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USING WOOD AND BONE ASH TO REMOVE METAL IONS FROM SOLUTIONS

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ABSTRACT

In the present work, wood and bone ash were used to remove metal cations from solutions. Cation-removal capacity of the ashes was analyzed by potentiometric titration. It was found that the capacity of wood ash was two times higher (37.3 meq g^{-1}) than bone ash (15.2 meq g^{-1}). Kinetics of metal ions removal by both ashes was described with pseudo-second order equation and Langmuir model was employed to describe equilibrium of the process. Wood ash had better removal properties than bone ash - at the same experimental conditions biosorption capacity at equilibrium for wood ash was 2 times higher (244 mg g^{-1}) than for bone ash (123 mg g^{-1}).

Promising results were also obtained for wood ash, which was capable of removing 67.9 % of Zn(II) ions, 70.4 % of Cd(II) ions, 92.8 % of Cu(II) ions and 99.1 % of Cr(III) ions from model solution of wastewater from metallurgical industry and 84.5 % of Cr(III) ions from the post-biosorption solution from the production process of biological feed additives. The utilization of ashes of biological origin was found to be a promising alternative to conventional processes of wastewater treatment.

KEYWORDS: wood and bone ash, kinetics, equilibrium, Cr(III), Cd(II), Zn(II), Cu(II), Ni(II) ions, removal of toxic metal ions, wastewater.

1. INTRODUCTION

In the recent years, there is an increasing interest in the application of materials of biological origin in heavy metal ions removal from aqueous solutions. In the future, such materials might gain a special attention, since the cost of these materials is much lower than the cost of commercial adsorbents, such as activated carbon or ion-exchange resins (Al-Asheh *et al*., 2002).

Many agricultural by-products, activated sludge, specially propagated the biomass of algae, fungi, yeast, bacteria, algae from the environment that are available at little or no cost have been reported to be capable of removing substantial amounts of toxic metals from aqueous solutions (Veglio` and Beolchini, 1997; Volesky, 1990). Removal of metal ions involves relatively rapid metal-sequestering mechanisms related to the cell surface. In most cases, the metal bound on the biosorbent can be eluted, biomass can be regenerated and reused in multiple cycles.

Apart form mentioned natural biosorbents, in the literature, a special attention was also paid to the application of fly ash, which is generated during burning of coal, as a useful adsorbent (Alinnor, 2007; Cho *et al*., 2005; Erol *et al*., 2005). Fly ash is a strongly alkaline material and its surface is negatively charged at high pH. Hence, it can be expected that metal ions can be removed from aqueous solutions by precipitation, electrostatic adsorption (Cho *et al*., 2005) and ion exchange (Erol *et al*., 2005).

In the present paper, wood and bone ashes are proposed as materials for removal of mainly Cr(III), Cd(II), Zn(II), Cu(II) and Ni(II) ions from aqueous solutions. For the removal of toxic elements, biosorption process was applied. It is a surface phenomenon and relies on the binding of metal ions to the functional groups present on the sorbent.

The combustion of wood and agricultural residues generates large amounts of ashes (Reijnders, 2007). The majority of these wastes is disposed to landfills. However, increasing costs and the difficulties in acquiring new landfill sites encourage to look for alternative methods of disposal (Demeyer *et al*., 2001). Wood ash, which is formed in the combustion process of wood as renewable fuel and the combustion of slaughter residues (Chojnacka, 2005), can be applied to soils. This enables to recycle nutrients Ca, K, Mg, P and to deacidify a soil (Górecka *et al*., 2006, Demeyer *et al*., 2001). Ribbing (2007) suggested that non-coal ashes could be also applied as a material in the construction of roads and surfaces in landfills, as ballast or filler in concrete. In the literature, an increasing attention is paid to the application of natural ashes as adsorbents. Das *et al*. (2007) used plant ash to remove iron from groundwater. The mechanism proposed was precipitation of ferric ions by increasing pH, achieved by dissolution of potassium hydroxide and oxide. Also, palm ash was proposed as biosorbent of Direct blue 71 dye ($C_{40}H_{28}N_7NaO_{13}S_4$). Very high adsorption capacity obtained in the experiment, suggested that palm ash could be employed as a low-cost alternative to commercial activated carbon (Ahmad *et al*., 2007).

