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COMPARISON OF ALUMINIUM SORPTION USING INORGANIC AND ORGANIC NATURAL SORBENTS

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Abstract: *Aluminium is the third most abundant element on the Earth. Most often it is tightly bound in rocks. On acidification of the environment with acid rain or civilization interventions, there is a release of aluminium in rocks bound to the soluble form of aluminum salts. The effects of acidification are in the final phase of ecosystems visibly unsafe (damage to crops, mortality of fish in lakes and rivers, etc.). The results of laboratory tests with a strain of Penicillium glabrum and Natural zeolit – cliniptilolit to estimate the sorption efficiency for removal of aluminum from water are presented.*

Keywords: *Water treatment, removal of aluminium, Penicilium glabrum, natural zeolites, drinking water*

1. Introduction

In the Earth´s crust, aluminum is the most abundant (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon). Because of its strong affinity to oxygen, it is almost never found in the elemental state; instead it is found in oxides or silicates. There are more than 270 different minerals containing aluminum.

After acidification of the environment by acid rain or civilization interventions leads to the release of aluminum bound in rocks to form soluble aluminum salts.

Aluminum concentration in the waters are significantly affected by pH, at neutral pH values are generally low, in the range 1-50 µg/l and more acidic waters are rising up to 500-1000 µg/l, the concentration greater than 700 µg/l Al it is toxic to fish [1]. The concentration 0.52 mg/l aluminum greatly reduces the growth of fish.

In seawater, the concentration of aluminum depends on the salinity of the water, normally is around 1-2 µg/l [2]. In the open oceans are aluminum concentration of about 0.5 µg/l [3].

Aluminum may be present in different forms, at a higher pH is dominated by ion $Al(OH)_4^-$, whereas the lower pH prevalent toxic Al^{3+} [4]. Higher concentrations of aluminum in surface water are in a period of high water levels, storm after rain or spring snowmelt in [5].

Aluminum levels in drinking-water vary according to the levels found in the source water and whether aluminum coagulants are used during water treatment [6]. In Germany, levels of aluminum in public water supplies averaged 0.01 mg/l in the western region, whereas levels in 2.7% of public supplies in the eastern region exceeded 0.2 mg/l. In a 1993–1994 survey of public water supplies in Ontario, Canada, 75% of all average levels were less than 0.1 mg/l, with a range of 0.04 - 0.85 mg/L. In a large monitoring program in 1991 in the United Kingdom, concentrations in 553 samples (0.7%) exceeded 0.2 mg/l. In a survey of 186 community water supplies in the USA, median aluminum concentrations for all finished drinking-water samples ranged from 0.03 to 0.1 mg/l; for facilities using aluminum sulfate coagulation, the median level was 0.1 mg/l, with a maximum of 2.7 mg/l. In another US survey, the average aluminum concentration in treated water at facilities using $Al_2(SO_4)_3$ coagulation ranged from 0.01 to 1.3 mg/l, with an overall average of 0.16 mg/l.

Despite its natural abundance, aluminum has no known function in biology. It is remarkably nontoxic, aluminum sulfate having an LD_{50} of 6207 mg/kg (oral, mouse), which corresponds to 500 grams for a 80 kg person [7]. Despite the extremely low acute toxicity, the health effects of aluminum are of interest in view of the widespread occurrence of the element in the environment and in commerce.

Some toxicity can be traced to deposition in bone and the central nervous system, which is particularly increased in patients with reduced renal function. Because aluminum competes with calcium for absorption, increased amounts of dietary aluminum may contribute to the reduced skeletal mineralization (osteopenia) observed in preterm infants and infants with growth retardation. In very high doses, aluminum can cause neurotoxicity, and is associated with altered function of the blood–brain barrier [8,9]. A small percentage of people are allergic to aluminum and experience contact dermatitis, digestive disorders, vomiting or other symptoms upon contact or ingestion of products containing aluminum, such as deodorants or antacids. In those without allergies, aluminum is not as toxic as heavy metals, but there is evidence of some toxicity if it is consumed in excessive amounts [10]. Aluminium in food may be absorbed more than aluminium from water [11].

