Effective removal of Cd (II), Co (II) and Ni (II) ions by using hypnum cupressiforme bioadsorbent

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Abstract: In this study, Hypnum cupressiforme, an effective bio-adsorbent was subjected to preconcentration, determination and removal of Cd (II), Co (II) and Ni (II) heavy metals in aqueous solutions. The Hypnum cupressiforme samples were collected from nature and dried for 24 hours at 40 °C after washing with distilled water. The optimization of preconcentration steps were evaluated for solution pH, sample volume and flow rate. The surface morphology of the adsorbent was evaluated by micrographic analysis. The heavy metal concentrations were determined by using flame atomic absorption spectroscopy. The Hypnum cupressiforme bio-adsorbent showed up to 95 % removal performance for Cd (II), Co (II) and Ni (II) heavy metals under optimum conditions. The obtained results suggest that Cd (II), Co (II) and Ni (II) heavy metal ions in aqueous solutions can be successfully removed by optimized technique.
Keywords: Hypnum cupressiforme, Heavy metals, preconcentration, FAAS.

1. Introduction

The contamination of waters from industrial effluents, causes a significant environmental and health problems (Raghu vd., 2009).

Large quantities of effluents are released continuously by industries containing high levels of toxic heavy metals. In general, there are no or not sufficient water treatment plants that can efficiently remove metal ions in these industrial plants. Even the concentrations of these metal ions are low, they may still represent serious threats to the environment and environmental related systems. These metal ions can block functional groups of essential enzymes and may cause damage of bones, kidneys, livers and nerves etc. (Malik, 2004). The removal of metal ions from waters is of prime importance to protect the water resources and nature. There are several extraction techniques to remove the metal ions from waters such as liquid-liquid extraction (LLE), electro-remediation (ER), cloud point extraction (CPE) and solid phase extraction (SPE). The SPE is a common technique involving a branch of adsorbents from synthetic to natural. Using biological materials in SPE technique (biosorption) is remarkable for scientist in recent years.

Biosorption is an environmental friendly branch of the adsorption techniques in which the sorbent is a biologically oriented material. This technique can be considered a simple, economical and environmentally friendly process which is used as an alternative for removing water soluble pollutants (Torres, 2020).

Bio-sorption phenomenon involves a series of chemical process with different mechanisms. The exact bonding mechanism of the bio-sorbent vary from physical electrostatic interactions, van der Waals forces, hydrogen bonding to chemical ionic and covalent bonding. Both living and dead organisms and their components can be

used in biosorption processes called biosorbent. In the biosorption involving processes, metal ions and related substances, and all kinds of soluble organic materials can be removed. Various types of biosorbents are fungi, algae, bacteria, fibres, peat, rice hulls, forest by-products, chitosan and agro-food wastes. Biosorbents are generally substances with high affinity, capacity and selectivity (Mathew vd., 2016).

Consequently, biosorption is an effective, economical and environmental friendly technique to remove soluble pollutants from waters (Qin vd., 2020).

Bryophytes are one of the ancestors of land plants and they are a group of the simplest land plants. Bryophytes are considered to have evolved from green algae. The bryophytes are widespread all over the world (Özkır vd., 2020).

Mosses are used as sensitive bioindicators for heavy metal contamination and have several advantages as indicators organisms. Mosses also show the concentrations of the most metals as a function of the amount of atmospheric deposition (Koz., 2014).

In this study, ***Hypnum cupressiforme*** is used as a bio-adsorbent for the preconcentration, determination and removal of Cd (II), Co (II) and Ni (II) heavy metals in aqueous solutions by using column technique.

2. Materials and Methods

2.1. Preparation of *Hypnum cupressiforme* for preconcentration process

Hypnum cupressiforme samples were washed carefully with distilled water three times to remove the dust and other impurities. The washed samples were dried in an oven for 48 hours at 40 °C. The dried samples were grinded by using Retsch PM-100 model grinder.

2.2. Removal of Cd (II), Co (II) and Ni (II) ions by column solid phase extraction method

Column solid phase extraction process was conducted in simple steps: In the first step, 0.05 g of grinded *Hypnum cupressiforme* samples were weighed by using Radwag Wagi Electroniczne AS 220/C/2 model analytical weigher and placed into a 250 mL mini adsorption column. Then a 100 mL of model solution containing 1.0, 5.0 and 5.0 ppm of Cd (II), Co (II) and Ni (II) ions were added in to the beaker. The pH of the solutions was adjusted by using 5 mL of appropriate buffer solutions. The model solutions were passed through the column. Adsorbed Cd (II), Co (II) and Ni (II) ions were desorbed into a 5 mL volumetric flask by using 1M HNO3 in methanol and metal concentrations were determined by flame atomic absorption spectrophotometer. A brief of the method was given in Fig 1.