Recently, the utilization of animal bones is of particular concern. Due to the recent problem with bovine spongiform encephalopathy (BSE) crisis in the European beef industry, the use of animal derived products to feed cattle is now restricted. Feeding with meat and bone meal (MBM) to cattle, sheep or goats has been banned within the European Union since July 1994. Also, import and export of MBM to/from/within the European Union has been banned since December 2000. As a consequence, it is necessary to elaborate new methods of utilization of animal by-products. One option of such disposal is the incineration of material such as meat and bone meal residues. Dedicated incineration plants for MBM, as currently used in e.g., Belgium and England, only appear reasonable when sufficient quantities of MBM can be guaranteed in the long term (Conesa *et al*., 2005). The second disposal option is pyrolysis. Animal wastes could be converted by pyrolysis into fuels, but it is also suggested, that the solid residue could be used for enrichment of agricultural soil with nutrients and minerals (Chaala and Roy, 2003). This is aimed to assure epidemiological safety. The problem of utilization of ash from thermal processing of slaughter wastes arose. There has not been found large-scale method of bone ash utilization so far. In the literature it can be found, that the main attention of researchers was paid to the application of animal bones in removal process of heavy metals from aqueous solutions (Chojnacka, 2005; Banat *et al*., 2000; Al-Asheh *et al*., 1999; Al-Asheh *et al*., 2002). Nevertheless, Deydier *et al*. (2003) used meat and bone meal combustion residue as a low-cost material to remove lead ions from effluents. This residue was considered as an apatite-rich material and was used as a low-cost substitute of hydroxyapatite in removal of lead ions from wastewater. The mechanism of metal ions removal was found to be as in pure apatite: surface complexation and calcium hydroxyapatite dissolution, followed by precipitation of less soluble lead hydroxyapatite (Deydier *et al*., 2003). In the present work, the sorption properties of two materials of biological origin - wood and bone ash were investigated. The experiments were divided into three groups: the first concerned the general characteristics of biosorption properties of the examined biosorbents, the second aimed to establish the effect of process parameters, such as initial concentration of metal ions (C_0), ash concentration (C_S), temperature, initial pH on process kinetics and the effect of ash concentration, initial pH, and temperature on process equilibrium. These preliminary experiments were conducted on Cr(III) ions. In the last experiment, the applicability of wood and bone ash to remove toxic metals (Cr(III), Cd(II), Zn(II), Cu(II), Ni(II)) from two model solutions was determined (the first came from metallurgical industry and the second from the production process of biological feed additives based on microalgal biomass).

2. MATERIALS AND METHODS

2.1. Ash preparation

Wood ash was obtained by the combustion of oak wood in a residential fireplace. The characteristic of the combustion process was as follows: power - 15 kW, combustion rate 0.06 - 0.07 m^3 of wood per day. The collected ash was mixed and grinded. Bone ash was obtained from chickens' bones, which were previously cooked, cleaned from the residual meat and finally grinded. Then, the bones were combusted in the temperature 600 ^{o}C for 4 hours in the laboratory oven (Carbolite CWF 1200).

2.2. Potentiometric titration of the ashes

Potentiometric titration of the ashes was performed in order to determine the acidic dissociation constants and the total concentrations of the functional groups present in ash that are responsible for cations binding. The deionized water (blank sample) and 0.2 g of bone ash (for wood ash 0.02 g of material was used) suspended in deionized water (200 ml) were titrated with HCl and NaOH in the range of pH 2.5 - 11.5. For the titration, the solutions of 0.1 mol l^{-1} HCl and NaOH were used. The procedure was described previously (Chojnacka *et al.*, 2005).

2.3. Batch biosorption experiments in single-metal system

The experiments were performed in 250 ml Erlenmeyer flasks containing 200 ml of Cr(III) solution (for kinetic experiments) and 20 ml (for equilibrium experiments) in thermostated water bath shaker at 150 rpm. The solutions of Cr(III) ions were prepared in deionized water (by dissolving appropriate amounts of $Cr(NO_3)_3 \cdot 9H_2O$ (from POCh S.A. Gliwice, Poland)). pH of the solutions was adjusted with 0.1 mol l^{-1} solution NaOH/HCl (from POCh S.A. Gliwice). pH was measured with pH - meter Mettler-Toledo (Seven Multi) equipped with an electrode InLab413 with compensation of temperature. Experimental conditions for kinetics and equilibrium of biosorption of Cr(III) ions is presented in Table 1.

Table 1. Experimental conditions for kinetics and equilibrium of biosorption of Cr(III) ions

Para-meter	Kinetic experiments		Equilibrium experiments	
	Wood ash	Bone ash	Wood ash	Bone ash
pH	3; 4; 5	3; 4; 5	3; 4; 5	3; 4; 5
	C_S 1.0 g l^{-1}	C_S 0.1 g l^{-1}	C_S 0.2 g l^{-1}	C_S 0.5 g l^{-1}
	T 20 ^{o}C	T 20 ^{o} C	T 20 ºC	T 20 ºC
	C_0 200 mg l^{-1}	C_0 100 mg l^{-1}	C_0 50-300 mg l^{-1}	C_0 25-300 mg l^{-1}
T (^{o}C)	20; 30; 40; 60	20; 30; 50	20; 40; 60	20; 40; 60
	C_S 1.0 g l^{-1}	C_S 0.75 g l^{-1}	C_S 0.2 g l^{-1}	C_S 0.5 g l^{-1}
	pH 4	pH 5	pH 5	pH 5
	C_0 200 mg l^{-1}	C_0 100 mg l^{-1}	C_0 50-300 mg l^{-1}	C_0 25-300 mg l^{-1}
C_S (g l^{-1})	0.05; 0.1; 0.2; 0.5; 1.0	0.1; 0.2; 0.5; 0.75; 1.0	0.1; 0.2; 0.5	0.1; 0.2; 0.5; 0.75; 1.0; 2.0
	pH 4	pH 5	pH 5	pH 5
	T 20 ^{o}C	T 20 ^{o}C	T 20 ºC	T 20 ºC
	C_0 100 mg l^{-1}	C_0 100 mg l^{-1}	C_0 50 - 300 mg l^{-1}	C_0 25-300 mg l^{-1}
C_0 (mg l^{-1})	100; 200; 300	100; 200; 300		
	C_S 1.0 g l^{-1}	C_S 0.75 g l^{-1}		
	pH 4	pH 5		
	T 20 ^{o}C	T 20 ^{o}C		

The contact time for all equilibrium experiments was 90 minutes for wood ash and 120 minutes for bone ash (determined from the kinetic experiments). Equilibrium experiments of biosorption of Cd(II) and Zn(II) ions were performed at the parameters, which were selected as the best in the case of biosorption of Cr(III) ions (1.0 g l^{-1}, T 20 ºC, pH 5, C_0 25 - 300 mg l^{-1}). The solutions of metal ions were prepared in deionized water by dissolving appropriate amounts of $Cd(NO_3)_2 \cdot 4H_2O$ and $ZnSO_4$ (from POCh S.A. Gliwice).

