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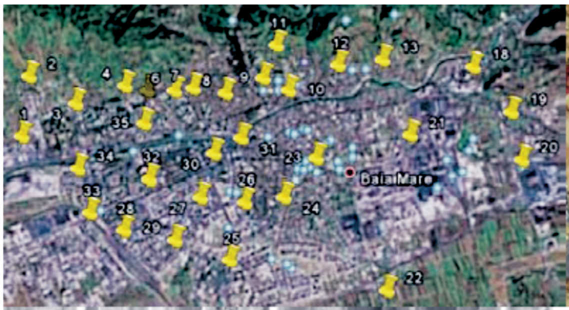

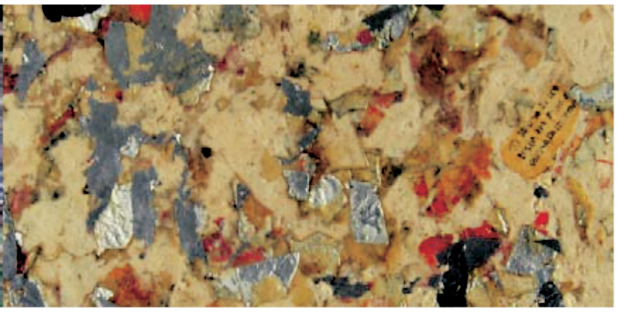

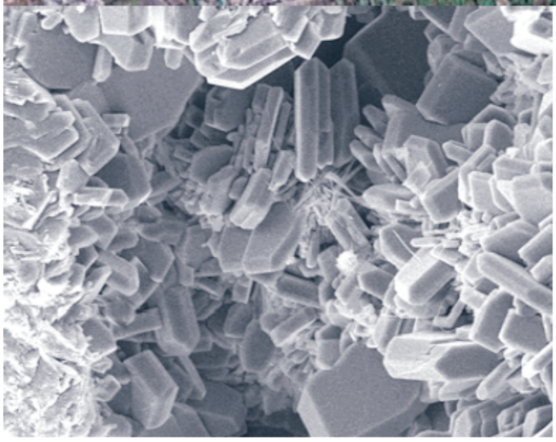

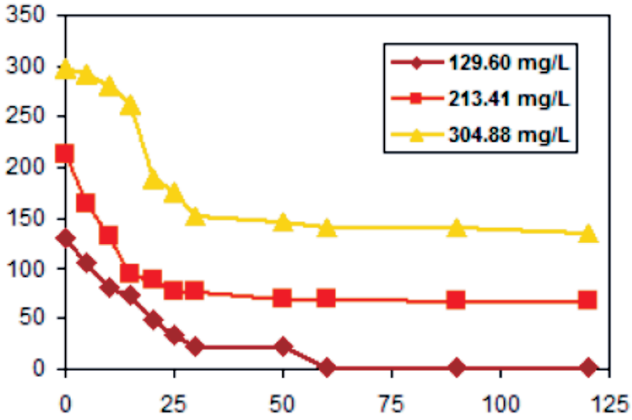

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This issue contains extended abstracts of talks given at the first TECHNIQUES OF CHEMICAL AND BIOCHEMICAL REMEDIATION CONFERENCE (BIOREMED) (September, 20-22, 2007) organized at the Faculty of Chemistry and Chemical Engineering of the "Babes-Bolyai" University.

We thank again all participants for their valuable contributions, and we particularly thank those who agreed to publish their abstracts in this journal.

Prof. Dr. Luminița Silaghi-Dumitrescu

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Fe/ZVT CATALYSTS FOR PHENOL TOTAL OXIDATION

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ABSTRACT. Zeolitic volcanic tuffs collected from Aluniş (A-ZVT) area (Cluj County, Romania) modified by ionic exchange with iron ions were tested, as catalysts, in the wet air oxidation process in order to remove phenol from synthetic wastewaters. The zeolitic volcanic tuff samples used as support for the oxidation catalysts were characterised by means of optical microscopy, scanning electron microscopy (SEM), X ray diffraction (XRD), chemical analysis and Fourier transformed infrared spectroscopy (FTIR). In order to realize phenol catalytic wet air oxidation we used a synthetic solution containing 1g phenol/dm^3 (100 cm^3), which was contacted with 4 grams of Fe/ZVT catalyst in a batch reactor with magnetic stirring. Air was introduced in the reactor using a glass frit at different flow rates. Effect of reaction conditions, temperature and air flow rate, over the phenol conversion and the overall efficiency of the oxidation process were investigated. With the increase of temperature and air flow rate we observed an increase of the oxidation process efficiency. Activation energy was also calculated.