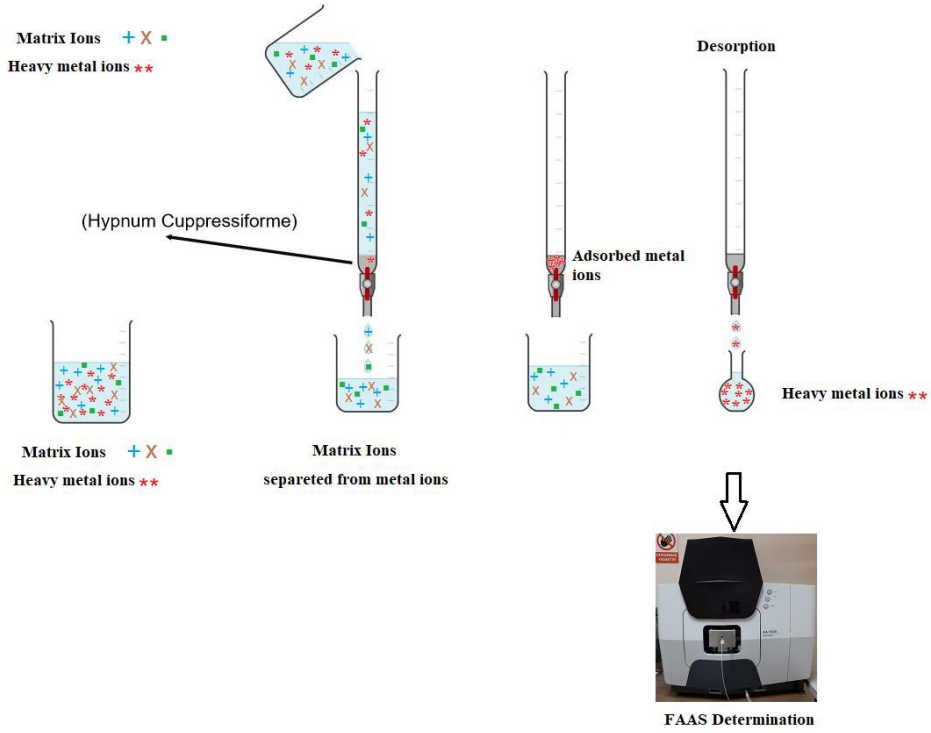

Figure 1. The column preconcentration process of heavy metal ions by using bio-adsorbent *Hypnum cupressiforme*

3. Results and Discussion

3.1. Surface structure of the bio-adsorbent

The surface structure of the grinded *Hypnum cupressiforme* was investigated by using micrographic analysis (Olympus SZX7 model computer integrated microscope) and the obtained results were given in Fig. 3.

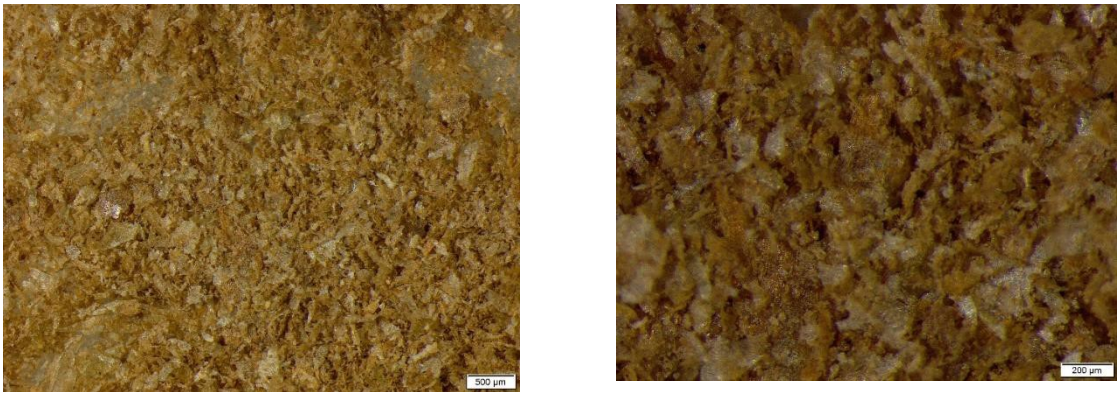

Figure 2. The surface structure of the *Hypnum cupressiforme* bio-adsorbent

The micrographs showed that the surface structure of the grinded bio-adsorbent is highly rough and irregular. This surface structure can be attributed to its suitability for adsorption in relation with its higher surface area.

