



Research article

Callitriche cophocarpa biomass as a potential low-cost biosorbent for trivalent chromium



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ABSTRACT

The present study focused on the use of the dry mass of the macrophyte *Callitriche cophocarpa* as an effective biosorbent for chromium removal from concentrated solutions, typical for industrial effluents. In order to evaluate the usability of *C. cophocarpa* as the Cr(III) sorbent, its detailed physicochemical characterization has been performed as well as the preliminary adsorption studies. The biosorbent was characterized by specific surface area (SSA), porosity, total organic carbon (TOC), inorganic content as well as the cation exchange capacity (CEC), dominant exchangeable cations and anion exchange capacity (AEC), point of zero charge (pH_{pzc}) and buffering capacity. The effect of the initial chromium concentration, solution pH and co-existing anions on the sorption effectiveness have been investigated. Based on theoretical isotherm models, the maximum adsorption capacity of the dry *C. cophocarpa* has been determined as 77.1 mg Cr(III)/g. Finally, the strength of Cr-binding onto the plant biomass has been evaluated using the BCR extraction method, stating that chromium was strongly and – under environmental conditions – irreversibly bound to the plant biomass.

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1. Introduction

Inorganic pollutants, especially heavy metals, pose a serious problem to the environment because of their toxicity and non-biodegradable nature. One of the major trace heavy metal pollutants in the aquatic environment is chromium, typically originated from industrial pollution sources. The effluents from electroplating and corrosion protection industries, steel works, tanneries, pigments or glass manufacturers, frequently contain chromium in a trivalent oxidation state. Cr(III) is a nutrient and an essential microelement at trace levels, however at large doses it exhibits toxic and carcinogenic properties for living organisms. In aquatic systems, the concentration of chromium is often significantly over-

limited (Kyzioł-Komosińska and Kukułka, 2008), being dangerous to aquatic life and humans. Therefore, chromium is regarded (i.e. by the Environmental Protection Agency, USA) as a priority-toxic pollutant, and the current European drinking water standard for chromium is 50 µg/L (Council Directive 98/83/EC, 1989). Moreover, the water quality standards for sewage introduced into the water or to the soil in Poland state that the concentrations of the total Cr depend on the kind of industry. The upper limit for Cr is 1 mg/L for sewage from tanning industry and 0.5 mg/L in the case of sewage from all other industries (Journal of Laws of the Republic of Poland, 2014). Thus, due to the low concentration limits for chromium in water, it is necessary to eliminate it thoroughly from contaminated effluents.

Conventional methods applied for chromium removal from aqueous solutions include: adsorption, coagulation, oxidation, precipitation, ozonisation, ultrafiltration and reversed osmosis (Babel and Kurniawan, 2004). However, due to their high costs, difficulty with removing of trace levels of chromium, or producing of chemical sewage sludge, many efforts have been recently made

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to develop “greener” and cheaper technologies. Among them, one of the most promising is biosorption. It is well known, that adsorption is one of the most suitable technique for treatment of diluted solutions, and the use of biosorbent, instead of synthetic one, significantly reduces its costs. Biosorption is a highly valuable method for heavy metals removal, considering its high effectiveness at relatively low costs (Fomina and Gadd, 2014; Jain et al., 2016). Some organic materials, such as agricultural by-products or peats have been tested for decontamination of Cr-containing effluents (Cardoso et al., 2017; Chen et al., 2017; Kostić et al., 2017; Kyzioł-Komosińska et al., 2014; Sarma et al., 2015). Yet, the spent sorbents have to be regarded as hazardous materials because of a relatively high content of the adsorbed heavy metals. Therefore, besides the sorption capacity, information about binding and mobility of heavy metals for tested materials are necessary. Many analytical procedures have been developed for the determination of mobile heavy metal fractions in various materials, soil, and sediments. Sequential extraction proposed by Tessier (1979), which has been later modified by several authors, is the most useful of them. Nowadays, a four-step extraction called the BCR method, as proposal of European Community Bureau of Reference, is also very popular (Mossop and Davidson, 2003; Ure et al., 1993).

This paper focused on the biosorption of Cr(III) species from aqueous solutions onto *Callitriche cophocarpa* dry biomass. *C. cophocarpa* (water starwort) is an aquatic, submersed, higher plant (macrophyte). It is the most common representative of *Callitriche* genus, widely distributed across temperate climate all over the world. The outstanding capability of this macrophyte to phytoremediate Cr was discovered by the group of Augustynowicz (2010). Studies also revealed that live plants treated by Cr(III) were able to accumulate up to 2.8% (28 mg/g) of dry weight of the element in semi-natural conditions (Augustynowicz et al., 2013b). The research on the use of *Callitriche* for chromium remediation carried out to date was done on live plants only. The main scope of the present research was to examine the potential of the dry *C. cophocarpa* as the Cr(III) biosorbent for its further biotechnological utilization. Since the studied plant species is widely distributed across the world and is a perennial one and shows relatively large biomass increments, introduction of the results into widely-applied use seems to be very beneficial.