Aluminium is presented at low concentration in foodstuff. It is being used in conservation of the food in a powder (instant coffee, milk-powder, firming agent for whipped cream, etc.). There is increased content of aluminium in the conditioner dough, tea leaves and in the drugs used against ill-digestion. Higher aluminium concentrations, that may toxically affect the organisms, enter the foodstuff by abrasion or by leaching of aluminium cookware.

Aluminium tocixocy is an serious factor that is limitating the growth of the plants and woody plants in the acid soils. Moreover, the toxicity of the aluminium is being expressed also in microorganisms and animals [12]. In a kidney function disorder diseases, the neurotoxical effects of aluminium on organism was proved. The utterances of aluminium intoxication represent the seizures, logagnosia and dementia utterances that is reffered to as Alzheimer's disease. Even if the opinions of the neuroendokrinologists are not completely united, they are affraid of water and food aluminium contamination may cause the emergence of Alzheimer's disease, which is the degenerative kind of disease related to reduction of the brain cells and by that also to decrease of brain functional capabilities, including the intelect.

There was recorded the aluminosis occurence in Germany (a severe lungs disease that is similar to silicosis). Aluminosis is caused by inhalant aluminium exposure or by alumina exposure. Moreover, in the presence of air the organometallic compounds of aluminium are self-igniting. The effect of aluminium organometallic compounds on the skin represents the epidermis irritation and after inhalation of these compounds the bleeding into lungs may occur. Encephalopathy (brain fever), osteodistrofia and anemia (increase in white blood cells) are among intoxication, which may be caused by aluminum. For alluminium salts toxicity determination, analogous to gallium and indium, the crutial point represents anion.Among the most toxic anions include Cl^-, NO_3^- and SO_4^{2-} [13].

The Regulation of the Government of the Slovak Republic No. 269/2010 sets the limit concentration for aluminum in surface water 0.2 mg/L, limit concentration for Al in streams intended for drinking water abstraction 0.2 mg/L in the category A1 (water requiring simple physical treatment and disinfection or rapid filtration and disinfection), 0.2 mg/L in the category A2 (water requiring physical-chemical treatment and disinfection, e.g. coagulation, flocculation, filtration and chlorine disinfection) and 1.0 mg/L in the category A3 (water requiring intensive physical-chemical treatment and disinfection, e.g. coagulation, flocculation, filtration, adsorption using active carbon, chlorine and ozone disinfection).

The Regulation of the Government of the Slovak Republic No. 496/2010 *establishing the requirements for water intended for human consumption and water quality monitoring* sets the permissible limit concentration 0.2 mg/L for aluminium in drinking waters. This limit complies with the recommendations of the WHO and the Council Directive 98/83/EU.

At the end of 80-ies were found in our deposit of natural zeolite with a high content of mineral zeolite - clinoptilolite in Nižný Hrabovec, in eastern neovol-canites. Besides this deposit, the Zeolite accumulations were discovered in the complex of the Central Slovakian neovolcanites, in the South – Western border of Kremnické vrchy and in Zemplínske pohorie on the territory of the Slovak Republic.

Natural zeolites were created by prolonged exposure of mineral alkaline solutions at different petrographic types of rocks of different ages at elevated temperatures. Not surprisingly, therefore, that these aluminosilicates bearings are close to hot dilute mineral or volcanic craters. Environment in which they were created, reflecting their structure and chemical composition. Zeolites are naturally not in a pure state, but usually in conjunction with other minerals and rocks that are part of them. Every deposit contains a rock of specific mineralogical composition.

Mineralogical and chemical analysis of Zeolitic material – Clinoptilolite is stated in Table 1 and Table 2.

Table 1

Mineralogical analysis of Zeolite from deposit Nižný Hrabovec [14]

Mineral	Content [%]
Clinoptilolite	84
Cristobalite	8
Feldspar	3-4
Illite	4
Quartz	Traces
Minerals of carbonates	Traces (<0.5 %)

Table 2
Chemical analysis of Clinoptilolite from deposits Nižný Hrabovec [14]

Compound	Content [%]
SiO_2	66.4
Al_2O_3	12.2
K_2O	3.33
CaO	3.04
Fe_2O_3	1.45
MgO	0.56
Na_2O	0.29
MnO	0.02
TiO_2	0.15
P_2O_5	0.02
Loss by ignition	12.2

The primary structural unit of the zeolite is an octahedron, formed of silicon and aluminum atoms with oxygen atoms coordinated tetratedricky. Representation of silicon and aluminum to oxygen is usually 1:2. This creates the crystal structure of relatively large cavities interconnected channels, which effectively averages range from 0.2 to 0.7 nm, and the total volume is empty space as 20 to 50% of the mineral. These cavities are stored mobile single or divalent cations of alkali metals and alkaline earth metals (Ca, K, Na) are surrounded by water molecules, which can be exchanged for other from the surrounding solution [15,16].

