

## The Adsorption Performance of *Urtica dioica* on the Removal of Cadmium from Aqueous Solutions

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### Authors' contributions

This work was carried out in collaboration between both authors. Author BE designed the study, managed the analyses of the study and wrote the first draft of the manuscript. Author DE managed the literature searches, supplied the adsorbent and prepared it for the experiments. Both authors read and approved the final manuscript.

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### ABSTRACT

Many contaminants (dyes, heavy metals and some inorganic substances) occur naturally through processes such as the weathering of rocks and human activities including the mining, processing and smelting of ore, and the nuclear and automotive industries. The release of contaminants, especially heavy metals to the media without any remediation process, has a very harmful effect on the environment and human health. Recently, scientists have been researching various methods to purify heavy metals from wastewater. Adsorption is an efficient method and many of materials are used as an adsorbent; activated carbons, clays, biopolymers, agricultural wastes etc. Among them, biosorbents have been preferred as they are cheap, practical, easy to find and environmentally friendly. In this study, the adsorption potential of *Urtica dioica* (*U. dioica*) on the removal of cadmium, one of the most dangerous poisons for the organisms and their environment, was investigated. The fact that the plant has low specific weight, rich functional groups and also lignocellulosic, porous structure led to the idea that it may be suitable for adsorption. *U. dioica* was

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used without any chemical modification only after being dried and passed through a 0.5 mm sieve. The effect of pH (4-10), adsorbent dose (0.2-0.8 g) and metal solution concentration (50-150 mgL<sup>-1</sup>) on adsorption was investigated. The great adsorption performance of 95% was obtained at pH 10 with 150 mgL<sup>-1</sup> metal solution concentration and 0.8 g adsorbent dose.

**Keywords:** Biosorbent; biopolymers; *Urtica dioica*; chemical modification; cadmium; automotive industries.

## 1. INTRODUCTION

Considering the increase in the population, the increase in the demand for water, irregular rains and drought, the protection of the existing water resources is very important. Heavy metals, dyes and some inorganic substances cause chemical pollution. Heavy metals are the most important pollutants in the aquatic media. As a result of industrial processes such as mining, metal, paper, plastic and petrochemical processing, metal, electrode plating, battery manufacturing, they are released into the environment as waste. Heavy metals accumulate in the soil and water and because their structures are stable to decomposition, they are very difficult to dispose of from the environment. It has known that a limited concentration of heavy metals is necessary for proper metabolism in living beings. High concentration of heavy metal causes many serious problems in both plants and animals. They also reduce soil fertility [1,2]. The major heavy metal pollutants are copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg) and nickel (Ni).

Cadmium (Cd<sup>2+</sup>) is a non-essential heavy metal and serious environmental pollutant. Cadmium has been identified as a human carcinogen according to The International Agency for Research on Cancer [3]. Cd<sup>2+</sup> causes inhibition of cell proliferation and induction of apoptosis in mammalian cells when it generates mutations in critical genes and/or it stimulates any of the cellular signals. Cd<sup>2+</sup> also damages a variety of biomolecules including nucleic acids and proteins by producing reactive oxygen species (ROS) [4,5]. Cd<sup>2+</sup> does not damage animals but also plants. Because Cd<sup>2+</sup> inclines inhibition of photosynthesis, respiration, nitrogen metabolism as well as the decrease of water and mineral uptake. Consequently, Cd<sup>2+</sup> leads to inhibition of plant growth [6].

There have been many techniques including precipitation, solvent extraction, electrochemical

methods, ion exchange, membrane separation and adsorption for heavy metal removal from contaminated water [7-9]. Adsorption is the most advantageous among these techniques with its economics, design and working flexibility, efficiency and high-quality purified product [9,10]. The commonly used adsorption materials are activated carbon, biosorbents, carbon nanotubes, clays, metal oxides, zeolites. Although there are many adsorption materials, biological materials are preferred because of being cheap, environmentally friendly and containing chitin, glucan, protein, mannan, etc. which they provide potential binding sites for pollutants [11].

