Hydrolysed biomass waste as a potential biosorbent of zinc from water

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Abstract. In the last 10 years recycling of various materials and metal recovery from waste with low cost biosorbents or agricultural biomass has become popular trend. Lignocellulosic biomass is regarded as a sustainable resource for biofuel production. In this process, lignocellulosic biomass is partly degraded during chemical or biological hydrolysis, as a result, these agricultural waste materials usually present a disposal problem and have no economic value. Therefore, reuse of lignocellulosic waste materials as inexpensive and alternative sorbent for heavy metals in polluted aqueous solution.

The aim of this research was to evaluate the applicability of hydrolysed biomass waste for zinc removal from water solution. To evaluate the potential use of lignocellulosic biomass for biosorption, experiments were performed with dry, washed from organic matter and hydrolysed hay. The results showed that hydrolysed hay have lower biosorption capacity than washed and dried hay, however, it still can be used as a low-cost biosorbent for the removal of Zn in polluted aqueous solutions, because it showed relatively high cink sorption capasity (336–391 mg g^{-1}).

Key words: biosorbent, lignocellulosic biomass, waste, heavy metal, zinc.

INTRODUCTION

Recycling of various materials and metal recovery from waste is applied more and more often in the World. The most popular methods for the recovery are chelator-forming agents (Xu & Zhang, 2006); ion exchange (Kang et al., 2004); ultrafiltration (Landaburu-Aguirre et al., 2010); reverse osmosis (Shahalam et al., 2002); nanofiltration (Murthy & Chaudhary, 2008); electro dialysis (Sadrzadeha et al., 2009); coagulation and flocculation (Charerntanyarak, 1999); flotation, dissolved air flotation (DAF) (Lundh et al., 2000); ionic flotation (Polat & Erdogan, 2007), electrocoagulation (Chen, 2004) or filtration through various materials. The most popular sorbents used as filter media are activated carbon (Kang et al., 2008), carbon nanotubes (first method is described in Iijima, 1991) and low-cost materials as kaolinite (Bhattacharyya & Gupta, 2008). However, most of these methods are expensive and often include the use of specific materials or chemicals. A good alternative is the application of biological materials (biosorbents) as filter media. Biosorbents can be divided into the following groups: (1) biological material, that can be used in bioreactors: fungi (Dhillon et al., 2016), yeasts (Amirnia et al., 2015), algae (Apiratikul & Pavasant, 2008) and bacteria (Kotrba et al., 2011), (2) agricultural material, that can be used as filter media: traditional biomass as

peat (Brown et al., 2000), garden grass (Hossain et al., 2012) or mixture of hay, manure or different agricultural wastes (Wang et al., 2009). The most important factor for the selection of the biosorbent is its applicability and cost-effectiveness.

Insufficiently treated industrial wastewater or various metallic waste (metal details, batteries etc.) (Sud et al., 2008) are one of the causes how various metal ions get into the environment. Many of them have a negative effect on human health due to their toxicity even at low concentrations and bioaccumulation properties (Kasiuliene et al., 2016). One of such metals is zinc. Despite zinc as a trace element is necessary for the human health and organism`s biochemical processes (Chapman, 2006), at high doses it is toxic and can cause problems such as stomach cramps, skin irritations, vomiting, nausea and anaemia (Oyaro et al., 2007). Zinc has excellent anti-rust properties and is usually used in the galvanization (zinc coating) of steel; therefore, it has great potential to be recycled (van Beers et al., 2007). The maximum concentration limit (established by USEPA) for Zn in the discharged wastewater is 0.80 mg L^{-1} (Babel & Kurniawan, 2003), however, industrial wastewater can have Zn concentrations of more than 100 mg L^{-1}, and thus, the biosorbent must be not only affordable but also efficient.

Along with the human health aspects and recovery of valuable chemicals, a major problem in global communities is an efficient production of energy. Plant biomass is regarded as a sustainable resource for biofuel production due to its wide abundance and high energetic value (Hahn–Hägerdal et al., 2006); Pauly & Keegstra, 2008). At the same time efficient fuel production is linked to generation of partially degraded lignocellulose or solid wastes that are usually discharged in the environment. However, re-introduction of this waste into industry would be of high importance.

Partially degraded lignocellulose or solid wastes that are not used further after chemical or biological extraction are usually discharged. The aim of this research was to evaluate if lignocellulosic biomass waste after hydrolysis can be used as a potential biosorbent for zinc recovery.