Wide range of uses of natural zeolites in various sectors of the economy is determined by their structure and physicochemical properties. One of the most important properties of zeolite minerals is their catalytic properties, the ability to exchange ions and adsorb organic or inorganic molecules of certain sizes [17,18].

In the last decades the Zeolitic mineral – Clinoptilolite has started to be also used in drinking water treatment. Zeolites are not to be found in the grained condition in the natural deposits, and before their use, Zeolites require crushing and sorting at the required fractions in the waterworks engineering. Sufficient mechanical strength, chemical stability and abrasion values, by which, though, they are classified among the soft filtering materials, and which permit to use the natural Zeolites as a filtering material [19].

Table 3
Filtration materials and some of their parameters

Material	Clinoptilolite	Filtration sand	Activated carbon
Grain size [mm]	0.3 – 2.5	0.3 – 1.0	0.3 – 1.5
Specific weight [$g.cm^{-3}$]	2.39	2.66	2.19
Apparent density [$g.cm^{-3}$]	0.84	1.55	0.40
Porosity [%]	64.8	41.7	81.7
Abrasion [%]	8.2	0.57	39.08

The specific weight of Clinoptilolite is lower as compared with the siliceous sand, and porosity and sludge capacity exceeds by 1.5-times the values of filtering sand. Clinoptilolite in combination with siliceous sand is more effective in elimination of Fe, Al, NH_4, etc. During slow sand filtration it enabled increasing the filtration speed up to quadruply. Clinoptilolite as compared with the classical materials used in the dressing and reparation engineering, has got the properties, which predestine it for utilization in the water treatment processes, and it meets the demands made upon the granular filtering materials.

2. Experimental

2.1Aluminium sorption using inorganic natural sorbents

The model laboratory experiments we observed sorption of aluminum on two natural sorbents of inorganic and organic origin. In our experiments we tested the natural zeolite - clinoptilolite, and compared the sorption capacity of the sorption capacity Penicillium glabrum.

Adsorption was studied for different initial concentrations of the aluminum in water.

A milled clinoptilotite of 1,2-1,6 mm granularity from Nižný Hrabovec deposite was used for alluminium sorption monitoring. The process of adsorption was discouous. The water containing Alluminium (400 ml) was in a contact with adsorbent for a certain period of time (**Table 4**, **Fig.1**). Solution of the monitored substance, c_o=50 mg.l^{-1} initial concentration, was mixed up with 100 g of clinoptilolite in a jar equipped with mixer. Samples were taken away in a certain latency and the alluminium content of the samples was subsequently analysed.

2.2 Aluminium sorption using organic natural sorbents

Three fungus tripes were used in monitoring of the alluminium sorption from water environment on a organic sorbent. *Penicillium glabrum* is one of the worldwide species [20]. It was isolated from various substrates, from a soil, plants, cereals, flavourings, wood mass, paper, composts, texture substances, fuelling and also from natural water, drinking and waste water [21-23]. Its occurence in air microflora is seasonal and this occurence was noticed also in a radioactive environment of the uran mines. The species, that were we working with it, was isolated from a moisty environment of drinking - water treatment plants. During testing the growing of some micromycetes, that were isolated from treatment plants, on a cultivation media containing zinc and alluminium, we have noticed the same growing rate of *P. Glabrum* species in both types of media - non-alluminium and alluminium containing media.

We inoculated this species by spore inoculation to the Roux flasks with a Sabouraud media (SAB) in which we added the solution of alluminium sulphate that way as the final alluminium concentration in particular flasks was : 65, 125, 250, 500 and 1 000 mg.l^{-1}.