2.4. Batch biosorption experiments in multi-metal system

For the biosorption experiments in multi-metal system two solutions were chosen: from the metallurgical industry (Łebkowska and Karwowska, 2003) and from the production process of mineral feed additives based on microalgal biomass (Chojnacka, 2007). The composition of the solutions was assumed to be as follows - the first one: range of the concentration of metal ions: 5 - 100 mg $l^{-1}$of Zn(II), 5 - 50 Ni(II) and Cu(II) ions, 1.5 - 30 mg l^{-1} of Cd(II) ions and 15 - 100 mg l^{-1} of Cr(III) ions and the second: 190 mg l^{-1} of Cr(III) ions. For their preparation, the following salts were used: $ZnSO_4$, $NiSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$. The experiments were performed at room temperature and pH 5. The concentration of wood ash was 0.2 g l^{-1} and of bone ash 1.0 g l^{-1} in both model solutions.

2.5. Analytical methods

2.5.1. Analysis of Cr(III) ions concentration

Samples of ash suspension were taken to determine residual concentration of Cr(III) ions in the solution. Before the analysis, samples were filtered through medium paper filter. The concentration of metal ions in the solution was determined directly spectrophotometrically by complexation with EDTA by Varian Cary 50 Conc. Instrument (Yongnian *et al*., 2002). The concentrations used in the preparation of the calibration curve were determined by Inductively Coupled Plasma-Optical Emission Spectrometer (Varian VISTA-MPX ICP-OES) in the Chemical Laboratory of Multielemental Analysis at Wrocław University of Technology accredited by ILAC-MRA and PCA. For the preparation of standard solutions (1.0, 10, 100 mg l^{-1}) the multielemental standard (100 mg l^{-1} Astasol®, Czech Republic) was used (Chojnacka, 2006). The presented data are the arithmetic average from three measurements.

2.5.2 Multielemental analysis of the wastewater and ash composition

Approximately 0.5 g of the natural ashes was digested with 5 ml of concentrated nitric acid (Supra pure grade from Merck) in a microwave oven (type Milestone MLS-1200 MEGA). The solution after mineralization was diluted to 50 ml. The concentrations of metal ions in the samples of digested ashes, as well as in model solution from metallurgical industry and in the wastewaters from biosorption process before and after treatment with wood and bone ash were determined by ICP-OES method.

3. RESULTS and DISCUSSION

3.1. Characterization of wood and bone ash

Table 2 shows the mineral composition of the ashes samples used in this study. The main constituents of wood and bone ash are alkali and alkaline earth metals (Ca, K, Mg, Na), microelements (Mn, Fe) and Al. Wood ash contained 17.4 % of Ca(II), 4.27 % of K(I), 1.15 % of Mg(II), 0.673 % of Na(I), whereas bone ash: 22.5 % of Ca(II), 1.34 % of K(I), 0.597 % of Mg(II) and 0.886 % of Na(I). From these results it can be expected, that theoretically bone ash will be a better material for the removal of heavy metal ions from wastewaters, due to higher concentration of light metals. The content of toxic metals in bone ash is smaller than in wood ash. It is important to check, whether wood and bone ash does not cause secondary pollution of treated wastewater.

3.2. Mechanism of the metal ions removal by ashes

The identification of functional groups on the ashes surface is one of the key issues in understanding the mechanism of metal binding. The acid site densities and acidity constants were determined by potentiometric titration. The experimental data were fitted to the models elaborated previously (Chojnacka *et al*., 2005a), which considered the presence of one, two or three types of functional groups. The highest regression coefficients were obtained for the assumption of the existence of three types of functional groups (R^2 0.999 for wood ash and R^2 0.989 for bone ash). For the titration of the 0.02 g suspension of wood ash, 1.77 meq of titrant was used, and for titration of deionized water - 1.01 meq of titrant. In the case of bone ash, for the titration of the 0.2 g suspension of ash, 4.26 meq of titrant was used and for water 1.22. From the difference between these two values, the total cation removal capacity was determined, which for wood ash was 38.0 meq g^{-1} and for bone ash as 15.2 meq g^{-1} (meq - milliequivalent is the molar unit, which considers the valency of an ion). It was found that cation-removal capacity of wood ash was two times higher than bone ash. The examined ashes possessed three functional groups with distinguishable pK_a on the surface: the first one is probably carbonate, the second phosphate and the third group hydroxyl. The acidity constants and acid site densities are shown in Table 3. Wood ash possessed similar values of acidity constants to coal fly ash reported in the literature, which for these three acid sites were 2.7, 7.8 and 11.0, respectively (Wang *et al.*, 2004).

