

New low cost sorbents for Cr(VI) – batch and column experiments

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Abstract. The use of agricultural byproducts and industrial biowaste materials has been shown to be an attractive technique for removing Cr(VI) from contaminated waste waters. In this study, used brewers draff, peat moss, sawdust, grape stalks and husks were investigated as novel biosorbents for Cr(VI). The material was tested in two different modifications. The material was dried, cut and sieved and part of it was subjected to acid (2 M H₂SO₄) and alkali (0.5 M NaOH) pre-treatments to remove starch, proteins and sugars. Fourier transform infrared rays analysis on solid phase (FTIR-ATR) was used to determine the main functional groups that might control the metal uptake. Batch experiments were performed at different pH values (3, 4.5, 6) and at various initial concentration of Cr(VI) (25–250 mg L⁻¹). Two equilibrium empirical models, Langmuir and Freundlich, were used to describe Cr(VI) adsorption. In order to identify possible reduction processes, ion exchange separation on the AG1-X8 resin was used to separate the anionic Cr(VI) and the reduced cationic Cr(III) from the aqueous phase after biosorption. As expected, Cr(VI) removal was pH-dependent and fitted well both the Langmuir and Freundlich isotherm models. The ion exchange separation showed that Cr(VI) reduction had occurred in the solution during biosorption. The efficiency of draff as a biosorbent was comparable (or even higher) to highly organic materials (e.g., composted peat) showing its potential application for Cr(VI) decontamination.

Key words: chromium, biosorption process, organic substrates, batch and packed bed column experiments

Introduction

Chromium can be found mainly in two forms in the environment, hexavalent and trivalent. Cr(VI) is highly soluble and mobile and it is a potential carcinogen (Kortenkamp et al., 1996). It is not typically naturally occurring in the environment but can be found in high concentrations in some regions of the Czech Republic (ultramafic rocks). Chromium as well as other metal elements is used widely in metallurgical and chemical industry. The majority of Cr is processed in stainless steel manufacturing followed by electroplating, leather and wood preservation, pigments production. Industrial wastewaters are the main pollution sources of Cr in natural waters and soils. Besides conventional processes used to remove Cr(VI) (precipitation as chromium hydroxide, ion exchange removal or adsorption). Recently, alternative sorbents have been investigated by many authors in order to find effective low cost technology for the treatment of metal-contaminated water (Fiol et al., 2008; Levankumar et al., 2009; Park et al., 2008).

This study is based on investigation of adsorption properties of five potential low-cost biosorbents for Cr(VI). The adsorption process under different conditions (various concentrations of Cr(VI) and various pH) will be studied using batch and column experiments. Also the ability of the sorbents to reduce Cr(VI) to Cr(III) will be investigated.

Materials and Methods

Biosorbents used in this study (brewers draff, peat moss, grape stalks and husks and digestate from biogas plant) were dried in an oven at 80°C for 24 hours and cut. Half of the material was subjected to pretreatment - an acid hydrolysis by 2 M H₂SO₄ (at 100°C for 1 hour) and an alkali treatment by 0.5 M NaOH (stirring for 24 hours at the room temperature). After each treatment the material was washed with deionized water several times until the pH reached 7 ± 0.5. Both types of the material were used for the batch and the column experiments.

Fourier transform infrared rays analysis (FTIR) was used to determine the main functional groups. The

specific surface area was measured using nitrogen as gas absorbent and the BET model.

Batch experiments were performed at plastic tubes by shaking a mass of 0.4 g of each material with 40 mL of chromium solution at different pH values (3, 4.5, 6) and different initial concentration of Cr(VI) (25-250 mg.L⁻¹).

Column experiments were carried out in plastic column (BioRad, USA). Initial Cr(VI) concentration was between 25 and 300mg.L⁻¹ and the initial pH values were 3, 4.5 and 6. Effect of different flow rates (5, 10 and 15 mL.min⁻¹) was investigated. Cr concentration was determined by ICP-OES.

Cr(VI) and Cr(III) exist in anionic and cationic forms, respectively. That is why the separation of both forms can be realized by exchange resin. Separation of Cr(VI) and Cr(III) by resin AG1-X8 (Bio-Rad) was performed in this study. Ion exchange columns were filled with 10 mL of the resin and initialized by 10 ml of 6 M HCl and 40 mL deionized water subsequently. The water sample was passed through the column. Cr(VI) was absorbed onto the resin and after that converted to Cr(III) with H₂O₂ and eluted by 6 M HCl (Ellis et al., 2002). The concentration of both Cr(III) and Cr(VI) in the filtrates was analyzed by ICP-OES (Agilent Technologies, USA).