Flasks were incubated at the day-light and laboratory temperature for 3 months. The growth of the *Penicillium glabrum* in the experimental flasks with alluminium sulphate lasted initially for 7-9 days and in consideration with the control sample, this growth was slowed-down, than the growth rate and the character of the growth of the experimental samples were in equivalence with the control samples in such way, no difference in mycelium mass increase and in sporulation was noticeable. After the end of the experiment the biomass was filtered out and dried at 105°C.

Dried biomasses as well the cultivation media filtrates were mineralized with the same measures, in HNO_3 environment, at the temperature of 300°C and the pressure of 130 bar in a high-pressure decomposition system HPA-S company of Anton Paar (Austria).

3. Results and discusion

The results of the alluminium sorption from water environment on the inorganic sorbent (clinoptilolite) for the initial alluminium concentration of 50 mg.l^{-1} are shown in the Table 4 and Fig. 1.

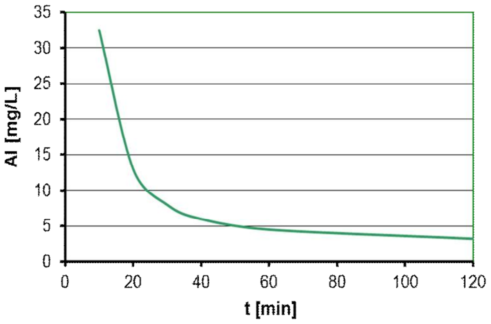

Fig. 1 Relation of alluminium concentration on the time, after the zeolite addition

Table 4
The removal of aluminium from water by using clinoptilolite

t [min]	10	20	30	40	60	120
c_m [mg/l]	32.5	13.0	8.0	6.0	4.5	3.5
η[%]	35.0	74.0	84.0	88.0	91.0	93.0
a_t [mg/g]	60	148	168	176	182	186

Instanteneous adsorption capacity a_t (1) and adsorption efficiency (2) we calculated by the following formula:

$$a_t = \frac{(c_0 - c_m)V}{m} \text{ [mg/g]} \quad (1)$$

$$\eta = \frac{(c_0 - c_m)100}{c_0} \text{ [\%]} \quad (2)$$

where c_0 (mg/l) represents the alluminium concentration before adsorption, c_m (mg/l) represents the alluminium concentration after adsorption at the time t, V (l) represents a volume of the water solution of the polutant, m (g) represents the weight of the adsorbent, η (%) represents the adsorption efficiency, a_t (mg.g^{-1}) represents the instanteneous adsorption capacity; the amount of the polutant which is adsorbed on the mass unit of the adsorbent at a time. AES –ICP was used for analysis of the alluminium content in the biomass samples and in media after the mineralisation. Results are shown in Table 5.

According to the results presented by Table 5 it is obvious that considering the biomass growth (1,8-2,0 g) of the experimental samples and the growth of control samples, the growth of experimental samples was not inhibited (2,1 g) in fact.

Initial pH value 4.5 of the growing solution has been changed in all the samples, during the cultivation.

Whereas the control medium stayed at the acidic reaction pH 5.2 during and also after the experiment, the pH value of the experiment samples has increased up to the neutral positions of pH spectrum (6.9-7.8). This fact may mean an active defence of *Penicillium glabrum* against a toxic effect of the alluminium, as it is known that in general the toxicity is being significantly decreased in neutral environment.

The differencies between the concentrations of the alluminium that is being added to experimental samples from adulterated stock solution and the measured alluminium concentrations can be explained by higher sensitivity and accuracy of the measuring device and AES-ICP method (in consideration with the other used and trace concentrations of the alluminium in used chemicals – were not included in added dose).

We noticed an non-inhibited growth of *Penicillium glabrum* in our laboratory experiments. This growth was noticed in a total testing range of high $Al_2(SO_4)_3$ concentrations, see (Tab.5) and in fact its complete (100%) sorption on a mycelia biomass. It is an interesting finding, in regard to the general knowledge, that alluminium is toxical when it is presented at the higher concentrations.

