Application of biomass from Greek juniper needles (*Juniperus excelsa* M. Bieb) for removal of Cr (VI) from aqueous solution

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Abstract. The main goal of present study was to examine the performance of biomass from Greek juniper needles (*Juniperus excelsa* M. Bieb), obtained after distillation of the raw material, for its ability to remove Cr (VI) ions from aqueous solution. The used biomass was characterized by FT-IR analysis. Batch experiments were conducted and the effects of different biosorption process parameters were determined. Maximum removal efficiency (99.58 ± 0.31 %) was obtained at pH = 1.0, adsorbent dose 0.5 g L⁻¹, agitation speed 250 rpm, initial Cr (VI) concentration 50 mg L⁻¹, temperature 30.0 ± 1.0°C and contact time of 30 min. The pseudo-second order model was found to provide the best fit to experimental kinetics data (*R²* = 1.000) and the calculated value of equilibrium metal uptake agree quite well with the experimental value. Results indicated that the Freundlich (*R²* = 0.975) and the Langmuir (*R²* = 0.976) isotherm models correlated very well to the experimental equilibrium data for Cr (VI) removal. Finally, the applied biomass could be used as a cheap biosorbent for the removal of Cr (VI) ions from aqueous solutions with high maximum adsorption capacity (*q_max* = 143.0 mg g⁻¹), compared to other biosorbents reported in the literature.

1. Introduction

Nowadays, the removal of heavy metal ions, including Cr (VI), from aqueous solutions based on the biosorption approach is consistent to green chemistry, simple and comparatively inexpensive. By-products or waste biomaterials are low cost and highly abundant materials which can be used as efficient biosorbents [1, 2]. In the last decades, there has been a tendency to use natural biosorbents, because in such lignocellulosic materials exists a large number of functional groups which have ability to bind metal ions [3, 4]. On the other side, chromium (VI) is commonly used in industrial applications and has been considered among the top sixteen toxic pollutants with harmful effects on human health [5-7].

In Bulgaria, forests occupy about 35% of the country's territory and 65% of which are coniferous plantations. According to statistical data of the Executive Forest Agency, the distribution of the afforested area by main tree species in our country is: white and black pines – 7.7 %, Norway spruce – 4.3 %, and firs – 0.9 %. Coniferous wood is mainly used in the timber industry, as well as for the...
production of pellets and briquettes. From the needles and thin twigs of pines and firs, by distillation and extraction, various aromatic products are obtained with application mainly in medicine, perfumery and cosmetics [8].

The needles of juniper (*Juniperus communis* L.), are also a raw material for industrial processing and the resulting essential oil finds the same application. In our country there are four more species of this genus, two of them - *J. sabina* L. and *J. excelsa* M. Bieb., are protected by law, which is why they are subject to research only. A number of authors have studied the chemical composition and properties of essential oils obtained from different Bulgarian species of the genus *Juniperus* [8].

To the best of our knowledge, only one study on the adsorption of dyes from biomass of the species *J. excelsa* growing in Turkey was found in the literature [9]. There were no reports in the literature about the use of biomass from Greek juniper needles (*Juniperus excelsa* M. Bieb), obtained after distillation of the raw material, for biosorption of chromium (VI) from aqueous solution. Therefore, the main goal of present study was to examine the performance of such biomass for its ability to remove Cr (VI) ions from aqueous solution.

### 2. Materials and methods

The biomass used as biosorbent (comprised of needles and the adjacent thin branches) is obtained after the water distillation of Greek juniper needles (*Juniperus excelsa* M. Bieb.) in laboratory scale [10]. Therefore, the biomass was converted to powder by cutting, drying (40°C), milling (Bosh MKM 6003, Germany) and sieving. Finally, biosorbent (the size classes 500/0 μm and the moisture 11.01%) was stored in plastic bag for further use. The infrared spectrum of biosorbent was recorded using a Nicolet iS 50 Thermo Scientific FT-IR spectrometer in the frequency region of 4000–400 cm⁻¹, with the biomass embedded in KBr matrixes.

All reagents used in the experiments were of analytical grade. Stock solution (500 mg L⁻¹) of Cr (VI) was prepared by dissolving of *K₂Cr₂O₇* in distilled water. This solution was diluted with distilled water to obtain desired concentrations of working solutions for the batch experiments study. The pH value of the samples was adjusted by adding 0.1 M NaOH or HCl solutions [7].