*U. dioica*, usually called as nettle, originated in South America and spread all over the world. The nettle is a perennial plant with pointed leaves and white to yellowish flowers. This plant of Plantae kingdom belongs to the order Rosales and family Urticaceae. It has been used as traditional medicine for anemia, dermatological disorders, arteritis anti-rheumatism and as a diuretic, antiviral and anti-proliferative agent [12]. Recently, the researchers have reported that the nettle includes important minerals, chlorophyll, amino acids, lecithin, carotenoids, flavonoids, sterols, tannins and vitamins, scopoletin, sterols, fatty acids, polysaccharides and isolectins. Therefore, the nettle has become crucial for human diet [12-14]. The nettle has soft, resistant and low specific weight fibres with efficient absorbent, anti-static, thermoregulatory, transpiration characteristics, and non-lignified cell wall [15].

As it is widely found in the world and its structure is very suitable as a biosorbent material, the adsorption potential of *U. dioica* was evaluated in this study. Biosorbent, *U. dioica* was used directly (only dried and ground) without any chemical modification and effect of some parameters such as pH (4-10), adsorbent dose (0.2-0.8 g) and metal solution concentration (50-150 mgL<sup>-1</sup>) on the removal of cadmium (Cd<sup>2+</sup>) have been investigated.

## 2. MATERIALS AND METHODS

### 2.1 Preparation and Characterization of the Biosorbent

*U. dioica*, collected from Giresun in the Black Sea Region was washed with tap water until removing the impurities, and then distilled water for two times. The plant was dried at room temperature for three days and at 80°C for 48 hours in the incubator. Then, it was ground, passed through a 0.5 mm sieve and stored in a dusky glass container with a cover for further experiments. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine functional groups of biosorbent in Giresun University Central Research Laboratory.

### 2.2 Preparation of Cadmium Nitrate Cd(NO<sub>3</sub>)<sub>2</sub> Solution

Cadmium nitrate Cd(NO<sub>3</sub>)<sub>2</sub> was supplied from Sigma-Aldrich Company. The stock solution was prepared as 1000 mgL<sup>-1</sup> (ppm) and the metal solutions at different concentrations were prepared by diluting of stock solution. The pH was adjusted using 0.1 N HNO<sub>3</sub> and 0.1 N NaOH.

### 2.3 Adsorption Experiment

Adsorption experiments were performed by using the batch method. The certain amounts of ground *U. dioica* were added into 50 mL of cadmium solutions at certain concentrations and incubated in a shaker incubator at room temperature, 200 rpm for 3 hours and then the solutions were centrifuged to separate the liquid phase. The metal concentration in the liquid phase was determined by using ICP-OES device (Inductively Coupled Plasma / Optical Emission Spectrometer Perkin Elmer Optima 7000 DV) in Rize Recep Tayyip University Central Research Laboratory and the operational conditions of ICP-OES are shown in Table 1. Adsorption experiments were performed to determine the effect of parameters such as pH, adsorbent dose and initial metal concentration on adsorption efficiency.

The percentage of Cd<sup>2+</sup> adsorption and the amount of Cd<sup>2+</sup> adsorbed at the moment of equilibrium can be calculated by using Equation 1 and Equation 2.

$$\%Adsorption = \frac{c_0 - c_e}{c_0} \times 100 \quad (1)$$

$$q_e = \frac{c_0 - c_e}{w} \times V \quad (2)$$

(c<sub>0</sub>: initial metal concentration (mgL<sup>-1</sup>), c<sub>e</sub>: metal concentration in solution after adsorption, q<sub>e</sub>: the adsorbed metal per gram of adsorbent at equilibrium time (mgg<sup>-1</sup>), V: the metal solution volume (L) and w: the adsorbent mass (g).

**Table 1. Operational parameters of ICP-OES**

Parameter	Value
RF incident power	1300 watts
Plasma argon flow rate	15 L/min
Auxiliary argon flow rate	0.2 L/min
Nebulizer argon flow rate	0.8 L/min
Source equilibration delay	15 sec
View distance	15.0 axial
Number of readings per replicate	3

All experiments were fulfilled threefold and the obtained results were used in data analysis.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of Biosorbent

The FTIR spectrum is used to determine the functional groups in the structure of *U. dioica*, which helps us explain the interaction between the adsorbate (metal ions) and the functional groups in the biosorbent.

