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BIOACCUMULATION OF CHROMIUM AND NICKEL APPLIED TO SINGLE AND BINARY FOR A SHORT TIME IN *Ceratophyllum demersum*, A ROOTLESS AQUATIC MACROPHYTE

Gülcan CINAR[1], Muhittin DOĞAN[1], Mustafa SEVINDIK[2]

[1]University of Gaziantep, Department of Biology, Faculty of Arts and Sciences, 27310 Gaziantep, Turkey
[2]Osmaniye Korkut Ata University, Department of Food Processing, Bahçe Vocational School, Osmaniye, Turkey

Corresponding author email: sevindik27@gmail.com

Abstract

This study was undertaken to investigate bioconcentrations of Cr and Ni in single and binary tratments by C. demersum. The macrophyte was treated with 0.1, 1 and 10 mg L^{-1} Cr and Ni concentrations their combinations (0+0, 0.1+0.1, 1+1 and 10+10 mg L^{-1} Cr plus Ni). Chromium and nickel accumulation capacities of the macrophyte were found to be different. Compared to Ni, more Cr was accumulated in the macrophyte tissues. Binary applications of Cr and Ni have generally reduced metal uptake compared to single applications. There was a decrease in bioconcentration factors with increased external the metal concentrations. It was concluded that the macrophyte can bioaccumulate in its tissues by uptake more metal from the environment at low concentrations.

Key words*: Ceratophyllum demersum, chromium, nickel, bioaccumulation.*

INTRODUCTION

The term heavy metal is used for metals or metalloids with a density greater than 5 g/cm³. The most common heavy metals include Pb, Cr, Fe, Cu, Ni, Zn, Co and Hg. The metals in our environment originate from natural and anthropogenic reasons (Ross, 1994). Heavy metal pollution in the environment has become an important problem, especially due to intensive industrial activities (Eick et al., 1999; Sevindik, 2018). Large areas are contaminated with heavy metals due to sewage or urban composts, pesticides and fertilizer use, municipal waste, car exhausts, mining waste and metal melting industries. Among these, a large part of Cr is used for stainless steel and chromate coating. In the chemical industry, Cr is mainly used in pigments, metal coatings and wood preservatives. The main source of Cr pollution is thought to be caused by dyes and leather tanning when wastes are discharged directly into waste streams as liquid or solid (Kabata-Pendias, 2011). Nickel is widely used for magnetic components and electrical equipment. Ni-alloys are used for different tools and containers used in medicine and food technology and kitchen equipment. It is also used as a dye in Ni ceramic and glass manufacturers and batteries containing Ni-Cd compounds (Kabata-Pendias, 2011).

The macrophytes are an important part of the aquatic ecosystem. Aquatic macrophytes include flowering and non flowering plants that live in streams such as rivers and stagnant waters such as lakes. These macrophytes are divided into three main groups according to the ecological characteristics of the environment in which they live. These are (i) emers type macrofites that grow on the shore, and a part of its stem and body, in water, (ii) the leaves whose roots are bound to sediment, swimmer macrophytes, and all morphological organs floating in water, (iii) completely underwater (in some species, genarative organs above the water). can be grouped as living submers type macrophytes (Dogan, 2011). They are known to have great importance, forming a substantial component of the primary production in many aquatic habitats (Pip, 1990). The macrophytes may accumulate considerable amounts of heavy metals in their tissues (Kovacks et al., 1984). In the recent past, the main groups of macrophytes are reported to bioconcentrate heavy metals in natural waters as well as after exposure to wastewaters (Greger, 1999). Previous studies have reported that macrophytes accumulate different heavy metals in their tissues. *C. demersum*, for example Cd (Saygideger and Dogan, 2004; Keskinkan et al., 2004; Dogan et. al., 2018), Cu (Rama Devi and Prasad, 1998), Cr (Garg and Chandra, 1990), Pb (Saygideger and Dogan, 2004; Dogan et al., 2018) and Hg (Suckcharoen, 1979) have been reported to take metals from contaminated solutions.

Although many studies have been conducted on heavy metal accumulation in aquatic macrophytes, studies on metal interaction are limited. Therefore, this experiment was designed to study determination of Cr and Ni accumulations at single and binary applications in *C. demersum*.