Table 2. Mineral composition of wood and bone ash

Element		Concentration (mg kg^{-1} of dry mass)	
		Wood ash	Bone ash
Microelements	Mn	5544	4.29
	Zn	518	215
	Cu	134	2.87
	Co	6.76	1.09
	Fe	1705	298
	Mo	1.64	1.22
	Cr	11.5	6.48
	B	302	4.16
Alkali and alkaline earth metals	K	42655	13372
	Ca	173879	225372
	Mg	11523	5968
	Na	6732	8861
	Ba	892	36.7
Toxic elements	Cd	2.89	0.232
	Ni	27.1	3.73
	Pb	29.4	1.92
Other elements	Ti	22.6	1.52
	Al	7251	14.8
	Ag	2.33	0.305
	V	125	56.8

Table 3. Functional groups on the surface of bio-ashes

Functional group	Acidity constant pK_a		Acid site density (meq g^{-1})	
	Wood ash	Bone ash	Wood ash	Bone ash
1	2.39	3.54	11.8	2.02
2	8.00	6.33	7.50	1.57
3	11.1	11.0	21.8	4.71

Multielemental analysis of digested ashes showed that bone ash contained more light metal ions than wood ash. Their concentration presented in Table 2 included the total concentration - inside and outside the sorbent. Biosorption is a surface phenomenon and in this process participate only light metal ions, which are present on the surface of the ash. Therefore on the basis of the total composition of light metal ions in ash it was supposed that bone ash would be better biosorbent than wood ash. However, potentiometric titration of the ash showed that the density of acidic sites on the surface of wood ash was higher than on the surface of bone ash. These functional groups play a key role in the biosorption process of cations through ion-exchange mechanism. Therefore, we concluded that wood ash possessed better biosorption properties than bone ash.

The expected mechanism of metal ions removal from aqueous solutions by wood ash can involve: precipitation, electrostatic adsorption (Cho *et al.*, 2005) and ion exchange (Erol *et al.*, 2005). As pH increased from 3 to 5, it can be expected that the number of positively charged sites decreases and the number of negatively charged sites increases on the surface of wood and bone ash. A negatively charged surface sites of the ashes favour the adsorption of cationic metal ions due to electrostatic attraction. Since the experiments were performed in pH range 3-5, it is necessary to consider the chemical speciation of Cr(III) ions under these conditions. In this range, Cr(III) ions occur as $CrOH^{2+}$, as a result of hydrolysis, according to the generalized expression: $M^{3+}(aq.) + nH_2O = M(OH)^{3-n} + nH^+$ (where $M^{3+}=Cr^{3+}$). At pH higher than 5, Cr(III) ions begin to precipitate as $Cr(OH)_3$ (Yun *et al*., 2001), and can be adsorbed on the surface of examined ashes.

At higher pH, ashes could act as a precipitant agent similarly to lime, which is used in chemical precipitation of heavy metals from inorganic effluent. In the case of removal of Zn(II), Cd(II), Mn(II), Mg(II) from the waste water with the use of lime, hydroxides are precipitated at elevated pH, but values of pH 9.5 or greater are necessary for the effective removal (Charerntanyarak, 1999). Similarly to lime or calcium hydroxide, which are the most commonly employed precipitant agents, ash could be also applied in wastewater treatment to precipitate heavy metal ions, because of the alkalization properties. The most important characteristic of fly ash is the Ca(II) content, that provides alkalinity. In the case of wood ash, examined in this study, Ca(II) constituted 17.4 % of all light metals determined by ICP-OES method, which occurred in the raw wood ash, and for bone ash 22.5 %. This means, that in higher pH, precipitation could constitute a dominant mechanism of toxic metal ions removal. Since Ca(II) in the ash is in the form of CaO, it can be assumed, that the following reactions occur: $Me_{alk.\mathbf{a}}O + H_2O + Me_{tox.}^{\mathbf{b+}} = Me_{tox}(OH)_{\mathbf{b}}\downarrow + Me_{alk.}^{\mathbf{a+}}$, where: a - charge $^{+1}$ or $^{+2}$; Me_{alk} - alkali (e.g. K(I), Na(I)) and alkaline earth metals (e.g. Mg(II), Ca(II), Ba(II)); Me_{tox}- toxic elements (e.g. Cd(II), Pb(II), Zn(II), Cu(II), Ni(II)). For example: $CaO + H_2O + Cu^{2+} = Cu(OH)_2\downarrow + Ca^{2+}$.

3.3. Batch biosorption experiments of Cr(III) ions in single-metal system

3.3.1. Kinetics of biosorption of Cr(III) ions

Kinetics of biosorption of Cr(III) ions by bio-ashes was described by pseudo-second order model (1):

$$\frac{dq}{dt} = k_{2,ad} \cdot \left(q_{eq} - q\right)^2 \tag{1}$$

where q_{eq} and q are the amounts of adsorbed metal ions on the adsorbent at equilibrium and at time t, respectively (mg g^{-1}) and $k_{2,ad}$ is the rate constant of second-order adsorption (g mg·min^{-1}). In the literature it is reported that pseudo-second order model was used to describe sorption of Direct blue 71 dye by palm ash (Ahmad *et al*., 2007). The kinetic experiments of the removal process of Cr(III) ions were conducted to determine the contact time required to reach the sorption equilibrium and to assess the impact of process parameters (pH, temperature, C_S, C_0) on q_{eq} and on $k_{2,ad}$. The contact time needed to reach equilibrium was evaluated as 90 minutes for wood ash and 120 minutes for bone ash (as an example the effect of pH on the kinetics of the biosorption of Cr(III) ions by wood (a) and bone ash (b) is presented in Figure 1).

The effect of process parameters on q_{eq} and on $k_{2,ad}$ is presented in Table 4.