When the spectrum was examined, the peak at 893 cm<sup>-1</sup> indicated aromatic stretching ring and the peak at 1022 cm<sup>-1</sup> was due to aliphatic fluorine compound. The peak at 1241 cm<sup>-1</sup> proved the presence of alcohol, ether, carboxylic acid or ester. The peak at 1600 cm<sup>-1</sup> showed C-C tension in the aromatic ring. The peaks observed at 2919 cm<sup>-1</sup> and 3274 cm<sup>-1</sup> belonged C-H bond of the alkane and the hydrogen bond in alcohol or phenol, respectively. The IR spectrum of the biomaterial has been scanned between 400-4000 cm<sup>-1</sup> and these results prove the existence of various functional groups that can bind metal ions in the structure of *U. dioica* during the adsorption process.

### 3.2 Adsorption Parameters

#### 3.2.1 The pH effect

pH is an important parameter to control the adsorption process. The ions in solution are affected by the pH since the medium in which the adsorption process will take place in acidic or

basic, that is, due to the strong adhesion of hydrogen ( $H^+$ ) and hydroxyl ( $OH^-$ ) ions to the surface. Different ions can adsorb at different pH values in the adsorption process. For example, cationic ions are expected to adsorb at high pH values, while anionic ions are expected to adsorb at low pH values. This is due to the negative or positive charge of the adsorbate surface. The effect of the pH parameter varies according to the characterization of adsorbent and adsorbed ions and their behaviors in solution [16,17].

100 ppm, 50 mL Cd solution was batch at pH 4, 6, 8 and 10 for 3 hours with 1 g of *U. dioica* at

room temperature. Metal adsorption percentages were presented in Fig. 2.

As seen in Fig. 2, it is observed that the percentage of adsorption increases as the pH increases and the pH reaches a maximum of 10. Hydrogen ion concentration is high at low pH values and it can be adsorbed more than metal ions. The increase in the pH value can be explained as the negative loading of the adsorbent surface due to the increase of the hydroxyl ion concentration and adsorption percentage is increase due to the electrostatic attraction between the negative hydroxyl groups and positive metal ions [18].

