



## Short communication

## The application of electroanalytical methods to determine affinity series of metal cations for functional biosorbent groups

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## ABSTRACT

The affinity of the selected heavy metal cations:  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  was determined for the functional groups located on the surface of leached barley middlings, so called Brewer's spent grain (BSG) – a by-product of the brewing industry. A simple method for determining the affinity series, with the use of a conductivity meter and a pH-meter, was described. It was demonstrated that the affinity of cations for the functional groups located on the surface of the BSG increases in the series:  $Na^+ < K^+ < Mg^{2+} < Mn^{2+} \approx Zn^{2+} < Ni^{2+} \approx Ca^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$ , and the series was determined by comparing concentrations expressed in gram equivalents, i.e. molar concentrations converted into the individual cation charge. The objective is to assess the possibility to use BSG as a biosorbent in the processes of treatment and post-treatment of waste waters from heavy metals.

## 1. Introduction

It has been known for many years that heavy metals, mainly discharged to surface waters in industrial waste water as well as waters drained from fields and industrial areas, are a major threat to aqueous ecosystems. The main sources of the pollution are metallurgy, power industry, galvanising and tanning industries, artificial fertilisers and pesticide paint, textiles production, electrochemical and automotive plants [1]. Most heavy metals are highly toxic and cause serious diseases when accumulated in the tissue of living organisms. A number of methods for removing heavy metals from waste water have been developed, including chemical precipitation, membrane filtration, flotation, coagulation and flocculation. The main disadvantages of these methods are high costs, low selectivity and, in some cases, the generation of secondary pollutants. The technical and economic limitations of these methods are particularly visible when heavy metal concentration in the treated waters is low ( $< 100 \text{ mg L}^{-1}$ ) [2].

Much attention has been focused in recent years on the sorption processes of pollutants from waste waters using various materials: synthetic, mineral and organic. Cheap and effective natural or by-product sorbents are highly sought after [3,4]. Research has been carried out regarding the possibility of using in sorption processes, of heavy metals in particular, lignocellulosic materials, for example: rice husk [5], agave fibers [6], straw [7–9], soybean meal [10], peat [11], sawdust [12], tree bark [13] and coffee husks [14]. These materials have numerous functional groups on their surface, including carboxylic

(–COOH), amine (–NH<sub>2</sub>) and hydroxylic (–OH) groups, which bind cations present in the solution during the ion exchange process [15–17]. Lignocellulosic materials have a certain advantage, which is their receptivity to various chemical modifications increasing the porosity of their surfaces, which in general increase their sorption capacity [18,19].

Brewer's spent grain (BSG), which is the subject of the presented research, is a by-product obtained during the beer brewing process. It contains the husks and non-leached remains of barley grains. The material is rich in arabinoxylan (22–28%), cellulose (17–25%), lignin (12–28%) and protein (15–24%) [20]. BSG is used as an addition to animal feed and food products [21], as a raw material for biogas, bioethanol and paper production, as a substrate for microorganism cultivation and the production of enzymes and organic acids [22], and as the matrix for the immobilization of microbes and enzymes [23,24]. BSG can also be used as a sorbent in the processes of removing dyes and heavy metals from waste water [23,25,26].

The assessment of the possibility to use a given material in the metal cation sorption process is usually based on a number of basic studies, in order to determine the process kinetics and equilibrium parameters [27]. An important element of such analyses is the definition of an affinity series of metal cations for the sorbent functional groups, which largely depends on the electric charge value, ionic radius and hydration level [15]. This is very significant if a selective sorption of cations from multicomponent solutions is required. The affinity series is determined mainly on the basis of equilibrium parameters, defined using the

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Langmuir isotherm model [16,28–30], which requires numerous measurements of metal concentrations in a solution or sorbent, prior to and after the sorption process.

This article proposes a method of determining the affinity series of metal cations for the functional groups located on the surface of BSG, using simple measurements of the conductivity and pH of metal solutions, prior to and after the sorption process. A hypothesis was presented that the number of sorbed metal cations in the prepared BSG is proportional to the number of hydrogen cations desorbed from BSG. The proposed method may be an alternative to currently applied methods of determining the affinity series of cations for functional groups of various biosorbents.

## 2. Materials and methods

### 2.1. Material preparation

Brewer's spent grain (BSG) – leached barley ground grain, which is a main by-product of the brewing industry, with a granulation of between 1.25 and 1.50 mm – was used in the study. The analysed BSG (40 g) was rinsed with demineralised water with a conductivity of  $\kappa = 0.5 \mu\text{S cm}^{-1}$ ; next, in order to saturate the functional groups with hydrogen cations, the material was conditioned for 60 min in a HCl solution with a concentration of  $0.03 \text{ mol L}^{-1}$ . After conditioning, the BSG was rinsed a few times with demineralised water until a stable pH was achieved of the water in which the BSG was immersed; next, the material was dried for approximately 24 h at a temperature of 323 K, until constant weight is achieved.

### 2.2. Equipment and reagents

The atomic absorption spectrometer (AAS) iCE 3500, made by Thermo Electron Corporation, USA, was used to determine the heavy metal concentrations in the solution, prior to and after the sorption process. The measurements were repeated 10 times, in order to assess the uncertainty of the measurement of the heavy metal concentrations in the solutions. The standard deviation from the mean value did not exceed 5% and, in the case of the solutions diluted below the upper limit of the determination characteristic for iCE 3500, the standard deviation was not higher than 7%. Detailed data for the equipment, together with an evaluation and quality assurance, were published in [31]. The conductivity of the solutions was determined with a CC-551 conductivity meter, made by Elmetron from Zabrze (PL), which has an absolute measurement error of  $\Delta\kappa = 0.1 \mu\text{S cm}^{-1}$ , while the pH of the solutions was measured using a CP551 pH-meter, made by Elmetron Sp.j. from Zabrze (PL), with an absolute measurement error of  $\Delta\text{pH} = 0.02$ . Reagents made by MERCK were used in the preparation of the solutions.