MATERIALS AND METHODS

Biosorbent preparation

Hay (Dry weight (DW) – 92.8 ± 1.3%) harvested in Latvia in June 2015 was used as the test material. The hay was grinded by mechanical cutting mill (Retsch SM100, Haan, Germany) with 1.5 kW drive and parallel section rotor with peripheral speed 9.4–11.4 ms^{-1}. Particle size was controlled by 10 mm-sieve size square holes. One part of the biomass was directly used further ('dried') at room temperature (RT) another was washed for 24 h with tap water at a flow rate of 15 mL min^{-1} ('washed'). Hydrolysed biomass was obtained after 24 h of enzymatic hydrolysis. In brief, 3% w/v of the biomass was diluted in 0.05 M sodium citrate buffer (mono–sodium citrate pure, AppliChem, Germany) and boiled for 5 min (1 atm) to eliminate any indigenous microorganisms. After cooling to RT, an enzyme (Viscozyme, Novozymes) was added and incubated on an orbital shaker (New Brunswick, Innova 43) for 24 h at 37°C and 150 rpm. Afterwards the solid fraction was collected, air-dried at RT and used for biosorption studies.

Experimental setup

Biosorption experiments were conducted in a glass column of 25 cm length and 3.2 cm of inner diameter, filled with of dry hay, washed hay and hydrolysed hay. Zn(II)

solutions with an initial concentration of 10 and 100 mg L^{-1} with pH 7.0 ± 0.5 were fed through the up-flow fixed-bed column at a flow rate of 15 mL min^{-1}. Samples were taken periodically and then analysed with Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer (AAS) for the determination of residual zinc concentration. Operation of the column was stopped when equilibrium between influent and effluent Zn(II) ion concentration was achieved (99% of an initial Zn(II) concentration). The pH, conductivity and temperature of the influent and effluent of collected samples were measured by using digital bench top meter (inoLab® Multi 9420 IDS, WTW, Germany). Each experiment was performed in triplicate.

Zn determination

The concentration of Zn was analysed using the AAnalyst 200 AAS (Perkin Elmer, USA) using a mixture of air-acetylene flame technique.

Samples of Zn(II) solution were taken periodically from the top of the column and have been acidified with concentrated nitric acid (HNO$_3$ 65%, Lach-Ner Ltd., Czech Republic) to reach a concentration of 2% v/v; then the samples were filtered with 0.45 μm membrane filter (Filtropur S, Sarstedt, Germany). All the results were expressed in milligrams of Zn(II) per litre (mg L^{-1}).

Zn solution

The synthetic Zn(II) solutions were prepared by dissolving the appropriate amount of ZnSO$_4$·7H$_2$0 (Reachem Slovakia, Slovakia) in tap water to simulate real water contamination. According to standard method maximal concentration for Zn determination in samples was 1 mg L^{-1}, thus dilutions were performed when necessary.

TOC determination

Total organic carbon (TOC) measurements were performed with a Scalar Primacs MCS TOC analyser based on high temperature and acidification of sample and by the difference of the total carbon and inorganic carbon measurement, according to standard method EN 1484:1997 (LVS EN 1484:2000). For TOC determination samples were filtered thought the 0.45 μm pore size membrane filters (Millipore Corporation, USA). Each sample was tested in duplicate and the mean values were calculated ($CV \leq 2\%$). The blank and control solutions were analysed with each series of sample in order to verify the accuracy of the results obtained by the method.

Statistical data analysis

The efficiency of Zn(II) removal or adsorption yield was calculated from the ratio of the amount of Zn(II) ions adsorbed and the biosorbent amount in fixed-bed column.

Total feed volume V (L) is calculated by the following equation:

$$V = Q \cdot T \tag{1}$$

where T is the total operating time in the biosorption experiment or retention time in hours (h), Q is the flow rate of Zn(II) ion solution which passed through the column in mL min^{-1}.

The total feed amount of Zn (g) biosorbed into the biosorbent in fixed-bed column experiments is calculated by the following integration:

$$\text{Total feed amount of Zn} = C \cdot V \qquad (2)$$

where C is the adsorbed concentration of Zn (mg L^{-1}) and V is total feed volume (L).

The Zn capacity (mg g^{-1}), the weight of Zn(II) sorbated per unit dry weight of biosorbent can be determined as following:

$$\text{Zn capacity} = \frac{\text{Total feed amount of Zn}}{m} \cdot 1,000 \qquad (3)$$

where m is the total mass of biosorbent in the column in g.