Comparing the parameters of pseudo-second order model for wood and bone ash at different pH, temperature, C_S and C_0, it can be seen, that wood ash showed better metal ions removal properties than bone ash. It was observed, that the higher pH and C_0 and the lower $C_{S,}$ the higher value of q_{eq}. The pH of the solution plays a very important role in the uptake of metal ions, since it determines the surface charge of the adsorbent (Alinnor, 2007). The highest sorption capacity for wood and bone ash was obtained at pH 5 and the smallest at pH 3. For both ashes q_{eq} in pH 5 was almost 2 times higher than in pH 3. The next parameter - temperature did not influence significantly the removal process of metal ions. For wood and bone ash, the values of q_{eq} and $k_{2,ad}$ were comparable in all examined temperatures. Considering the influence of C_S on q_{eq}, it can be seen, than wood ash had much better removal properties than bone ash. For example: q_{eq} for wood ash (C_S 1.0 g l^{-1}, C_0 100 mg l^{-1}, pH 4) was 103 mg g^{-1} and for bone ash only 36.0 mg g^{-1}, although the pH was even higher for the second ash (C_S 1.0 g l^{-1}, C_0 100 mg l^{-1}, pH 5), which should influence the q_{eq} value positively. The same trend was observed also for C_S 0.1, 0.2 and 0.5 g l^{-1}. For both bio-ashes, the lower concentration of material in the solution, the higher the value of q_{eq}. It is beneficial to conduct removal process of metal ions at higher biomass concentrations, because with increase of C_S, the amount of ions bound from the solution also increased - for example for the concentration of wood ash 0.05 g l^{-1} (q_{eq} 270 mg g^{-1}) - 13.5 mg of Cr(III) ions were bound by the material from 1 L of the solution, for C_S 1.0 g l^{-1} (q_{eq} 103 mg g^{-1})- 103 mg l^{-1} (almost 8 times more). This conclusion is very important in design of wastewater treatment plant. As it was shown previously, the higher value of pH and the lower of C_S, the higher value of q_{eq}.are. Although biosorption of Cr(III) ions by wood ash was performed in different biosorption conditions (C_S 0.75 g l^{-1}, 20 °C, pH 5) than by wood ash (C_S 1.0 g l^{-1}, 20 °C, pH 4) for C_0 range 100 - 300 mg l^{-1}, the value of q_{eq} were averagely 2.52 ± 0.27 higher for wood than for bone ash.

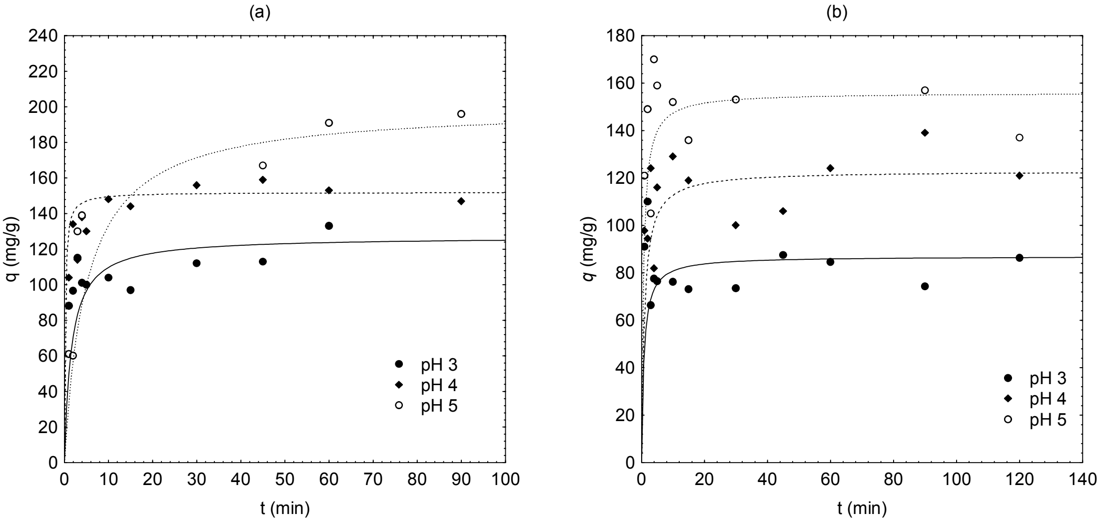

Figure 1. The effect of pH on the kinetics of the biosorption of Cr(III) ions by (a) wood (20 °C, C_0 200 mg l^{-1}, C_S 1.0 g l^{-1}) and (b) bone ash (20 °C, C_0 100 mg l^{-1}, C_S 0.1 g l^{-1})

Table 4. The comparison of parameters of pseudo-second order model for wood and bone ash at different pH, temperatures, C_S and C_0

Parameter	Wood ash			Bone ash		
	q_{eq} (mg g^{-1})	$k_{2,ad}$ (g mg·min^{-1})	R^2	q_{eq} (mg g^{-1})	$k_{2,ad}$ (g mg·min^{-1})	R^2
pH						
3	127	0.005	0.987	87.0	0.015	0.999
4	152	0.04	0.998	123	0.009	0.997
5	200	0.001	0.991	156	0.011	0.999
T (°C)						
20	200	0.001	0.991	40.7	0.012	0.999
30	208	0.002	0.997	40.2	0.019	0.998
40	227	0.002	0.999	NA	NA	NA
50	NA	NA	NA	51.0	0.003	0.983
60	200	0.002	0.989	NA	NA	NA
C_S (g l^{-1})						
0.05	270	0.006	0.994	NA	NA	NA
0.1	244	0.002	0.996	159	0.007	0.999
0.2	263	0.002	0.998	75.2	0.161	0.998
0.5	208	0.001	0.993	46.7	0.005	0.965
0.75	NA	NA	NA	40.7	0.012	0.999
1.0	103	0.009	0.982	36.0	0.004	0.979
C_0 (mg l^{-1})						
100	103	0.009	0.982	40.7	0.012	0.999
200	152	0.044	0.998	67.8	0.005	0.998
300	238	0.001	0.994	85.5	0.004	0.995