3.2. The heavy metal removal characteristics of the *Hypnum cupressiforme*

The optimization of heavy metal uptake ability of *Hypnum cupressiforme* was investigated by column method on heavy metals Cd (II), Co (II) and Ni (II) in terms of solution pH, sample volume, flow rate and matrix ions. Obtained results were given in Fig 3-4-5 respectively.

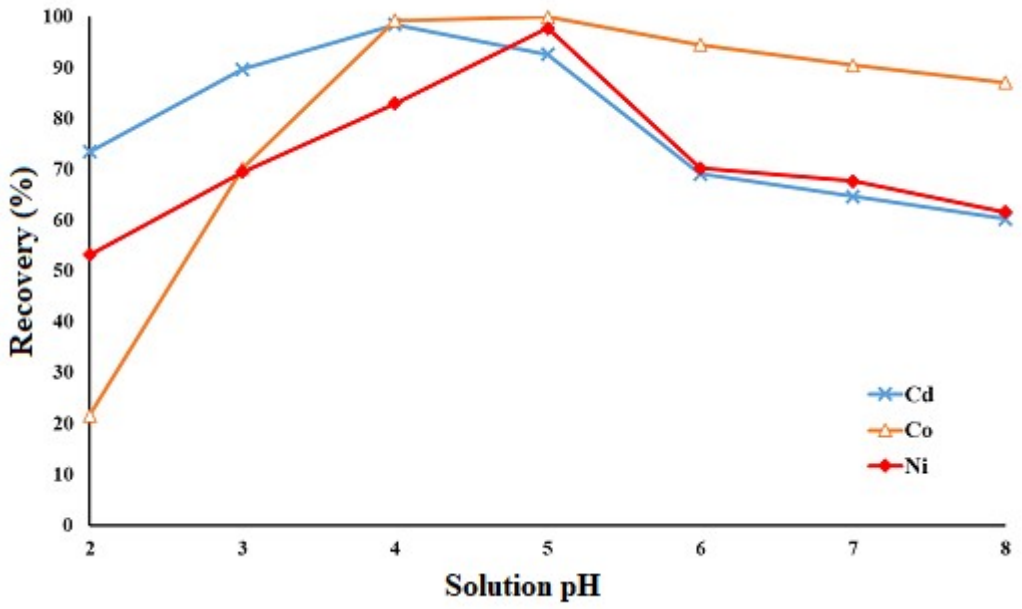

Figure 3. Effect of solution pH on the recovery of Cd (II), Co (II) and Ni (II) metal ions

The pH of the adsorption medium is one of the key factors on the removal of metal ions. According to Fig 3. the optimization of heavy metal uptake ability of *Hypnum cupressiforme* was investigated by column method all three metal ions Cd (II), Co (II) and Ni (II) were quantitatively removed from aqueous medium. The optimum solution pH was chosen as pH=5 and the rest of the experiments were conducted at this value.