2. Materials and methods

2.1. Materials

Callitriche cophocarpa was collected from the unpolluted natural stands located in the Dłubnia River in Southern Poland (N 50°15'58"/E 19°56'24.9"). The plants were harvested and immediately transferred to the laboratory, then rinsed exhaustively to remove sand, soluble impurities, and clays, and finally flushed several times with deionised water. Clean plants were air-dried, ground to particles of size fraction <200 μm, and stored for further use. All chemicals were of analytical grade. The stock solutions (1000 mg Cr/L) were prepared from CrCl₃·6H₂O and KCr(SO₄)₂·12H₂O.

2.2. Characterization of the sorbent

The external specific surface area of the studied sorbent was identified by nitrogen sorption/desorption measurements at 77 K using Sorptomatic ASAP instrument (Micromeritics) and calculated by the BET method. An Autopore IV 9500 (Micromeritics, INC, USA) mercury porosimeter was used for determination of the pore size distribution. Total organic content was measured using TOC-5000 A (Shimadzu) and inorganic content was measured by calcinating at

550 °C at constant weight (approximately 8 h).

The Cation Exchange Capacity (CEC) of the sorbent and exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) were determined in 1M NH₄OAc at pH = 7 using ICP-AES with a Perkin Elmer spectrophotometer (Optima, 2000 DV) (Tamayo et al., 2012). The Anion Exchange Capacity (AEC) was determined by extraction method using ammonium chloride solution as the index anion and nitrate ion from potassium nitrate solution as the replacing anion (Wada and Okamura, 1977). The concentration of Cl⁻ was estimated using ion chromatography (ICS-1100, Dionex, California, USA). Moreover, compounds soluble in water using leaching test under batch mode contact at ratio sample: water 1:100 during 24 h were set out. All pH values for the biomass suspension in water (1:10) were measured with a pH-meter equipped with a combined glass electrode. The point of zero charge (pH_{PZC}) was determined using method described by Calvete (2009) and Cardoso (2011). The buffering capacity results essentially from the dissociation of acidic functional groups (Ceppi et al., 1999), and may be expressed quantitatively as the number of moles of strong acid or strong base required to change the pH by the unit. The buffering capacity was measured by titration and calculated from the difference of surface area in coordinates (pH, V) between the linear relationship between pH versus the amount of 0.1M acid added to studied sorbent and quartz sand, which serves as a blank test. All values were calculated from triplicates.

2.3. Adsorption studies

The sorption capacity of the *Callitriche* dry mass was determined under batch contact mode, at the sorbent dose of 10 g/L, at 23 ± 2 °C and the shaking time 24 h. Experiments were carried out by shaking 0.5 g of the sorbent with 50 mL of chromium solutions with various initial concentrations (0.005–0.8 g/L) in polyethylene bottles. Such high concentrations of chromium provided a necessary excess of the sorbate with respect to the biosorbent sample, ensuring an almost complete saturation of the active sites of the sorbent. Chloride and sulfate concentrations were in the range of 0.01–1.6 g and 0.02–2.9 g/L, respectively. A horizontal shaker was applied with an intensity of agitation set at 0.03 m/s². Afterwards, the solution was separated from the solid phase during a 20-min centrifugation process (12 850 g). Simultaneously, the pH values and concentration of main exchangeable cations (Ca²⁺, K⁺, Mg²⁺ and Na⁺) in equilibrium solution were measured. Sorption experiments were performed at two moderate initial acidities (pH: 5.0 and 3.0), adjusted by the addition of 0.1M KOH or 0.1M H₂SO₄ solutions. The pH value was kept below 5, due to Cr(OH)₃ precipitation at higher pH levels. In each series of measurements, two kinds of quality control experiments were carried out: (1) a blank experiment with the sorbent and working solutions, but without the addition of chromium, and (2) experiments with various concentrations of chromium in working solutions, but without the sorbent. Chromium concentrations in aqueous solutions were determined by the flame atomic absorption spectrometry method (FAAS) (GBC spectrometer, Avanta model).

2.4. Desorption studies

In order to determine the strength of the chromium-sorbent binding and the leachability of adsorbed chromium species, desorption experiments and sequential chemical extraction method (BCR) were used. A desorption experiment with double distilled water was performed according to the standard leaching test for granular wastes and sediments (EN 124571-4, 2002). The dry mass of the spent sorbent loaded with Cr(III) species adsorbed at the maximal initial concentration in solution was shaken with

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