The efficiency of Zn(II) removal or adsorption yield (%) was calculated from the ratio of the amount of Zn(II) ions biosorbed and the total mass of biosorbent (g) in fixed-bed column using the following equation:

$$\text{Adsorption yield} = \frac{\text{Amount of Zn(II)biosorbed}}{m} \cdot 100 \qquad (4)$$

General MS Excel statistical data analysis was used for data processing. Probabilities of ≤ 0.05 were considered as significant.

RESULTS AND DISCUSSION

In this study, the application of hydrolysed biomass waste for zinc removal from water solution was evaluated with the aim to determine the potential of lignocellulosic biomass as a biosorbent.

Biosorption experiments were conducted in a glass column, filled with dry, washed and hydrolysed hay. Zn(II) solutions with an initial zinc concentration of about 10 and 100 mg L^{-1} (pH 7.0 ± 0.5) were fed through the up-flow fixed-bed column. The concentrations were selected to represent moderately or heavily polluted water. The comparison of dried, washed and hydrolysed hay showed similar tendencies of Zn adsorption (Figs 1, 2). The efficiency of adsorption process was determined as the changes in Zn concentration in influent and effluent samples.
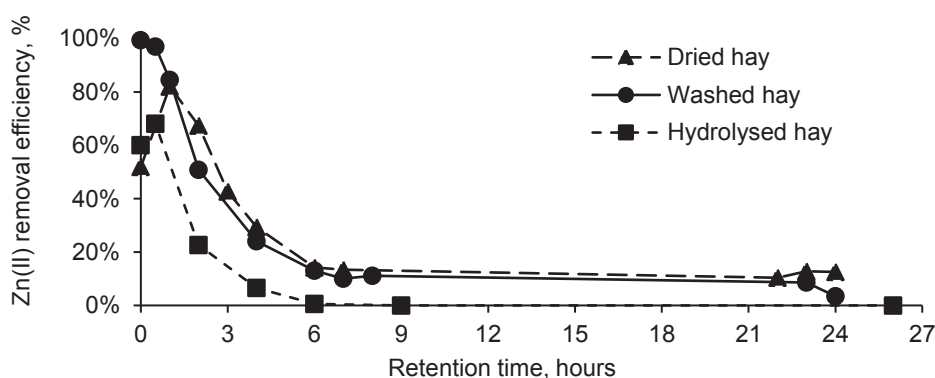

Figure 1. Zinc removal efficiency from solution with initial concentration of around 100 mg Zn mg L^{-1} during the biosorption process. The data are the mean of three separate experiments.

Figure 2. Zinc removal efficiency from solution with initial concentration of around 10 mg Zn mg L^{-1} during the biosorption process. The data are the mean of three separate experiments.

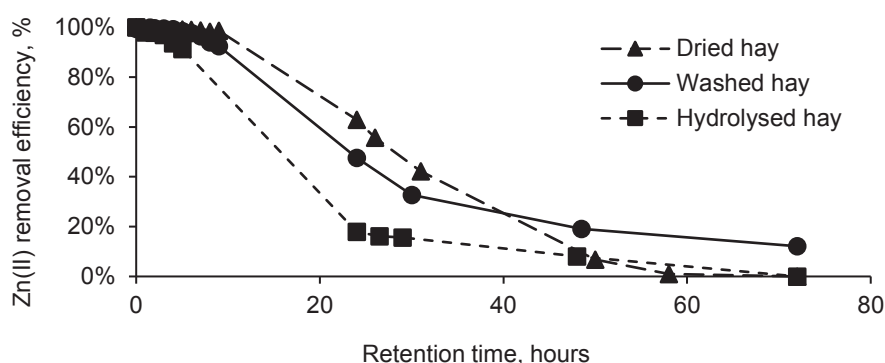At high initial zinc concentration (around 100 mg L^{-1}), Zn(II) removal for dried, hydrolysed and washed hay at the initial stage was 52, 60 and 99%. During the next 60 minutes of biosorption, Zn removal efficiency with dried hay biosorbent increased to 82%, and to 68% for the hydrolysed one. The residual concentration of Zn increased to the initial concentration after 24 hours of treatment through both hay types.

The experiments with dried and hydrolysed hay showed that in the first effluent samples high amount of humic substances (HS) that affected biosorption capacity were observed (Table 1). To determine the effect of HS on the biosorption process, hay samples were washed with tap water at a flow rate of 15 mL min^{-1}. Concentration of HS, determined as TOC, reached up to 6,999 mg L^{-1} (with dried hay and 100 mg Zn L^{-1} solution). Higher TOC concentration was observed in the first minutes of biosorption process and afterwards it slowed down. The final concentration of TOC stayed at the same level with influent solution 6–8 mg L^{-1}.

