997; Xiao *et al.*, 2008). The third treatment recorded the lowest concentration of nitrogen in both shoots and roots. This could be attributed to the biosorption of $NO_3^-$ ions by the biosorbent material.

**Table 6: Effect of hydroponic treatments on macronutrients concentration (%) in shoots and roots of different vegetable crops.**

| Vegetable crops | | Macronutrients concentration (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Shoots | | | | | | Roots | | | | | |
| | | N | P | K | Ca | Mg | S | N | P | K | Ca | Mg | S |
| Radish | First | 6.59 | 0.85b | 5.99b | 2.36c | 0.74c | 1.24c | 3.47a | 0.83b | 3.86c | 1.22c | 0.35b | 0.95c |
| | Second | 6.54 | 1.14a | 5.99b | 3.17a | 0.98a | 1.29b | 3.31b | 0.92a | 4.25b | 1.51a | 0.43a | 1.15b |
| | Third | 6.40 | 0.89b | 7.63a | 2.75b | 0.84b | 1.75a | 3.29b | 0.85b | 4.43a | 1.29b | 0.39ab | 1.20a |
| Arugula | First | 6.40a | 0.74b | 6.96b | 2.59c | 0.70c | 1.60c | 3.71a | 0.89b | 3.26c | 1.11c | 0.29b | 0.98c |
| | Second | 6.34a | 0.95a | 7.01b | 2.86a | 0.89a | 1.69b | 3.45b | 0.96a | 3.41b | 1.49a | 0.34a | 1.11b |
| | Third | 5.96b | 0.76b | 8.51a | 2.74b | 0.79b | 1.77a | 3.34b | 0.85b | 3.76a | 1.24b | 0.32ab | 1.16a |
| Chicory | First | 5.98a | 0.75c | 7.20b | 0.96c | 0.34c | 0.45c | 4.21a | 0.71b | 5.50c | 0.56b | 0.23b | 0.43c |
| | Second | 5.83a | 0.83a | 7.21b | 1.13a | 0.48a | 0.51b | 4.15a | 0.82a | 5.69b | 0.68a | 0.29a | 0.57b |
| | Third | 5.25b | 0.79b | 8.22a | 1.04b | 0.39b | 0.64a | 3.47b | 0.75b | 5.81a | 0.58b | 0.26ab | 0.63a |
| Corchorus | First | 2.84 | 0.48 | 3.81b | 1.62 | 0.48 | 0.35b | 1.41a | 0.25b | 1.89b | 0.64 | 0.36b | 0.56b |
| | Second | 2.81 | 0.50 | 3.83b | 1.69 | 0.52 | 0.40a | 1.38a | 0.28a | 1.93b | 0.67 | 0.40a | 0.62a |
| | Third | 2.77 | 0.50 | 4.29a | 1.64 | 0.49 | 0.37ab | 1.31b | 0.25b | 2.07a | 0.65 | 0.36b | 0.61a |

**Mean values followed by the same letter within treatments are not significantly different ( $p < 0.05$) according Duncan's multiple range test.**

Phosphorus has another trend, as it increased in the second treatment more than other treatments. Probably, because of the imbalance of water status in plant tissues. Excessive concentrations of heavy metals significantly affected plant water status, which caused water deficit, and subsequent changes in nutrients concentration (Kastori *et al.*, 1992). There was no significant difference in P concentration between the control and the third treatment in most cases. This is attributed to the biosorbent material, which mitigated the harm of water deficit in plant tissues.

Concerning K concentration, it was noticed that its values were the highest in the third treatment. This is due to the desorption of $K^+$ ions from the biosorbent material to the nutrient solution. On the other hand, K concentration in the second treatment was higher than the control treatment. Presumably due to the concentration effect, which attributed with the imbalance of water status in plant.