MATERIALS AND METHODS

C. demersum L. (coontail) belongs to the family Ceratophyllaceae (hornworts). The macrophyte is commonly available aquatic macrophyte in Turkey. *C. demersum* was collected from the local water bodies. This was acclimatized in 10% Arnon and Hoagland nutrient solution under 25-27ºC, 16 h light and 8 h dark periods during two weeks in a climate chamber. Then, the macrophytes were treated with 0, 0.1, 1 and 10 mg L^{-1} Cr as $K_2Cr_2O_7$ and ($NiCl_2.6H_2O$) and their combinations (0+0, 0.1+0.1, 1+1 and 10+10 mg L^{-1} Cr+Ni) in 500 mL beher glass. A sample of 10% nutrient solution was used as control. pH's of the test solutions were adjusted to 6.4-6.6. All experiment carried out in triplicate.

After two days of application, macrophytes were collected. they were washed three times with distilled water. The macrophytes were then dried to an constant weight at 80°C in an electric furnace and pulverized. The samples were dissolved in 14 M $HN0_3$ and the residue was dissolved in 1 M HCl. After mineralization, Cr and Ni were determined using a flame AAS. Control macrophytes were treated in the same way.

Bioconcentration factor (BCF) was computed as follows:

$$BCF = C_{metal\ content\ in\ macrophyte} / C_{metal\ in\ solution}$$

The statistical analysis of the data obtained was made using the SPSS program. The significance of the differences between the values was determined by LSD test.

RESULTS AND DISCUSSIONS

Accumulations of Cr and Ni in single treatments are given in Figure 1. According to this, Cr accumulations of the *C. demersum* tissues were increased with increasing Cr concentrations. Chromium contents of the macrophye at 0.1, 1 and 10 mg L^{-1} were found about 14.8, 24.2 and 33.0 times greater than with respect to control, respectively (Figure 1A). Moreover Ni content in the macrophyte tissues was increased up to 45.8-fold at 10 mg L^{-1} concentration with respect to control (Figure 1C). BCF, defined as the concentration ratio of the metal in the plant, was used to measure the effectiveness of the macrophyte in concentrating Cr and Ni on tissues. Accordingly, there was a decrease in BCF with increased external Cr and Ni concentrations (Figure 1B and D). The highest BCFs were calculated at 0.1 mg/L Cr and 0.1 mg L^{-1} Ni concentrations as 311 and 164, respectively. According to the findings, macrophyte has more Cr bioaccumulation ability than Ni. It also showed that the macrophyte can bioaccumulate more the metals at low concentrations.

Co-occurrence of heavy metals is observed in environment. However, their individual and combined uptakes by macrophytes are not well documented. Cr and Ni contents in all tested binary treatments are given Figure 2. In the applications, both Cr and Ni accumulations were increased with increasing the metals concentrations. The maximum Cr and Ni contents in the combine treatment were measured at 10 + 10 mg L^{-1} Cr + Ni. These are about 23.1 for Cr and 8.0, for Ni, times greater than control respective metal contents (Figure 2A and C). However both the metal accumulations were decreased compared to individul Cr and Ni applications exception of 0.1 + 0.1 Cr + Ni application for Cr. While Cr content increased by 70.0% in 0.1 + 0.1 Cr plus Ni interaction compared to single Cr application, it decreased by 43.5% and 29.8% in 1 + 1 and 10 + 10 Cr + Ni interactions.

Besides Ni content decresed by 59.1%, 76.9% and 82.5% with respect to individual Ni application. So in the combination Ni accumulations was decreased by Cr. In addition, as in single metal applications, in the binary metal application, decreases in BCF ratios were found with increasing metal concentration (Figure 2B and D).