Table 1. Average pH, EVS and TOC values during the biosorption process

Hay	pH		EVS range, μS cm^{-1}		TOC range, mg L^{-1}	
Zn, mg L^{-1}*	*10*	*100*	*10*	*100*	*10*	*100*
Dried	7.58 ± 0.24	7.29 ± 0.38	614–9,574	839–10,586	8–1,640	8–6,999
Washed	7.56 ± 0.18	7.45 ± 0.16	640–716	759–884	8–29	8–43
Hydrolysed	10.94 ± 1.14	6.49 ± 0.94	952–2,612	864–2,516	6–1,100	7–1,268

* – initial zinc concentration, mg L^{-1}.

At low initial zinc concentration (10 mg L^{-1}), 99% removal was observed for dried and hydrolysed hay after 9 h and 3 h, respectively. Zn removal efficiency decreased after 24 h to 63% for dried and 18% – for hydrolysed hay. Biosorbent capacity was exhausted after 51 h for dried and after 72 h – for hydrolysed hay, when Zn increased to initial concentration.

Washed hay showed higher Zn(II) adsorption rates in the first 60 minutes (100 mg L^{-1} Zn(II)). Afterwards the adsorption kinetics slowed down and the effluent had Zn(II) at the same level as in the inlet water. In samples with 10 mg L^{-1} Zn(II) the greatest decrease was obtained within the first 24 h. Afterwards the decrease slowed down. After 30 hours no significant reduction in Zn concentration was observed ($p < 0.05$).

Similar tendency was observed for electro conductivity (EVS) measurements (Table 1). Higher EVS (10,586 μS cm^{-1}) was obtained in solutions with higher TOC concentration (with dried and hydrolysed hay). EVS was the highest during the first minutes of biosorption process and afterwards it slowed down and the final concentration of EVS stayed at the same level as in the inlet water – 614–952 μS cm^{-1}. At the same time zinc removal efficiency at the highest TOC and EVS levels was low in systems with dried and hydrolysed hay.

The total adsorbed Zn(II) on three types of hay was calculated as the difference in Zn between the inlet sample and the Zn value in the effluent sample during the overall biosorption cycle (Table 2). The efficiency of Zn(II) removal or adsorption yield was calculated from the ratio of the amount of Zn(II) ions adsorbed and the biosorbent amount in fixed-bed column.

Table 2. Comparison of Zn load and adsorption yield depending on the biosorbent used.

| Parameters | Hay | | | | | |
	Dried		Washed		Hydrolysed	
Zn, mg L^{-1}*	*10*	*100*	*10*	*100*	*10*	*100*
Flow rate, mL min^{-1}	15	15	15	15	15	15
Retention time, h	51	24	72	25	48	26
Total feed volume, L	45.9	21.6	64.8	22.5	43.2	23.4
Adsorbed concentration of Zn, mg L^{-1}	193	398	206	642	84.8	184
Total feed amount of Zn, g	8.9	8.6	13.4	14.4	3.7	4.3
Biosorbent mass, g	18	16	17	17	11	11
Zn capacity, mg g^{-1}	494	538	788	847	336	391
Adsorption yield, %	50	53	81	88	33	40

* – initial zinc concentration, mg L^{-1}.

Differences in the retention time can be explained by operation mode: the column experiments were stopped when an equilibrium between the influent and effluent Zn(II) ion concentration was achieved (99% of an initial Zn(II) concentration).

The results showed that pH level increased up to 10.94 ± 1.14, higher EVS level (952 μS cm^{-1}) and lower TOC (6 mg L^{-1}) in effluent samples from fixed-bed column with hydrolysed hay and 10 mg L^{-1} Zn(II) effluent solution. The hydrolysed biomass prior biosorption was only slightly washed and it is possible that certain amount of enzymes and hydrolysis intermediates have remained and in the presence of metal ions, resulted in formation of certain basic products that caused pH increase. Partially thermally and enzymatically degraded biomass reaction with lower Zn(II) concentration in influent solution can be the reason for these results. The scanning electron microscope (SEM) analysis in other parallel studies (Gruskevica et al., 2017) have shown than sorbent is covered by thin white film with some drop shaped inclusions, as well as energy dispersive X-ray spectroscopy (EDX) analysis confirmed that the film consist of organic substances and inclusion were made of Zn. Some other studies (Denisova et al., in Press) showed that reaction with lower influent concentration can be more intensive and also the Zn(II) biosorption capacity was higher at lower Zn(II) influent concentration. Some other reaserchers (Singha & Guleria, 2015) have shown a decrease in feasibility of adsorption at higher temperatures, and also the percentage removal of Zn ions increases in the pH range of 5.0–7.0.