Calcium and magnesium concentrations increased significantly as the concentration of heavy metals increased in the nutrient solution. The highest concentrations of Ca and Mg were associated with the second treatment, followed by the third treatment. However, the control treatment recorded the lowest values. Several defense strategies against heavy metals stress were described in higher plants. One of these mechanisms is the plant selectivity toward the absorption of $Ca^{2+}$ and $Mg^{2+}$ ions to mitigate the stress of heavy metals (Abul Kashem and Kawai, 2007; Wang and Song, 2009). This could be the reason of increasing Ca and Mg in the second treatment, which exposed to more stress of heavy metals. Furthermore, the negative effect of heavy metals on the water balance in plant tissues could be another possible reason for increasing Ca and Mg concentrations in the second and the third treatment.

Sulfur concentration in shoots and roots has been affected significantly by different hydroponic treatments. The highest concentration of S was associated with the third treatment, followed by the second treatment. Whereas, the control treatment recorded the lowest concentration. It is recognized that high S concentration is associated with the accumulation of Cd in plant tissues. This is revealed to the enhancement of sulfate uptake and assimilation by plant, due to the stimulation of Cd accumulation in plant tissues. Cadmium-induced sulfate uptake was related to a higher level of mRNA encoding for a putative high-affinity sulfate transporter in roots (Nocito *et al.*, 2002). In addition, Cd exposure induces the activity of ATP-sulfurylase and 5'- phosphosulfate reductase, and these are the first two enzymes in the sulfate assimilation pathway (Nussbaum *et al.*, 1988)

**Effect of different hydroponic treatments on micronutrients concentration in shoots and roots.**

Iron concentration in shoots decreased significantly ($p<0.05$) in the second and the third treatment (Table 7). Whereas, the concentration of Fe in roots increased. Heavy metals contamination, especially with $Cd^{2+}$, inhibited the translocation of Fe from roots into shoots. This led to an accumulation of Fe in roots (Kovács *et al.*, 2010).

Manganese concentration in roots showed a reduction in the second treatment as a result of heavy metals contamination. Perhaps due to the antagonistic effect between $Ni^{2+}$ and $Mn^{2+}$ ions. In addition to a possible antagonism between $Cd^{2+}$ and $Mn^{2+}$ ions (Khalid and Tinsley, 1980; Dong *et al.*, 2006; Wu *et al.*, 2007). Meanwhile, a slight increase in Mn concentration in shoots appeared in the second treatment as compared with the control treatment. This is due to the inhibitory effect of water uptake by plants due to heavy metals contamination. The highest concentration of Mn was recorded in the third treatment. This is revealed to the desorption of $Mn^{2+}$ ions from the biosorbent material to the nutrient solution as mentioned before.

Zink concentration in both shoots and roots increased significantly in the second treatment as compared with the control treatment. This could be attributed to the synergistic effect between $Cd^{2+}$ and $Zn^{2+}$ ions (Liu *et al.*, 2003). In addition to a possible synergism between $Ni^{2+}$ and $Zn^{2+}$ ions (Kabata-Pendias and Pendias, 2001). Concerning the third treatment, Zn concentration in shoots and roots marked the lowest values. This is revealed to the high ability of the biosorbent material to bind $Zn^{2+}$ ions (Mosa *et al.*, 2010).

Copper concentration in roots increased significantly as the accumulation of Cd increased in plant tissues. The highest concentration of Cu was associated with the third treatment, which recorded the highest values of Cd accumulation in plant tissues. However, the control treatment was associated with the lowest values of Cu concentration. Synergistic effect between high Cd concentration and Cu uptake and accumulation in roots have been reported (Larbi *et al.*, 2002; Liu *et al.*, 2003). The concentration of Cu in shoots showed a different trend, as it increased in the control treatment, and decreased in the second and third treatment in most cases. These results are in accordance with those obtained by López-Millán *et al.* (2009).