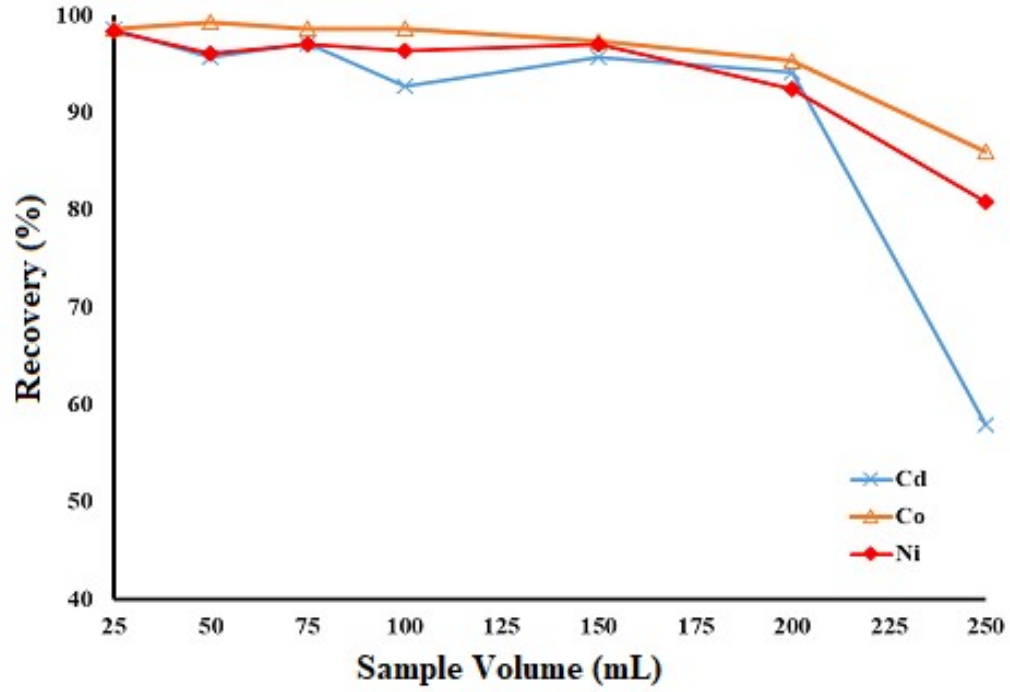

Figure 4. Effect of sample volume on the recovery of Cd (II), Co (II) and Ni (II) metal ions

Sample volume optimization is important to gain higher preconcentration factors and to remove higher values of metal ions from waters. Fig 4 revealed that *Hypnum cupressiforme* successfully adsorbed the Cd (II), Co (II) and Ni (II) ions up to 200 mL and the optimum value was chosen as 200 mL of sample volume.

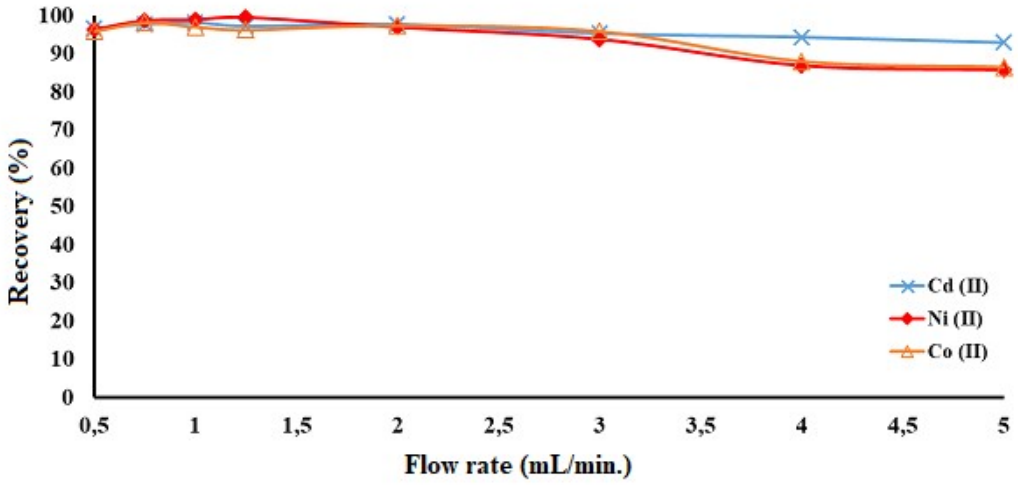

Figure 5. Effect of sample flow rate on the recovery of Cd (II), Co (II) and Ni (II) metal ions

It is well known that the adsorption is a equilibrium dependent process and optimization of the sample flow rate is important to remove the metal ions at optimum rate and maximum quantity. According to results from Fig 5, Cd (II), Co (II) and Ni (II) metal ions

quantitatively removed from aqueous medium up to 3 mL/min. sample flow rate and this value is accepted as optimum flow rate.

4. Conclusions

This study is based on the application of *Hypnum cupressiforme* on the removal of heavy metals Cd (II), Co (II) and Ni (II) as an environmentally friendly bio-adsorbent. The *Hypnum cupressiforme* acted as an efficient adsorbent for Cd (II), Co (II) and Ni (II) ions whom removal values were above 90%. In conclusion, the *Hypnum cupressiforme* can be used for the removal of these three heavy metal ions. Considering the environment, using an eco-friendly and easily bio-degradable material can be a better alternative to synthetic adsorbents.

Acknowledgement

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