### 2.3. The research method

The analyses were carried out with the use of  $0.5 \pm 0.02 \text{ g}$  samples of the prepared and homogenised BSG, which were immersed in vigorously stirred metal solutions ( $V = 200 \text{ mL}$ , each metal separately). During stage one, the water used to prepare the solutions was acidified to pH 4.0–4.1, in order to avoid the creation of metal hydroxides, mainly Cu and Pb. Acids were applied with the same anion as the salts of the metals used in the experiments:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  ( $\text{Cl}^-$ ),  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ( $\text{SO}_4^{2-}$ ),  $\text{Pb}^{2+}$  ( $\text{NO}_3^-$ ). The conductivity and pH in the metal solutions were determined prior to and after the sorption process, which lasted 60 min. Additionally, for comparison, concentrations of the following were determined prior to and after the sorption process:  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ .

### 2.4. Results interpretation method

The ion exchange process, taking place according to the formula:  $\text{M}^{z+} + \text{H}_z\text{R} \rightleftharpoons z\text{H}^+ + \text{MR}$ , where:  $\text{M}^{z+}$  – the sorbed metal cation with valence  $z$ , R – functional group on the surface of BSG, can be described taking into consideration the changes of three related parameters: the metal concentration in the solution  $c_{\text{M(s)}}$ , the solution conductivity  $\kappa$  and pH, and the hydrogen ion concentrations in the solution  $c_{\text{H(s)}}$ . The changes occurring during the exchange of ions, with the participation of cations of different valence, can be interpreted more easily by expressing their concentrations in gram equivalents:  $c^*$  ( $\text{mmol L}^{-1}$  or  $\text{mmol g}^{-1}$ ) =  $z \cdot c$ , where:  $z$  – cation valence (–),  $c$  – concentration ( $\text{mmol L}^{-1}$  or  $\text{mmol g}^{-1}$ ). Then the reaction model can be simplified to the form:  $\text{M}^+ + \text{HR} \rightleftharpoons \text{H}^+ + \text{MR}$ .

Such a reaction process may be registered by the solution pH and conductivity measurements during the sorption process. In real conditions, during the process of ions exchange, apart from the desorbed hydrogen cations, also other cations are desorbed, naturally connected with BSG active centres. Therefore, the observed changes result from achieving mutual equilibria:  $\text{M}^+ + \text{CtR} \rightleftharpoons \text{Ct}^+ + \text{MR}$  and  $\text{M}^+ + \text{HR} \rightleftharpoons \text{H}^+ + \text{MR}$ , where  $\text{M}^+$  – sorbed cation,  $\text{H}^+$  – desorbed proton,  $\text{Ct}^+$  – desorbed cation naturally connected with active centres R, e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ . Interactions between these cations are also possible [32].

For the diluted solutions ( $c^* < 2 \text{ mmol L}^{-1}$ ), conductivity changes depending on the cation concentrations are linear. Moreover, as a consequence of the mobility of the cations, the empirically determined direction coefficient of the straight line for cations:

$$\kappa (\mu\text{S cm}^{-1}) = a \cdot c_{\text{M(s)}}^* + \kappa_0 \quad (1)$$

(where:  $\kappa_0$  – initial solution conductivity at  $c_{\text{M(s)}} = 0$ ) has a similar value:  $a = 115 (\mu\text{S cm}^{-1}) \cdot (\text{mmol L}^{-1})$ , which is different in relation to the more mobile hydrogen cations:  $a' = 400 (\mu\text{S cm}^{-1}) \cdot (\text{mmol L}^{-1})$ . The following relation describes conductivity of the solution containing metal and hydrogen cations:  $\kappa (\mu\text{S cm}^{-1}) = a \cdot c_{\text{M(s)}}^* + a' \cdot c_{\text{H(s)}}^* + \kappa_0$ .

Assuming the additivity of conductivity, it can be stated that the exchange process, occurring according to the simplified formula:  $\text{M}^+ + \text{HR} \rightleftharpoons \text{H}^+ + \text{MR}$ , can be described by a straight line illustrating the increase of conductivity, as a consequence of the release of more mobile hydrogen cations into the solution and equilibrium sorption of less active metal cations:

$$\Delta\kappa (\mu\text{S cm}^{-1}) = b \cdot \Delta c_{\text{H(s)}}^* \quad (2)$$

with the direction coefficient, in reference to different metals and bearing in mind measurement uncertainty, remaining within the range:  $b \in (260; 290)$ . The discussed correlations were described in [32,33].

The presented correlations indicate that the initial concentrations in the solution from which sorption will be carried out can be determined on the basis of conductivity measurement, and that the number of hydrogen cations desorbed from the surface of BSG is proportional to the number of the metal cations sorbed as a consequence of the ion exchange on the surface of the BSG. As a result, conductivity measurements enable the preparation of solutions of metals with a comparable initial gram equivalent  $c^*$  concentration, whereas sorption efficiency can be estimated on the basis of pH measurements. Therefore, it can be stated that the affinity series of metals for functional groups previously saturated with hydrogen cations can be determined by measuring the conductivity and pH values of the solution from which sorption is carried out. The initial and final statuses of the process were marked in the lower index by 0 and 1.

## 3. Results and discussion

In order to verify the correlation between pH and metal concentration changes in the solution during the sorption process, three

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