NA - not available

3.3.2. Equilibrium of sorption of Cr(III) ions

Langmuir equation was used to model equilibrium between metal ions adsorbed to the biosorbent and metal ions in the solution at a given temperature. This model is simple and gives a good description of experimental behavior in a wide range of operating conditions (Yun *et al*., 2001). The main advantage of this model is the possibility of evaluation of q_{max} - maximum possible quantity of metal ions adsorbed per gram of adsorbent (mg g^{-1}) and b - constant related with the affinity of binding sites for the metal ions (l mg^{-1}). In the literature it is reported, that Langmuir model was used to describe sorption of Direct blue 71 dye by palm ash (Ahmad *et al*., 2007) and cadmium and nickel onto bagasse fly ash (Srivastava *et al*., 2006).

The model parameters of Langmuir equation for sorption of Cr(III), Cd(II) and Zn(II) ions were determined by nonlinear regression (*Mathematica v. 3.0*). Table 5 presents the effect of temperature, pH and C_S on model parameters.

Table 5. Model parameters of Langmuir isotherm for Cr(III) ions sorption by wood and bone ash

Parameter	Wood ash			Bone ash		
	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2
pH						
3	133	0.036	0.963	39.0	0.056	0.984
4	196	0.786	0.971	63.5	0.025	0.951
5	340	0.532	0.986	75.0	0.037	0.962
T (^{o}C)						
20	315.7	1.03	0.973	75.0	0.037	0.962
40	339.8	0.224	0.995	121	0.038	0.993
60	325.1	0.653	0.991	140	0.160	0.996
C_S (g l^{-1})						
0.1	498	0.106	0.978	277	0.090	0.973
0.2	316	1.03	0.973	116	0.022	0.979
0.5	252	0.963	0.957	56.9	0.069	0.989
0.75	NA	NA	NA	75.0	0.037	0.962
1.0	NA	NA	NA	55.0	0.014	0.991
2.0	NA	NA	NA	42.0	0.030	0.994

NA - not available

Results obtained in the equilibrium experiments confirmed the results from kinetic experiments. pH influenced the removal process in the highest extent. With increase of pH, increase of q_{max} for both bio-ashes was observed. From the Table 5 it can be seen that wood ash had much higher affinity towards Cr(III) ions, than bone ash (for example in pH 4: 0.786 l mg^{-1}and 0.025 l mg^{-1} for wood and bone ash, respectively). The influence of temperature on the model parameters of Langmuir isotherm was slight for wood ash similarly to its influence on pseudo-second order model parameters. This indicates that biosorption process is due to ion-exchange mechanism (Wang and Chen, 2006). For wood ash, q_{max} was 327 mg g^{-1} (±12.1). The highest affinity of wood ash towards Cr(III) ions was observed at 20 ^{o}C (1.03 l mg^{-1}). In the case of bone ash, the highest q_{max} was obtained at 60 ^{o}C. With increase of temperature, the increase of affinity was observed. The effect of ash concentration on the equilibrium of sorption of Cr(III) ions by both ashes was investigated for C_S 0.1, 0.2 and 0.5 g l^{-1} and for bone ash also for three additional concentrations: 0.75, 1.0 and 2.0 g l^{-1}. The concentration of Cr(III) ions in the solutions after removal process was below detection limit (LD<0.0027 mg l^{-1}). This means, that the removal process for both ashes was very efficient. The highest amounts of removed Cr(III) ions were observed for the concentration of wood ash - 0.5 g l^{-1} (126 mg l^{-1}). In the case of bone ash, the highest q_{max} and b, were obtained at C_S 0.1 g l^{-1} (277 mg g^{-1} and 0.090 l mg^{-1}, respectively). Preliminary experiments, which concerned the evaluation of the effect of temperature, pH and ash concentration on the equilibrium of Cr(III) ions sorption by wood and bone ash, were necessary to establish the best operation conditions, that would be used to remove toxic elements on larger scale. On the basis of the obtained results, the best process parameters for wastewater treatment with the utilization of wood ash are: pH 5, T 20 ^{o}C, C_S 0.2 g l^{-1}, and for bone ash: pH 5, T 20 ^{o}C, C_S 1.0 g l^{-1}. Additionally, equilibrium experiments were also conducted for Zn(II) and Cd(II) ions, which commonly pollute wastewaters. The experiments were performed at the following parameters: 1.0 g l^{-1}, T 20 ºC, pH 5, C_0 25 - 300 mg l^{-1}. The aim of these experiments was to determine Langmuir parameters: $q_{\max}$ and b. The obtained results are presented in Table 6. The maximum sorption capacity of wood ash obtained for Cd(II) and Zn(II) ions was 4 and 12 times higher, than $q_{\max}$ obtained for bone ash, for these two metal ions, respectively. On the other hand, the affinity of the bone ash towards Cd(II) and Zn(II) ions was 9 and 6 times higher, than the affinity of wood ash towards these metal ions, respectively.