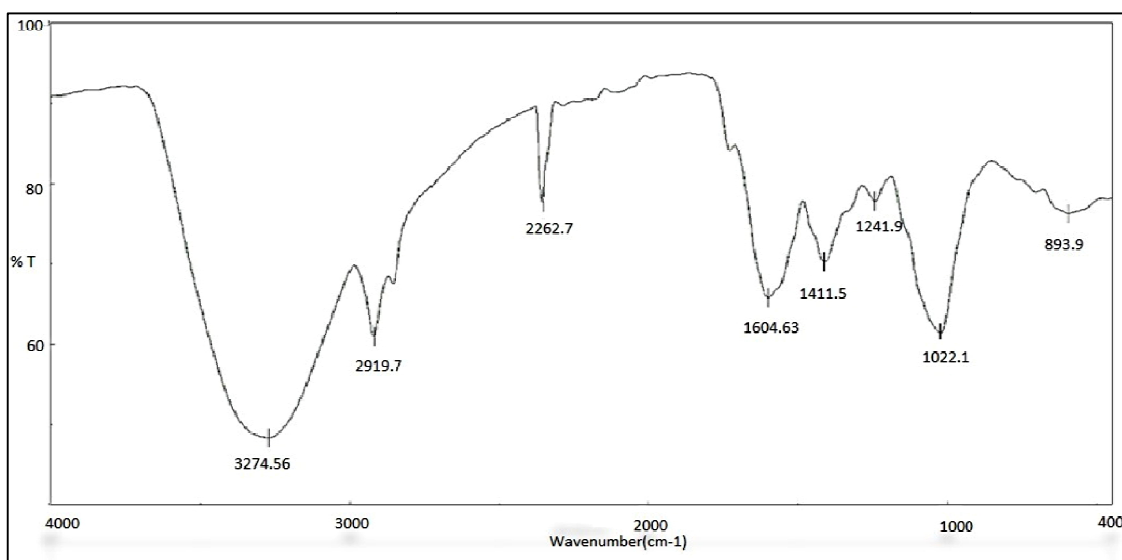


Fig. 1. The FTIR spectra of *U. dioica*

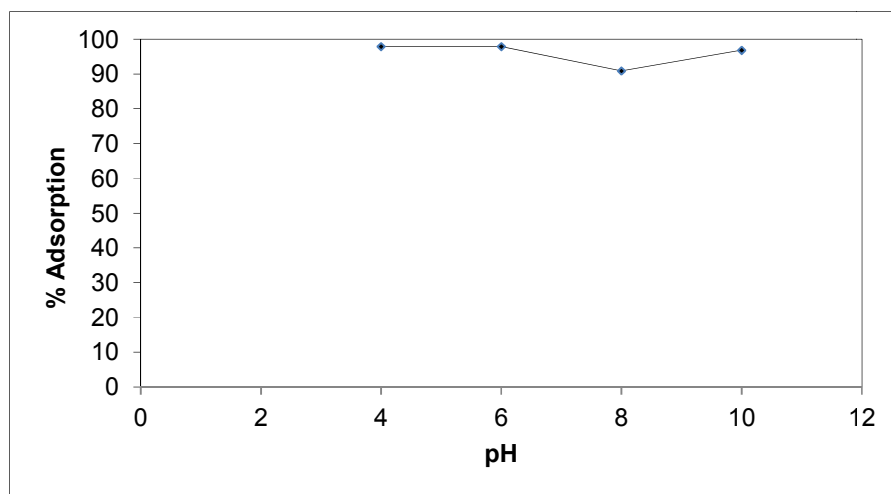
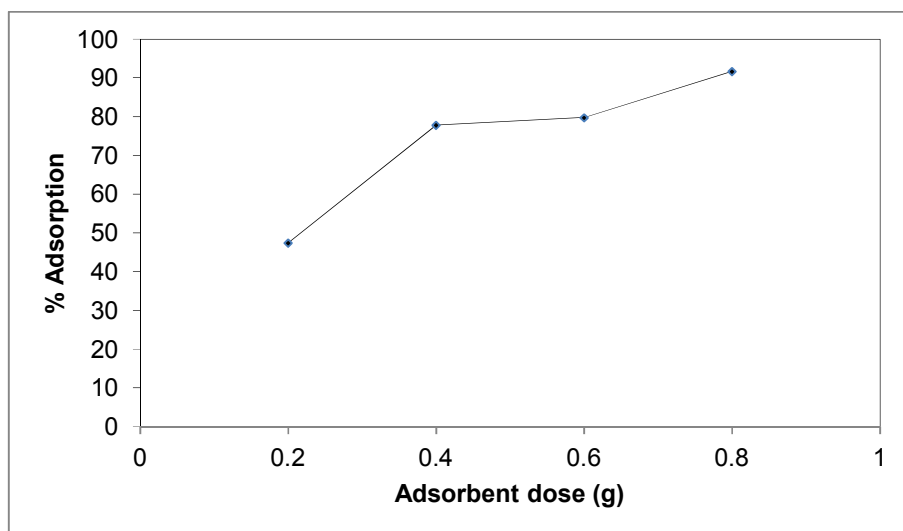


Fig. 2. The pH effect on the adsorption of Cd(II)



