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Research paper

# Cross-flow leaching of alkali and alkaline-earth metals from sawdust and wheat straw – Modelling of the process

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Cross-flow washing of wheat straw and beech sawdust with water was carried out in order to leach the alkali and alkaline earth metals from them. Incremental concentration change ($C = \Delta m/\Delta V$) of alkali and alkaline-earth metals in the leachate was plotted against the wash water volume. Maximum increase in $\Delta m/\Delta V$ was achieved after passing 0.04 to 0.06 $dm^3$ of water through the washed biomass. After passing 0.2 $dm^3$ of water through the biomass, leaching of alkali metals was practically completed. Concentration of potassium ion was predominant in the leachate. From the whole amount of alkali and alkaline-earth metal ions, found in the aqueous phase after washing, $K^+$ ions make about 80% in case of wheat straw and 64% in case of beech sawdust. Concentration of other considered metal ions was much less comparing to the potassium ones.

Change in the pH and electrical conductivity (EC) were measured after passing of each portion of wash water through the biomass. Change of the EC against the wash water volume follows fairly the change of leachate composition. Based on the experimental results, the process of alkali and alkaline-earth metals leaching was modelled assuming the cross-flow scheme of leaching process. Proposed model follows fairly the experimental data. Discrepancy between the experimental and calculated values for alkaline-earth metals in case of beech sawdust is attributed to a different leaching mechanism.

## 1. Introduction

Many papers have been published in the past two-three decades on the usage of various natural waste materials, or by-products from agricultural, as well as from timber and wood industry. Two ecologically important aspects stand particularly out of investigating such materials:

- To be utilized as adsorbents – so-called *biosorbents* for adsorption of heavy metal ions from the industrial and mine water streams [1–10,13,16].
- To be used as a renewable fuel for the "*green*" *energy production* [11,12,14,15,17–19,22–24].

In these investigations the sawdust, leaves and barks of various trees [1–3,7,9,13,20], as well as straw and husks of different cereals, were investigated to be used as adsorbents for metal ions [4,8,16]. Besides them, the stalks, fruit stones, peels, shells and grains were investigated for the same purpose [5,8,10]. The aim was usually to obtain the information on the ability of a particular biosorbent to adsorb targeted heavy metal ions, as well as on the importance of some parameters affecting the adsorption. Data about the adsorption capacity and selectivity towards targeted metal ions, as well as the adsorption kinetics, mechanism and equilibrium, were presented in the cited papers. An overall, for now only declarative, intention of these studies, was to replace the conventional adsorbents with cheaper and easily available ones that can be found everywhere around us. That would be an important step towards establishing a new process for heavy metal ions removal from different wastewater, which could be equally efficient, economically beneficial and ecologically sustainable for wastewater treatment as the existing adsorption processes are.

On the other side, particularly straw of different cereals, but also some by-products from wood and timber industry, have been already in use as a renewable fuel for the "green" energy production [11,12,14,15,17–19,22–24]. This aspect gives a new dimension to straw being an important energy source particularly in the

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countries having developed agriculture [11,12,17,18,22–24]. Even for this purpose, burning of raw straw will cause the undesirable technological and maintenance problems on the boilers and heat exchangers due to formation a layer of slag, consisting mainly from alkali and alkaline-earth, oxides as well as salts - mainly chlorides and sulphates [12,22]. These deposits on the outer surface of tubes bundles in the combustion chamber slow down the heat transfer rate changing by them the dynamics of gases in the boiler and heat exchangers. Due to this reason, the washing of biomass to be used as a fuel, was investigated in order to wash out troublesome constituents responsible for production of fusible ash [12,15,17,23]. Washing of biomass with water, to be used as adsorbents, leads to an increase in the adsorption capacity for almost twice - though not so spectacular but anyway increasing [1–4,16,20]. Washing of biomass, irrespective of their further use (either as a fuel or as an adsorbent), has a beneficial contribution mainly due to the leaching of alkali and alkaline-earth metals.

The aim of this work was to study the multi-step cross-flow washing of wheat straw and beech sawdust with water in order to reduce the alkali and alkaline earth metal content, as a pretreatment step to be used either as adsorbents or as a fuel. A particular attention will be paid to the concentration of each element in the leachate at every step of washing, in order to estimate the mass of metal removed from biomass with each portion of wash water, i.e. $\Delta m/\Delta V$. Determination the extent to which alkali and alkaline-earth metals could be leached from considered biomass at gradual washing will be one of the tasks in this study. Measuring the change of pH and especially EC of the leachate could interconnect their change with the alkali and alkaline-earth metal leaching, what could be utilized as an indicator on the progress and completion of the process. A particular aim will be also paid in developing a mathematical model of the cross-flow biomass washing and to verify it using the obtained experimental data. Establishing the model would provide a possibility to predict conditions of the cross-flow biomass washing at an enlarged scale.