Table 6. Model parameters of Langmuir equation determined at pH 5, 20 ^{o}C, bio-ash concentration 1.0 g l^{-1}

Metal ion	Wood ash			Bone ash		
	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	q_{max} (mg g^{-1})	b (l mg^{-1})	R^2
Cd(II)	210	0.278	0.984	57.1	2.61	0.982
Zn(II)	255	0.190	0.904	21.2	1.18	0.980

3.4. Batch sorption experiments in multi-metal system

The efficiency of the sorption process in wastewater treatment depends not only on the ash properties but also on the sewage composition. The final aim of this paper was to determine the usefulness of wood and bone ash to remove toxic metals from effluents, which are generated by industry. In order to do that, two effluents were examined.

3.4.1. Treatment of model wastewaters from metallurgical industry

The treatment of the solution was performed at the best process parameters, which were established for equilibrium of sorption of Cr(III) ions. The concentrations of metal ions in the solution before and after treatment with bio-ashes are presented in Table 7.

Table 7. Treatment of wastewater from metallurgical with wood ash (0.2 g l^{-1}) and bone ash (1.0 g l^{-1}) at pH 5, 20 ^{o}C

Element		Concentration (mg l^{-1})		
		Before treatment	After treatment with	
			wood ash	bone ash
Toxic elements	Cd	15.5	4.59	9.24
	Cu	7.22	0.52*	0.77*
	Cr	19.6	0.18*	7.78
	Ni	9.48	3.04	8.71
	Zn	6.26	LD<0.0651*	3.21
Alkali and alkaline earth metals	K	6.48	21.5	15.2
	Mg	0.08	1.82	3.67
	Ca	2.63	32.7	23.1
	Mn	0.002	0.06	LD<0.00091
	Ba	0.070	0.23	LD<0.0003*

LD - below detection limit
*fulfil the Directive of Polish Minister of Agriculture and Rural Development - the acceptable concentrations of metal ions in discarded to soil and water solutions (2006)

The analysis of the Table 7 showed, that wood ash turned out to be very efficient material for toxic metal ions: Cr(III), Cu(II), Cd(II), Ni(II) and Zn(II). The percentage of the metal ions removed from the model solution was as follows: 99.1 %, 92.8 %, 70.4 %, 67.9 % and >99.0%, respectively. The efficiency of bone ash to remove metal ions was lower and the percentage of the removal of metal ions ranged from 8.2 % for Ni(II) ions to 89.3 % for Cu(II) ions. In spite of the relatively high efficiency of both ashes, obtained solutions can not be discarded into water or soil, because they do not fulfil Polish law - the concentration of metal ions was too high. According to the Directive of Polish Minister of Agriculture and Rural Development (2006), the concentration of metal ions in the discarded solutions should be as follows: Cd 0.05-0.4 mg l^{-1}, Zn 2.0 mg l^{-1}, Cr total 0.5-1.0 mg l^{-1}, Cu, Ni 0.1-0.5 mg l^{-1}, Ba 2.0-3.0 mg l^{-1}. Generally, wood ash was found to be an efficient material for removal of Cu(II), Cr(III), Zn(II) and Ba(II), but not for Cd(II) and Ni(II). In the case of bone ash, removal of Cu(II) and Ba(II) ions fulfilled Polish norms. In order to decrease the concentration of metal ions in the treated effluent, higher concentrations of ash should be applied. It is also important to emphasize, that the concentration of all toxic elements in the solution after treatment with bio-ashes was smaller than before removal process. This means that bio-ashes did not cause secondary pollution of the effluent.

The multielemental analysis of the model solutions after removal process revealed the presence of higher concentrations of alkali (K(I)) and alkaline earth metals (Mg(II), Ca(II), Ba(II)) than in the initial solution. These ions, which originate from natural ashes, were released during treatment, which caused precipitation of toxic metals hydroxides. In the case of wood ash, 10.2 meq g^{-1} of light metals (Mg(II), Ca(II), Ba(II), K(I), Mn(II)) were released from the ash to the solution during removal process, and 8.72 meq g^{-1} of toxic metals (Cd(II), Cr(III), Cu(II), Ni(II)) were removed from the effluent by the wood ash. For bone ash, the sum of light metals (Mg(II), Ca(II), K(I)), released was equal 1.54 meq g^{-1}, and the sum of toxic metals (Cd(II), Cr(III), Cu(II), Zn(II) and Ni(II)) bound by the ash was 1.12 meq g^{-1}.

3.4.2. Treatment of effluent from the production process of biological feed additives with microelements from microalgae using a biosorption process

The second solution for the removal of toxic elements was acquired from the production process of biological feed additives. This process relies on the enrichment of the biomass of alga with microelements (e.g. Cr(III) ions) via biosorption process. As a result, after the process, the solutions with high concentration of Cr(III) ions were obtained.