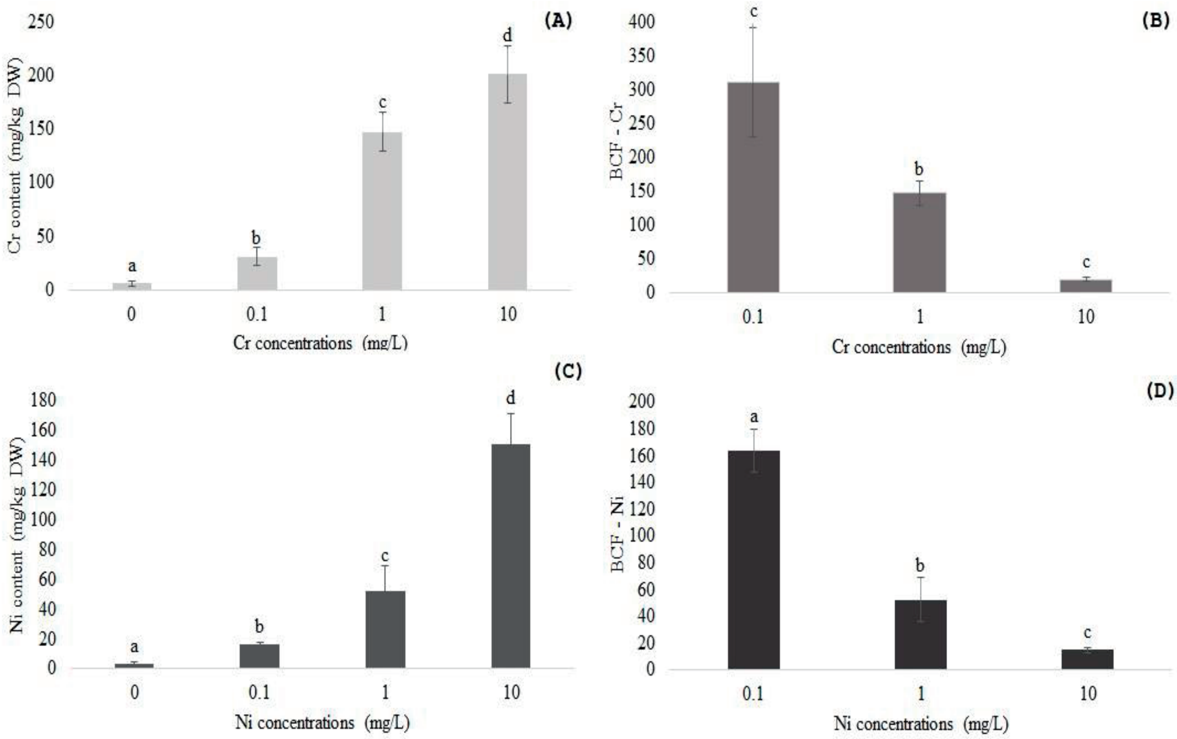

Figure 1. Chromium (A) and nickel accumulations (C) and their bioconcentration factors (BCFs) (B and D) in single treatments by *C. demersum*. Values expressed as mean ± standard deviation. Different letters on the bars indicate their significance according to the LSD test ($p<0.05$)

Heavy metals are important environmental pollutants and are toxic even at low concentrations (Krupodorova and Sevindik, 2020; Mushtaq et al., 2020). Macrophytes have an important role in the heavy metal cycle in water directly and indirectly. The accumulation of heavy metals by aquatic macrophytes has been studied by many researchers (Manny et al., 1991; Rama Devi and Prasad, 1998; Keskinkan et al., 2004; Saygideger and Dogan, 2004; Dogan et al., 2018). Macrophytes living in wetlands have been found to accumulate metal at high concentrations in the roots and shoots (Fritioff and Greger, 2001). Submerged macrophytes *Ceratophyllum demersum*, *Myriophyllum brasiliense* and *Hippuris vulgaris*, living in metal-contaminated waters, have also been reported to accumulate metal at high concentrations in their tissues (Rai et al., 1995; Quian et al., 1999; Saygideger and Dogan, 2004; Saygideger and Dogan, 2005). As a result, according to the findings, *C. demersum* was able to accumulate a significant amount of metals in its tissues with increased Cr and Ni concentrations. In addition, it has accumulated more Cr than Ni, showing that it has metal specific accumulation capacity. Previously, accumulation capabilities of heavy metals in Potamogetonaceae species were determined as Pb> Cu> Ni> Cr. So *C. demersum* differed in their accumulation capacities with respect to each particular ion. Similar results have been reported by other researchers (Saygideger and Dogan, 2004; Demirezen and Aksoy, 2006). As also described by Denny (1980), one reason of this may be differences in cellular mechanisms of metal ions uptake in the macrophytes.

According to findings, Cr-Ni interaction generally showed an antagonistic effect on absobtion of both metals compared to the single Cr and Ni applications. Interactions between metals can be both antagonistic and synergistic. Antagonism occurs when the combined physiological effect of two or more metals is less than the sum of its independent effects. Synergism occurs when the combined metals are greater. These interactions may also refer to a metal ability to inhibit or stimulate the absorption of other metals in plants (Kabata-Pendias, 2011). Chromium has been observed to have both antegonistic and synergetic effects with metals (Turner and Rust, 1971; Dong et al., 2007; Kabata-Pendias, 2011). In addition, similar interactions of Ni with other metals have been reported (Kabata-Pendias, 2011).