Results and Discussion

Langmuir and Freundlich isotherms were used to describe the sorption process and both fitted well the batch experimental data. As seen in Fig. 1, all the studied materials are able to adsorb Cr to some extent. Comparing non-pretreated materials, the most efficient one was grape husks (the maximal sorption capacity

evaluated from the Langmuir isotherm is 350 mg.g⁻¹), followed by grape stalks (331 mg.g⁻¹), peat moss (237mg.g⁻¹), brewers draff (139 mg.g⁻¹) and sawdust (63 mg.g⁻¹). FTIR-ATR analyses showed that the composition of the materials has changed by the acid and alkali pretreatment. Maximal sorption capacities of all the materials were enhanced: grape husks (378 mg.g⁻¹), grape stalks (336 mg.g⁻¹), peat moss (298 mg.g⁻¹), brewers draff (261 mg.g⁻¹) and sawdust (99 mg.g⁻¹). By this treatment, starch, proteins and sugars are removed from the structure of biomaterial accessing thus the functional groups, such as carboxyl and hydroxyl, and increasing the specific surface area (Dupont and Guillon, 2003).

Chromium sorption proved to be pH-dependent. The sorption efficiency was the highest for all the materials at initial solution pH 3. At low pH values the sorption sites bound largely H⁺ and these can be easily exchanged by toxic metal ions.

It was generally observed that increasing the initial Cr(VI) concentration led to adsorption decreases. In the range 0 – 100 mg.L⁻¹ the adsorption percentage was between 25 and 90% for most of the materials (except sawdust); in solution with concentrations between 100 – 200 mg.l⁻¹, from 15 to 50 % of the Cr has been removed and in the range 200 – 300 mg.L⁻¹ only 0 to 30 % of Cr was removed.

After the sorption process, Cr(III) was detected in the solution. This proves the presence of reduction reactions during the sorption process. Cr(VI) is partly reduced to Cr(III) by the sorbents. To ascertain the sorption mechanism and the oxidation state of Cr on the biomaterial surface more experiments are necessary. To characterize the oxidation state of Cr bound X-ray adsorption spectrometry might be used as a next step (Park et al., 2008).

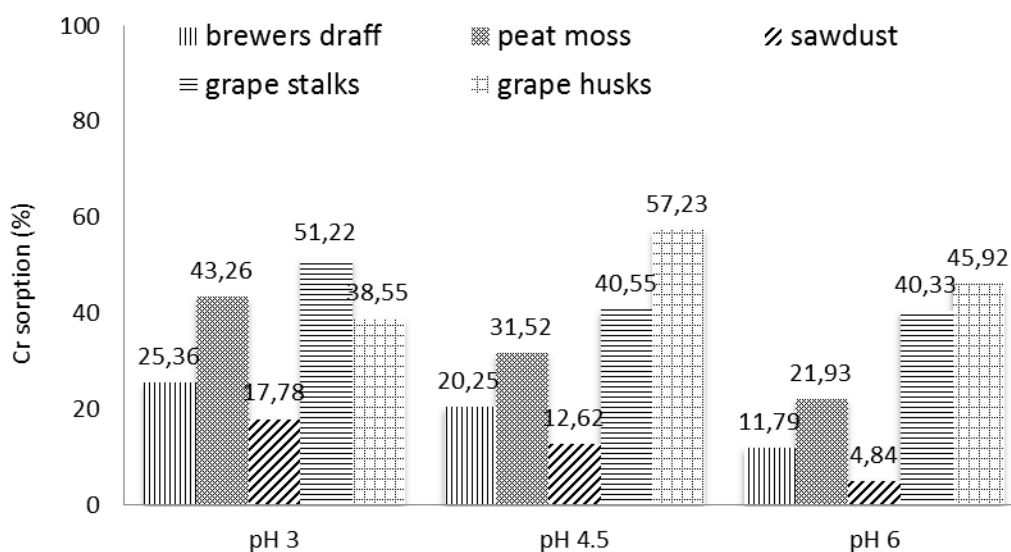


Fig. 1. Biosorption efficiency of non-pretreated brewers draff, peat moss, sawdust, grape stalks and husks on chromium solution at different pH.

Conclusion

All of the used materials, except sawdust, show good efficiency in removal of chromium from aqueous solution. The efficiency of the newly tested material, brewers draff, was comparable (or even higher) to highly organic materials (e.g., composted peat) showing its potential application for Cr(VI) decontamination. Chromium sorption is pH-dependent and the maximum sorption capacity is found at initial pH 3. Part of Cr(VI) is reduced to Cr(III) during the sorption process (5 - 15 % of the chromium at equilibrium concentration conditions). More experiments are necessary to ascertain the oxidation state of the chromium bound on the biomaterial.

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