Biosorption experiments were carried out in 250 mL Erlenmeyer glass flasks with 100 mL volume of Cr (VI) solution, as described in our previous studies [7, 11]. Batch experiments were conducted to investigate the effect of pH (1.0, 2.0, 3.0, 4.0, 5.0 and 6.0), initial Cr (VI) concentration (10, 30, 50, 70 and 100 mg L⁻¹), biosorbent dosage (0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 g L⁻¹), agitation speed (150, 200, 250 and 300 rpm) and contact time (5, 10, 15, 20, 25, 30, 60 80 and 100 min). The effects of biosorbent particle size and temperature were not under investigation in present study. The values of investigated factors were selected from a practical point of view and based on the literature preview [7, 11].

Kinetic study was carried out to determine the equilibrium time of Cr (VI) biosorption [11]. The pseudo-first-order and pseudo-second order models in their linearized forms were applied to model experimental kinetics data [11, 12].

Equilibrium sorption experiments were performed and adsorption isotherm was plotted [7, 11]. The Freundlich and the Langmuir isotherms models were used to correlate the equilibrium data for Cr (VI) removal [7, 11, 12].

For determination of Cr (VI) concentration in the solutions before and after biosorption, samples were vacuum filtered (MN640 de filter paper) and the filtrate was analyzed spectrophotometrically at 540 nm by using the standard Diphenilcarbazide method [13].

The equilibrium metal uptake $q_e$ (mg g⁻¹) was determined by employing the mass balance (1) [7]:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where: $C_0$ and $C_e$– the initial and the final metal concentrations (mg L⁻¹);

$m$ – the mass of biosorbent material (g);

$V$– the initial volume of Cr (VI) solution (L).
The performance of biosorption was evaluated in terms of its removal efficiency as \( \text{RE} \) (%), estimated by the following equation (2):

\[
\text{RE} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

(2)

where \( C_t \) is the Cr (VI) concentration at time \( t \) [7].

All experiments were carried out in triplicate at ambient temperature 30.0 ± 1.0°C. The data were analyzed and presented as mean values. Statistical techniques, incl. ANOVA and Duncan’s Multiple Range Test were applied to determine the significant differences at 95 % confidence (\( P < 0.05 \)) level [7, 11].

3. Results and discussion

The used biosorbent were characterized in terms of moisture content (11.01 %), ash (5.91 %), cellulose (22.05 %), chlorophyll (372.8 \( \mu \text{g g}^{-1} \)), and total carotenoids (187.7 \( \mu \text{g g}^{-1} \)) [10].

The FT-IR spectrum of used biosorbent was presented in figure 1 and some of the bands for typical functional groups were summarized in table 1.

![Figure 1. FT-IR spectrum of biomass from Greek juniper needles (J. excelsa).](image-url)
Table 1. Assignments of the characteristic bands in the FTIR spectra of biomass from Greek juniper needles.

| Characteristic bands (cm⁻¹) | Group type |
|-----------------------------|------------|
| Biomass | Reference data |  |
| 3441 | 3550 – 3400 | γ OH intramolecular H – bond |
| 2919 | 2940 – 2915 | γₚ –CH₂– groups |
| 2853 | 2970 – 2950 | linear γₚ CH₃- group |
| 1734 | 1740 – 1720 | γ C = O conjugated aliphatic esters |
| 1623 | 1660 – 1580 | –CH₂–CO– Vibrations of ketones, δ CH₂ |
| 1464 | 1480 – 1440 | –CH₃–CO– Vibrations of ketones, δ CH₃ |
| 1318 | 1368 – 1320 | a structural fragment of the type γ C–H and –CH₃ groups |
| 1260 | 1260 – 1240 | γₚ C–O–C, ether bond |
| 1056 | 1150 – 1050 | γₚ C–O–C, ether bond |
| 1044 | 1070 – 1020 | –C–O–C, γₚ C–O–C, aromatic and vinyl |
| 864 | 893 – 761 | a structural fragment of the type δₚ –HC=CH–, cis- group |
| 819 | 820 – 761 | a structural fragment of the type δₚ (–CH₂)n and (–HC = CH–, cis-) groups |
| 805 | 820 – 761 | a structural fragment of the type δₚ (–CH₂)n and (–HC = CH–, cis-) groups |

The analysis of FT-IR of studied biomass represents mainly strong vibrations of major components and showed that the biosorbent had several functional groups available for binding Cr (VI) ions. Determination of the optimal pH value, agitation speed, biosorbent dose, initial metal concentration and contact time at which the maximum metal removal efficiency could achieve is very important from the practical point of view [14].

The effect of pH on Cr (VI) removal efficiency from the aqueous solution by the studied biosorbent is illustrated in figure 2.