**Table 7: Effect of hydroponic treatments on micronutrients concentration (mg $kg^{-1}$) in shoots and roots of different vegetable crops.**

| Vegetable crops | | Micronutrients concentration (mg$kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Shoots | | | | Roots | | | |
| | | Fe | Mn | Zn | Cu | Fe | Mn | Zn | Cu |
| Radish | First | 606a | 62b | 197b | 177a | 596b | 85b | 566b | 87c |
| | Second | 444c | 66b | 206a | 145b | 720a | 71c | 680a | 94b |
| | Third | 511b | 93a | 171c | 172a | 548c | 97a | 425c | 104a |
| Arugula | First | 437a | 49b | 163b | 57a | 490c | 74b | 348b | 53b |
| | Second | 319c | 52b | 217a | 47c | 743a | 50c | 690a | 55b |
| | Third | 347b | 61a | 139c | 51b | 596b | 85a | 278c | 64a |
| Chicory | First | 365a | 57b | 172b | 110b | 681c | 99a | 500b | 36c |
| | Second | 280b | 61b | 219a | 125a | 840a | 91b | 615a | 40b |
| | Third | 357a | 68a | 157c | 107b | 783b | 71c | 232c | 49a |
| Corcho-rus | First | 560a | 55a | 100a | 14a | 346 | 60b | 469a | 23a |
| | Second | 494b | 52a | 81b | 11b | 353 | 45c | 393b | 21b |
| | Third | 542a | 89b | 72c | 8c | 348 | 76a | 382b | 22ab |

Mean values followed by the same letter within treatments are not significantly different ( $p < 0.05$) according Duncan's multiple range test.

## Conclusion

In conclusion, results obtained from this study increased our knowledge concerning the effect of biosorption process on mitigating heavy metals accumulation in plant tissues. The biosorbent material decreased the concentration of $Cd^{2+}$, $Pb^{2+}$ and $Ni^{2+}$ ions in the contaminated nutrient solution. Heavy metals contamination decreased fresh and dry weight yield, and altered the concentration of plant nutrients in shoots and roots. The concentration of Pb and Ni decreased significantly in the third treatment comparing with the second treatment, as a result of the biosorption process. However Cd concentration increased, due to reactions between metal ions, which increased Cd uptake. The accumulation of heavy metals in root tissues was higher than shoots, and it reached the excessive levels. Thereby, it is recommended to avoid the consumption of vegetable roots, as it is considered as a pool for accumulating heavy metals. Finally, we should mention that a further hydroponic study should be conducted by changing the plant nutrition technique to the foliar nutrition instead of the nutrient solution to avoid the reaction between plant nutrients, and the investigated heavy metal ions. This will lead to a more consistent background about the effect of biosorption process on heavy metals uptake by plants.

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## هل عملية الامتصاص الحيوي قادرة علي تقليل إجهاد العناصر الثقيلة ؟

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هناك نقص في المعلومات فيما يتعلق بتأثير عملية الامتصاص الحيوي علي نمو النبات تحت تأثير إجهاد العناصر الثقيلة. لهذا الغرض، أجريت تجربة مزارع مائية لتقييم قدرة حطب القطن المعامل بهيدروكسيد الصوديوم كمادة مدمصة لدرأ التأثير الضار للكادميوم والرصاص والنيكل علي بعض محاصيل الخضر.تكونت التجربة من ٣ معاملات للمزارع المائية وهي محلول غذائي ملوث مع أو بدون المادة المدمصة بالإضافة إلي معاملة المقارنة (محلول غذائي غير ملوث). أزالت المادة المدمصة كميات كبيرة من العناصر الثقيلة من المحلول الغذائي الملوث خاصة أيونات الرصاص. أدت العناصر الثقيلة إلي تقليل للمحصول الطازج والجاف للمجموعين الخضري والجذري. تأثر تركيز العناصر الكبرى والصغرى بالتلوث بالعناصر الثقيلة. ازداد تراكم العناصر الثقيلة في الجذر مقارنة بالمجموع الخضري. وصل تركيز العناصر الثقيلة في الجذور إلي الحدود الحرجة خاصة في المعاملة الثانية (بدون المادة المدمصة). أدت المادة المدمصة إلي تقليل تراكم الرصاص والنيكل في المجموعين الخضري والجذري. بينما ازداد تركيز النيكل.

إجمالا يمكن القول أن حطب القطن المعامل بهيدروكسيد الصوديوم يمكن أن يكون مادة مدمصة واعدة لإزالة العناصر الثقيلة من المياه العادمة قبل الري.

**قام بتحكيم البحث**

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