Table 5

Alluminium accumulation in a biomass of Penicillium glabrum

			SAMPLES					
			Control	1	2	3	4	5
Growing medium	Before the inoculation pH		4.5 ± 0.1					
	After the cultivation pH		5.2	6.9	7.2	7.3	7.8	7.5
	$Al_2(SO_4)_3$	added [mg.l^{-1}] Al	0	1000	500	250	125	65
		Measured after kultivation v [mg.l^{-1}] Al	0 ± 3.6					
Biomasa	Total dry mass [g] pri 105 °C		2.10	1.90	1.89	1.80	2.00	1.95
	Dose of dry mass for analysis		0.232	0.244	0.253	0.232	0.189	0.195
	Al [mg.l^{-1}] measured		2.867	141.4	78.83	38.78	13.75	8.341
	Al [mg.l^{-1}] adsorbed from the solution and adjusted for total biomass		4.5	1007	506	259	128	67

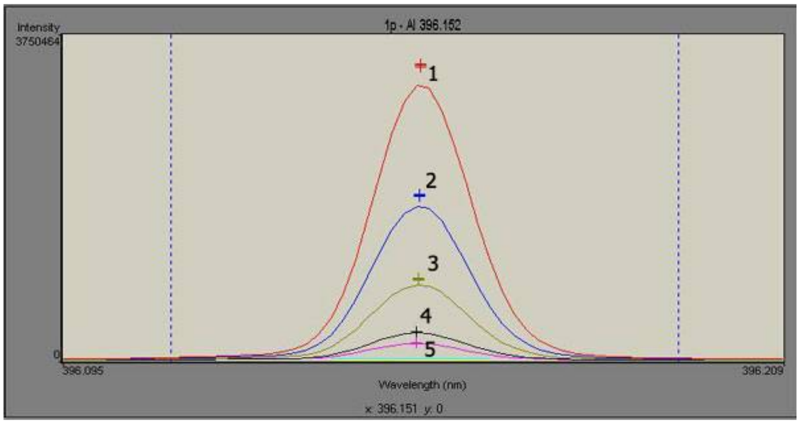

Fig. 2 Alluminium content in the biomass, method of AES analysis with inductance-coupled plasma as the driving source, after the mineralisation of the samples (1-5) in hydrogen nitrate in high-pressure decomposition system HPA-S company A. PAAR (Austria).

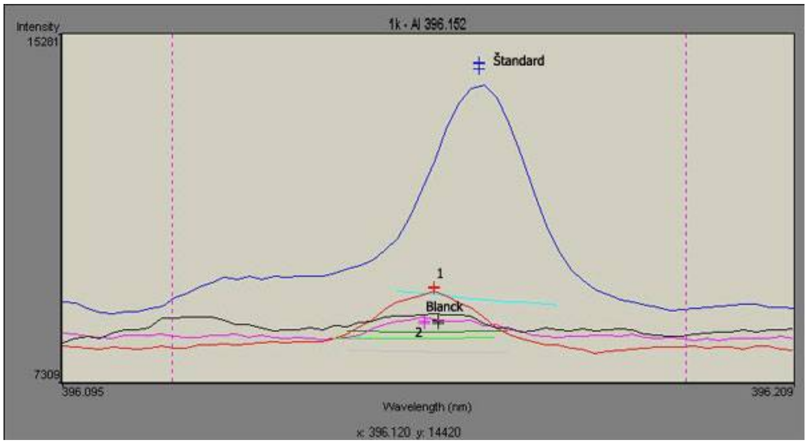

Fig. 3. Alluminium content in growing media no.1 and no.2, after the grown biomass separation, determined by AES-ICP method and the consideration with the standard and blank

Although many of the authors in Slovakia and abroad deal with the sorbtion characteristics of filamentous micromycets, especially in terms of the case of heavy metals and cations of the toxic and radioactive elements [24,25].

4. Conclusion

At this experiment work was tested two natural sorption materials of inorganic and organic origin in removal of aluminium from water. Sorption capacity of natural zeolite – clinoptilolite was compared with sorption capacity of organic material *Penicilliumglabrum*, one of the worldwide species. Adsorption tests were studied for different initial concentrations of the aluminum in water. Clinoptiloliteachieved 93 % efficiency after two hours of contact with water containing aluminium, *Penicilliumglabrum* needed longer time – from seven7 to 9 days to achieve 100% efficiency. Results obtained from laboratory experiments shown, that both tested materialsclinoptilolite and *Penicilliumglabrum*effectively removed aluminium from water.

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