Adsorption is an effective and economic method for heavy metal wastewater treatment, when it is possible to produce high-quality treated effluent (Fu & Wang, 2011). The obtained results showed that it was possible to immobilize at least 84.8 mg L^{-1} of Zn on hydrolysed hay during the biosorption cycle from a solution with 100 mg L^{-1} Zn(II) (Zn capacity is 336 mg g^{-1} or adsorption yield – 33%). Maximal adsorbed Zn concentration (642 mg L^{-1}), maximal Zn capacity (847 mg g^{-1}) and adsorption yield (88%) was obtained in columns with washed hay and 10 mg Zn L^{-1} solution. The obtained adsorption capacity of hay was higher than reported in other studies (Chen et al., 2011), where Zn removal was performed by biochar and varied at about 10–55%. The capacity was as low as 11 mg g^{-1}. Some other researchers presented Zn sorption capacities on different sorbents: HCl-treated clay – 63.2 mg g^{-1} (Vengris et al., 2001), pecan shells activated carbon – 13.9 mg g^{-1} (Bansode et al., 2003), bacillus – bacterial biomass – 418 mg g^{-1} (Ahluwalia & Goyal, 2006). According to other studies (Gruskevica et al., 2017) the obtained Zn adsorption capacity of hay was by 30% higher in experiments with standard solutions than in multicomponent solution or real wastewater. Partially degraded lignocellulose or solid wastes that are not used further after chemical or biological extraction are usually discharged. Thus, the key factor to investigate the possibility of potential recovery of the biosorbent material is the regeneration of the biosorbent. Usually desorption efficiency for lignocellulose biosorbents was is higher than 99 % (Denisova et al., in Press).

Thus, the highest Zn adsorption capacity was obtained with washed hay that had low free organic content. Zn adsorption capacity in experiments with dried hay that had high free TOC content was lower. Subsequently, the lowest capacity was determined in samples with hydrolysed hay.

Some studies showed that the modification of the adsorbent can increase the removal efficiency of pollutants: modified rice husk – 80% (Roy et al., 1993) or algal was greater than 90% (Guo et al., 2002). Of course, all sorbent modifications increase the costs of metal removal processing technology (Bailey et al., 1999). Other authors have reported that heat-treatment of biosorbents could affect sorption capacity significantly. As example, Sharma et al. (2013) showed that NaOH and HCl washed soybean and cottonseed hulls were better adsorbents for Zn (sorption capacity varied from 69.5 to 90.3%) than water-washed (control) hulls (51.9 and 59.5% respectively) and heat-treated cottonseed and soybean hulls (sorption capacity varied from 33.3 to 59.8%).

Zinc pollution of water is a major problem faced worldwide. Zinc adsorption capacity on low cost adsorbents has been presented in different studies and depends on various environmental conditions, such as, pH, temperature, contact time and sorbent modifications.

This study showed that hay and hydrolysed hay can be used as a potential low-cost biosorbent for the removal of Zn(II) in moderately and heavily polluted aqueous solutions.

The advantages of used biosorbent are the ease of production, low price, availability of raw materials including waste materials such as recycling waste and the potential to use agricultural wastes for immobilization of heavy metals from polluted environmental solutions with different engineering systems. Further research on the hay properties and adsorption capacities for other metals should be performed to evaluate the full potential of this waste-resource.

CONCLUSIONS

The present study showed a potential for the removal of heavy metals from wastewater using washed, dried and hydrolysed hay. Biosorption efficiency of hay decreased with the increase of organic matter concentration. As well as the sorption capacity depended on this type of the adsorbent. Washed hay was a better adsorbent than dried and hydrolysed hay.

The highest Zn adsorption capacity was obtained with washed hay with low free organic content, Zn adsorption capacity obtained in experiments with dried hay and high free TOC content was lower, and finally, the lowest – with hydrolysed hay. Adsorption yield of Zn was 81–88% for washed hay, 50–53% for dried hay and 33–40% for hydrolysed hay.

This study showed that the hydrolysed hay can be used as a potential low-cost biosorbent for the removal of Zn(II) in polluted aqueous solutions, but non-modified hay (washed and dried) still showed higher Zn sorption potential.

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