## 2. Experimental part

### 2.1. Materials

Fresh wheat straw was collected behind a combine harvester from the local fields of the Bor region, Eastern Serbia, just after grain harvesting and before any rainfall. Sampled straw was then naturally dried on air to avoid mould development and stored for further characterization and to be used later for the adsorption experiments. Wheat straw was sampled, and then cut, grinded and sieved.

Beech sawdust was obtained from a local sawmill by sawing the beech timbers originated from Ozren mountain – Sokobanja, Eastern Serbia. Sampled sawdust was processed in the same way as well as straw, i.e. drayed on air, packed and stored for further characterisation to be then used in the adsorption experiments. Beech sawdust was only sieved. For the washing experiments, particles size in a range from 0.4 mm to 1 mm of each sample of biomass was used. The specific surface area was determined and published elsewhere [1,16]:

- for the sawdust sieve fraction, 1.08 $m^2\ g^{-1}$,
- for the wheat straw, 1.54 $m^2\ g^{-1}$.

Usually either distilled or tap water or both [1,12,16] were used in washing the sawdust and wheat straw prior their use in further experiments. In this study, washing of wheat straw and beech sawdust was carried out with distilled water in order to be sure that there are no traces of metal ions in the water. Beside the chemical analysis of leachate, a change in electrical conductivity and pH were also measured during washing. Washing experiments were performed at the ambient temperature.

### 2.2. Experimental procedure

Experiments were carried out in a similar way as it is described in the literature [12,16], i.e.: One gram of previously dried biomass was placed on a filter paper in a laboratory funnel and repeatedly washed ten times with equal portions (0.02 $dm^3$) of distilled water, having the initial conductivity of 1.9 $\mu S\ cm^{-1}$ and pH around 5–5.5, due to the absorbed atmospheric $CO_2$. Each portion of water was filtered through a biomass and collected in a laboratory beaker to be used for analysis and the pH and EC measurements. The pH was measured by means of WTW inoLab-720 pH-meter, while the EC measurements were performed by a conductivity-meter WTW inoLab-720. Samples of filtrate were taken and analysed on alkali and alkaline-earth metal ions using the PerkinElmer 403 AAS-ICP analyser.

### 2.3. Modelling the biomass cross-flow washing

As it was described above, the procedure of biomass washing could be considered as a multistage cross-flow leaching process as illustrated in Fig. 1, where the numerated circles represent the leaching stages. The water of volume $\Delta V$ flows through each stage and metal content in both the solid ($m_i$) and the aqueous phase ($C_i$) will be changed along the washing stages as indicated in Fig. 1. This way of leaching is characterised by a stepwise depletion of the solid phase in components, which have to be washed out, as well as with different quality of leachate from one stage to the other.

Here, as it is presented in Fig. 1, the process of biomass washing consists from *n* identical stages serving as the contactors of phases. Biomass, which has to be washed, enters into the first stage, bringing in $m_o$ quantity of elements, which have to be leached out. In this case, the leaching of Na, K, Mg and Ca from beech sawdust and wheat straw will be considered. Biomass will be repeatedly washed with a constant volume of water $\Delta V = 0.02\ dm^3$, equal for each stage. Passing through the biomass, each portion of water will take out a certain amount of considered elements. Concentration of metal ions in filtrate (leachate) is denoted as $C_1$. The subscript 1 corresponds to the first stage, numerated as 1 in Fig. 1. Drained solid phase contains the mass of considered metals $m_1 < m_o$. It will be washed again with the same volume of water $\Delta V$, as it was in the stage 1. Concentration of leached metals will be now $C_2$, while the residual mass of considered elements, in the treated biomass, is $m_2 < m_1$. Repeating the operation of washing *n* times, the final quantity of metals in biomass will be $m_n$, while their concentration in corresponding filtrate is $C_n$.

According to Fig. 1, the mass balance of leached chemical element for the first stage could be written as:

$$m_o - m_1 = \Delta m_1 = \Delta V \cdot C_1 \tag{1}$$

This means that a decrease in alkali and alkaline-earth metals from biomass, because of leaching, is equal to the water volume multiplied by the concentration of corresponding element in filtrate.

For the 2nd stage, in the same way, the mass balance equation will be:

$$m_1 - m_2 = \Delta m_2 = \Delta V \cdot C_2 \tag{2}$$

While for the nth stage:

$$m_{n-1} - m_n = \Delta m_n = \Delta V \cdot C_n \tag{3}$$