**Figure 2.** Effect of pH on the removal efficiency of Cr (VI) from aqueous solution by biomass from Greek juniper needles (initial metal concentration 50 mg L⁻¹, biosorbent dosage 1 g L⁻¹, 30°C, 60 min, agitation speed 250 rpm).
In our study maximum removal efficiency (99.06 ± 0.18 %) was obtained at pH = 1.0. Wang et al., also reported maximum removal efficiency (97.3 %) of Cr (VI) at pH = 1 by using of walnut hull as biosorbent [15]. Another studies also indicated that at low pH chromium existed as negatively charged HCrO$_4^-$, Cr$_2$O$_7^{2-}$ and CrO$_4^{2-}$ forms, while the positively charged surface of the adsorbent enhances the sorbent-sorbate interaction, thus resulting in high Cr (VI) removal [5-7, 11, 16].

The removal of Cr (VI) as a function of agitation speed was studied by varying the speed from 150 to 300 rpm. The results obtained are presented in figure 3. Increasing of the agitation speed up to 250 rpm results in improvement of the diffusion toward the biomass surface and increases the metal removal efficiency. Than the increasing of speed above 250 rpm lowered the metal removal, not allowing enough time to metal ions to adsorb [17, 18].

![Figure 3. Effect of agitation speed on the removal efficiency of Cr (VI) from aqueous solution by biomass from Greek juniper needles (pH = 1.0, initial metal concentration 50 mg L$^{-1}$, biosorbent dosage 1 g L$^{-1}$, 30°C, 60 min).](image-url)

The effect of biosorbent dose on the removal efficiency of Cr (VI) is illustrated at figure 4.

![Figure 4. Effect of biosorbent dose on the removal efficiency of Cr (VI) from aqueous solution by biomass from Greek juniper needles (pH = 1.0, initial metal concentration 50 mg L$^{-1}$, 30°C, 60 min, agitation speed 250 rpm).](image-url)

The results indicated increasing of the Cr (VI) removal efficiency with the increase in biosorbent dose up to 0.5 g L$^{-1}$ because of availability of more surface area for contact between the adsorbent and the adsorbate, but removal efficiency then decreased due to aggregation of the biomass particles and disturbance of the mass transfer of the metal ions from the liquid to the solid phase. This effect was reported similarly by other studies [5-7, 11, 19].
Results obtained for the influence of the initial Cr (VI) concentration in the solution on metal removal showed that when the initial Cr (VI) concentration increased from 10 to 100 mg L\(^{-1}\) the equilibrium metal uptake increased from 19.85 to 199.06 mg g\(^{-1}\), may be due to the increase in the number of Cr (VI) ions competing for the available binding sites in the surface of used biomass, as similarly reported by another researches [6, 15]. The highest removal efficiency of Cr (VI) ions (99.58 ± 0.31 %) was established at an initial metal concentration of 50 mg L\(^{-1}\), pH = 1.0, biosorbent dose 0.5 g L\(^{-1}\), 30°C and agitation speed 250 rpm.

Contact time between biosorbent and sorbate is another important parameter affected the biosorption process. Results for the effect of contact time on biosorption of Cr (VI) ions were plotted on figure 5.

![Figure 5](image-url)

**Figure 5.** Effect of contact time on the removal efficiency of Cr (VI) from aqueous solution by biomass from Greek juniper needles (pH = 1.0, initial metal concentration 50 mg L\(^{-1}\), biosorbent dose 0.5 g L\(^{-1}\), 30°C, agitation speed 250 rpm).

Based on the kinetics data obtained (figure 5) we established that the biosorption process going on two phases. The rapid initial phase within the first 5 min and a second gradual biosorption until the system reached equilibrium, as similarly was reported in other studies [6, 11, 15]. The determined equilibrium time for Cr (VI) ions biosorption was 30 min with established removal efficiency 99.58 %. The experimental kinetics data were fitted to two kinetic models of pseudo-first and pseudo-second order and the obtained kinetic parameters are listed in table 2.

**Table 2.** Kinetic parameters for the biosorption of Cr (VI) ions onto biomass from Greek juniper needles.

| Experimental equilibrium metal uptake \(q_e^{\text{exp}}\) (mg g\(^{-1}\)) | Pseudo-first order model | Pseudo-second order model |
|---------------------------------|---------------------|------------------------|
| \(q_e^{\text{cal}}\) \(\text{mg g}^{-1}\) | \(K_{1\text{ads}}\) \(\text{min}^{-1}\) | \(R^2\) | \(q_e^{\text{cal}}\) \(\text{mg g}^{-1}\) | \(K_{2\text{ads}}\) \(\text{g mg}^{-1} \text{min}^{-1}\) | \(R^2\) |
| 99.58 | 3.76 | 0.127 | 0.906 | 100.00 | 0.200 | 1.000 |