**Fig. 3. The adsorbent dose effect on the adsorption of Cd(II)**

### 3.2.2 The adsorbent dose effect

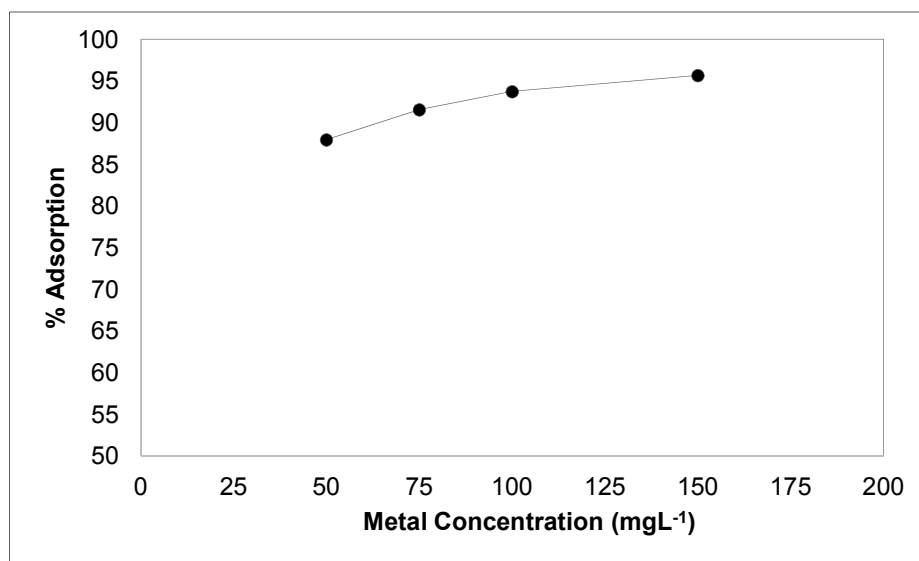
100 ppm, 50 mL Cd solutions were batch at room temperature with 0.2, 0.4, 0.6, 0.8 g of *U. dioica* at pH 10 for 3 hours. Metal adsorption percentages are given in Fig. 3.

In the experiments, the amount of adsorbent was studied between 0.2-1.0 g and when 1 g was used, it was observed that almost all of the metal was adsorbed. As the number of adsorbent active surfaces that will bind metal ions increases as the number of adsorbent increases.

Therefore, the adsorption is increased, too. When 0.2 g adsorbent was used, the percentage of adsorption was 47.39% for Cd, this value reached 91.64% when 0.8 g adsorbent was used. The excess of the biosorbent amount also means the excess number of adsorbent active sites and hence the adsorption rate increases.

### 3.2.3 The metal concentration effect

The metal solution in 50 mL, pH: 10 was batch with 0.8 g of *U. dioica* at room temperature as seen in Fig. 4.



**Fig. 4. The adsorbent dose effect on the adsorption of Cd(II)**

Adsorption increased as the ion concentration of the metal solution increased. As the adsorption will increase with the attraction force between the metal ions and the active sites on the adsorbent surface, the increase of the metal ion concentration increases the adsorption. This continues until the adsorbent is saturated.

#### 4. CONCLUSION

As a result of rapid industrialization, the increase in environmental and water pollution have become a global problem. It is important to protect limited clean water resources and to remediate wastewater before releasing the media. Recently, searches for cheap, easily applicable, environmentally friendly adsorbents have become a remarkable research topic.

The fact that *U. dioica* is widely grown on the world and has lignocellulosic structure, many functional groups and harmless effect has shown that the plant can be used as an adsorbent. It was applied directly without any chemical pretreatment and a little dose of adsorbent (0.8 g) was able to enough the adsorption rate above 95% for Cd (II). Removal of Cd(II) ions was increasing with increasing pH value because of the surface charge of the adsorbent as expected. It is also explained that at low pH values,  $H_3O^+$  ions increase in the solution and metal ions are harder to bind to available adsorbent sites. The optimum pH value was 10. When initial metal concentration is increased, adsorbed metal ions by per amount of adsorbent is increased. Then the active sites on the adsorbent surface become filled and adsorption decreases. A significant increase in adsorption was observed until the metal concentration was  $100 \text{ mgL}^{-1}$ , and when the metal concentration was  $150 \text{ mgL}^{-1}$ , almost all of the metal ions were adsorbed. As a result of our studies, it has been revealed that the *U. dioica*, which is used with all parts of the plant in many areas, can also be used as an ideal adsorbent.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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