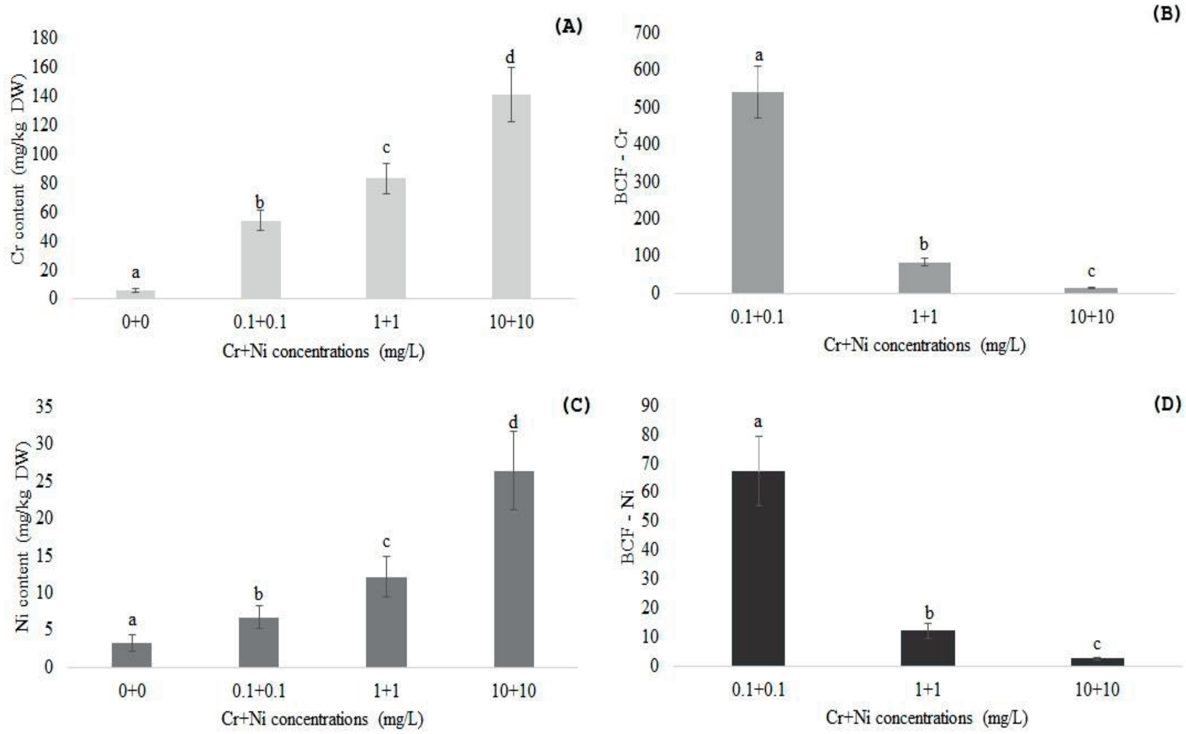

Figure 2. Chromium (A) and nickel accumulations (C) of *C. demersum* after Cr plus Ni applications and their bioconcentration factors (BCFs) (B and D). Values expressed as mean ± standard deviation. Different letters on the bars indicate their significance according to the LSD test ($p<0.05$)

CONCLUSIONS

As a result, metal accumulation capacity of *C. demersum* was found to be different. Compared to Ni, more Cr was accumulated by the macrophyte. In addition, the application of metals together has generally reduced metal uptake compared to single applications. It was also concluded that the macrophyte can bioaccumulate in its tissues by removing more metal from the environment at low concentrations. Rapid urbanization, increase in industrialization and intensive use of pesticides increase heavy metal contamination in the environment. Aquatic macrophytes have the ability to accumulate metals from contaminated waters by taking into consideration their levels. Removal of such pollutants from the environment or reduction of their effects has recently become a popular practice. Phytoremediation is known as a promising cost effective and environmentally sustainable technology, especially for the treatment of water contaminated by heavy metals. Macrophytes are often used for the phytoemediation of water contaminated with heavy metals. The high metal accumulation capacity, especially Cr, can make *C. demersum* a choice for phytoremediation of heavy metals.

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