Multielemental analysis of the solution before and after treatment with bio-ashes revealed that mainly alkali and alkaline earth metal ions were released to the solution: Ca(II), K(I), Mg(II), Na(I) (Table 8). For wood ash 31.4 meq g^{-1} of light metals were released and for bone ash 5.15 meq g^{-1}. The concentration of Cr(III) ions was reduced from 190 mg l^{-1} to 29.4 mg l^{-1} by wood ash (0.2 g l^{-1}) and to 114 mg l^{-1} by bone ash (1.0 g l^{-1}) and the concentration of Cd(II) was reduced by 45.1 % by wood ash and by 84.5 % by bone ash. Nevertheless, the concentration of Cr(III) ions in the solution after treatment with wood and bone ash did not fulfil Polish norms (Directive of Polish Minister of Agriculture and Rural Development, 2006). The concentration of other elements in the solution after removal is in an acceptable by Polish law range (with exception of Sb for bone ash - 0.3 mg l^{-1}). Higher removal efficiencies are possible after treatment with higher concentrations of bio-ashes.

4. CONCLUSIONS

In the present paper, sorption process was used to remove toxic elements from aqueous solution using two natural materials - wood and bone ash. The preliminary studies showed, that the removal process depended on pH, ash concentration, initial metal ions concentration and in slight extent on temperature. These studies enabled to characterize sorption properties of bio-ashes and to establish the experimental conditions, in which the highest efficiency of metal ions removal was observed. The best experimental conditions for removal of metal ions from wastewaters were established as: pH 5, T 20 ^{o}C and C_S 0.2 g l^{-1} for wood ash and pH 5, T 20 ^{o}C, C_S 1.0 g l^{-1} for bone ash. Wood ash was found to be a better sorbent for toxic cations than bone ash. At the same experimental conditions (C_S 0.1 g l^{-1}, C_0 100 mg l^{-1}, pH 4, T 20 ^{o}C), q_{eq} for the removal of Cr(III) ions by wood ash was 2 times higher (244 mg g^{-1}) than for bone ash (123 mg g^{-1}). The same effect was observed for other toxic elements. The maximum sorption capacity of wood ash obtained for Cd(II) and Zn(II) ions was 4 and 12 times higher, than q_{max} obtained for bone ash, for these two metal ions, respectively.

Table 8. Treatment of wastewater from biosorption process containing high concentrations of Cr(III) ions with wood ash (0.2 g l^{-1}) and bone ash (1.0 g l^{-1}) at pH 5, 20 °C

Element		Concentration (mg l^{-1})		
		Before treatment	After treatment with	
			wood ash	bone ash
Toxic elements	Cd	0.071	0.039*	0.011*
	Cu	0.010	0.012*	0.015*
	Cr	190	29.4	114
	Ni	0.016	LD<0.0153*	0.039*
Alkali and alkaline earth metals	K	73.6	92.1	91.3
	Mg	11.0	13.4	14.5
	Ca	13.8	71.9	47.2
	Mn	0.097	0.190	0.111
	Ba	1.02	0.77*	0.679*
	Na	194	256	257
Micro-element	Fe	0.088	0.061	0.118
	Co	0.025	0.019	0.025
	B	0.181	0.211	0.168
Other elements	Al	0.049	0.013	0.024
	Sb	8.30	0.162*	5.20
	Ti	0.031	0.005*	0.018*
	Tl	0.285	0.038*	0.207*
	V	0.053	0.070	0.068

LD - below detection limit

* fulfil the Directive of Polish Minister of Agriculture and Rural Development - the acceptable concentrations of metal ions in discarded to soil and water solutions (2006)

The key issue of this paper was to determine the usefulness of wood and bone ash in the removal of toxic metal ions from effluents, which are generated by industry. The promising results were obtained for wood ash. The percentage of the metal ions removed from the model solution from metallurgical industry by wood ash ranged from 67.9 % for Ni(II) ions to 99.1 % for Cr(III) ions at only 0.2 g l^{-1} of the ash, whereas for bone ash from 8.2 % for Ni(II) ions to 89.3 % for Cu(II) ions, even if 5 times higher concentration of the ash was applied. After the treatment of the effluent from the production process of biological feed additives from microalgae, which was rich in Cr(III) ions, wood ash was capable of reducing Cr(III) ions concentration 84.5 % and bone ash only 40 %.

It is also important to emphasize, that removal of metal ions from aqueous solutions is a complex process. It can be expected that metal ions can be removed from aqueous solutions by precipitation, electrostatic adsorption and ion exchange. The presence of light metals in the solution after removal process indicated, that one of the possible mechanisms was ion-exchange or dissolution of light metals and precipitation of toxic hydroxides. The potentiometric titration of ashes confirmed, that on the sorbent surface were present three functional groups, which were responsible for cation removal. The total cation removal capacity of wood ash was 37.3 meq g^{-1} and of bone ash 15.2 meq g^{-1}. This means, that theoretical q_{max} of wood ash towards toxic elements was evaluated as: q_{max}Cr(III) 647 mg g^{-1}, q_{max}Cu(II) 1185 mg g^{-1} and q_{max}Cd(II) 2096 mg g^{-1}, and for bone ash as: q_{max} Cr(III) 264 mg g^{-1}, q_{max}Cu(II) 483 mg g^{-1} and q_{max}Cd(II) 854 mg g^{-1}. These results showed, that wood ash has higher potential to remove toxic elements from wastewaters. Theoretically, wood ash is able to bind 2.5 times more of toxic metals than bone ash.

Removal process described in this paper incorporating the utilization of bio-ashes as sorbents can be used in the future as an alternative method of wastewater treatment. These biosorbents could be therefore substituted in place of activated carbon or ion-exchange resins as metal ions removal agents due to their availability, high adsorption capacity and low cost. Nevertheless, there is a necessity to perform further experiments, especially on real industrial effluents.

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