Kinetic parameters \(q_e^{\text{cal}}\), \(K_{1\text{ads}}\), and \(K_{2\text{ads}}\) are calculated value of equilibrium metal uptake and rate constants, respectively.
The pseudo-second order model was found to provide the best fit to experimental kinetics data ($R^2 = 1.000$) and the calculated value of equilibrium metal uptake ($q_{eq}^{cal}$) agree quite well with the experimental value ($q_{eq}^{exp}$). Most of the studies also reported that biosorption of Cr (VI) ions by different biosorbents followed the pseudo-second order kinetics, indicated of chemisorption mechanism [6, 11, 20, 21, 22].

Equilibrium isotherms study is of fundamental importance in the design of adsorption systems. An adequate mathematical modeling of the experimentally obtained isotherm is essential for the efficient design of the system [7, 11, 12, 20]. Adsorption isotherm was plotted as the equilibrium metal uptake ($q_e$) versus the equilibrium metal concentration remaining in the solution ($C_e$). The Freundlich and the Langmuir isotherm models and their linearized forms (figures 6 and 7) were used to fit the experimental data for Cr (VI) removal, as described in our previous studies [7, 11]. The isotherm model’s parameters were determined and the values are summarized in table 3.

Figure 6. Linearized Freundlich isotherm for biosorption of Cr (VI) from aqueous solution by biomass from Greek juniper needles (pH = 1.0, biosorbent dose 0.5 g L$^{-1}$, 30°C, 60 min, agitation speed 250 rpm).

Results indicated that the Freundlich ($R^2 = 0.975$) and the Langmuir ($R^2 = 0.976$) isotherm models correlated very well to the experimental equilibrium data for Cr (VI) removal. Similar results were reported by other studies [7, 11, 22, 23].

Calculated values of Langmuir separation factor ($R_L$) was found to be between 0 and 1 indicating favorable adsorption of Cr (VI) ions under experimental conditions of present study [7, 11, 24]. Compared to different biosorbents used for Cr (VI) removal from aqueous solutions reported in the literature, the calculated maximum adsorption capacity by Langmuir isotherm model for the biomass from Greek juniper needles (Juniperus excelsa M. Bieb) was high ($q_{max} = 143.0$ mg g$^{-1}$). For example, the reported values of maximum adsorption capacity of osage orange peel, modified groundnut hull, walnut hull and activated coconut shell are 93.67, 131.00, 98.13 and 5.32 mg g$^{-1}$, respectively [5, 6, 15, 23].
Figure 7. Linearized Langmuir isotherm for biosorption of Cr (VI) from aqueous solution by biomass from Greek juniper needles (pH = 1.0, biosorbent dose 0.5 g L\(^{-1}\), 30°C, 60 min, agitation speed 250 rpm).

Table 3. Isotherm parameters for the biosorption of Cr (VI) ions onto biomass from Greek juniper needles.

| Freundlich isotherm model | Langmuir isotherm model |
|---------------------------|-------------------------|
| 1/n                       | K\(_F\) (mg g\(^{-1}\)) | R\(^2\)          |
|                           | q\(_{\text{max}}\) (mg g\(^{-1}\)) | K\(_L\) (L mg\(^{-1}\)) | R\(^2\) |
| 1.26                      | 593.8                   | 0.975            | 143.0   | 1.71 | 0.976 |

Freundlich parameters K\(_F\) and n are related to adsorption capacity and adsorption intensity of the biosorbent, respectively. Langmuir parameters q\(_{\text{max}}\) and K\(_L\) representing the maximum monolayer adsorption capacity and the energy constant related to the heat of adsorption, respectively.

4. Conclusion
The results from present study indicated that the biomass from Greek juniper needles (Juniperus excelsa M. Bieb), obtained after water distillation of the raw material could be applied as a cheap biosorbent for the removal of Cr (VI) ions from aqueous solutions with high maximum adsorption capacity (q\(_{\text{max}} = 143.0\) mg g\(^{-1}\)), compared to other biosorbents reported in the literature. Maximum removal efficiency (99.58 ± 0.31 %) was obtained at pH = 1.0, adsorbent dose 0.5 g L\(^{-1}\), agitation speed 250 rpm, initial Cr (VI) concentration 50 mg L\(^{-1}\), temperature 30.0 ± 1.0°C and contact time of 30 min. Adsorption kinetics followed pseudo-second order model and the Langmuir and Freundlich models were found to represent very well equilibrium adsorption isotherm data.

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