Keywords: *zeolitic volcanic tuff, clinoptilolite, wastewaters, phenol, catalytic wet air oxidation (CWAO)*

INTRODUCTION

Pollutants removal from wastewaters and water disposal in nature or recycling in the economic circuit is one of the main strategies applied to avoid environmental pollution.

Effluents containing organic pollutants from chemical, petrochemical or pharmaceutical industries can create many problems in choosing an appropriate method to remove them. Many times, concentration of these pollutants is too small to make recovery profitable but too high to be treated by conventional methods. Between pollutants, which create problems due to their difficulty to remove by conventional methods (mechanical and biological treatment) are refractory organic pollutants [1-3].

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Because of their toxicity and the frequency of their presence in industrial wastewaters, phenol and phenolic compounds have gained increased attention in the last two decades. Moreover, phenol is considered to be an intermediate in the oxidation route of higher molecular weight aromatics and so usually is taken as a model compound in research studies [4].

Phenol is produced through both natural and anthropogenic processes. It is naturally occurring in some foods, in human and animal wastes, in decomposing organic material and it is produced endogenously in the gut from the metabolism of aromatic amino acids. Currently, the largest use of phenol is as an intermediate in the production of phenolic resins (which are used in the plywood, adhesive, construction, automotive, appliances industries), synthetic fibbers (nylon) and as epoxy resins precursors. Phenol is toxic to bacteria and fungi, and is used as a slimcide and disinfectant. The greatest potential source for exposure to phenol is in the occupational setting, where phenol is used in manufacturing process. People are also exposed via consumer products, such as medicines and lotions, some foods and tobacco smoke. Phenol was also found in drinking water. Phenol is readily adsorbed by the inhalation, oral and dermal routes. Once adsorbed, phenol is widely distributed in the body [5]. A wide range of adverse effects has been reported following well-documented human exposure to phenol. Gastrointestinal irritation has been reported following ingestion. Local effects following dermal exposure range from painless blanching or erythema to corrosion and deep necrosis. Systemic effects include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects (including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion (death occurred within 10 minutes). Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

Adequate human data on the carcinogenicity of phenol are not available [6]. Aquatic life can also be affected if wastewaters containing phenol are discharged in surface waters. At extremely low phenol values, there are two effects apparent in phenol-contaminated waters: toxicity to aquatic life, and the generation of an unpleasant taste in fish and shellfish [7].

Different methods for treating industrial wastewaters containing organic pollutants, including phenol, have been reported. The choice of treatment depends on the concentration, economics, efficiency, easy control and reliability [8].

Several processes for phenol removal have been studied, such as adsorption-floculation [9], adsorption on activated bentonites [10], activated carbons [11], membrane-based solvent extraction [12], separation techniques using composite membranes [13], electrochemical treatment [14-15], sonochemical processes [16], biodegradation [17, 18], photochemical degradation [19,20], wet air oxidation [21], advanced oxidation processes [22-24] and supercritical water oxidation [25].

Chemical oxidation with all its alternatives is widely used for treatment of wastewaters in order to remove organic pollutants, and has as final objective the mineralization of the organic contaminants to CO_2, H_2O and inorganics or, at least at their transformation into harmless products [22].

A reference parameter in case of using chemical oxidation as treatment process is the chemical oxygen demand (COD). Only waters with relatively small COD contents ($< 5 g\cdot L^{-1}$) can be suitably treated by means of advanced oxidation processes (AOP) since higher COD contents would require the consumption of too large amounts of expensive reactants. In those cases, it would be more convenient to use wet oxidation or incineration. Wastewaters with COD higher than $20\ g\cdot L^{-1}$ may undergo with wet oxidation, while those with COD $> 200\ g\cdot L^{-1}$ are suitable for incineration [26].

Many of the oxidation processes are catalytic processes and are used for the oxidation of organic pollutants in dilute aqueous solutions, using air or oxygen as oxidation agent. Non-catalytic aqueous-phase oxidations requires long residence times and relatively severe temperatures (200-450°C) and pressures (70-250 atm) [27], therefore the catalytic processes become useful alternative processes. Catalysts used to destroy, organic pollutants including phenol, comprise Ru, Rh, Pt, Ir, Ni, Ag supported on TiO_2, CeO_2, Al_2O_3 [27, 28], metal oxides CuO, CoO, Cr_2O_3, NiO, MnO_2, Fe_2O_3, ZnO, CeO_2 [8, 27, 29, 30] and activated carbon [31]. Synthetic zeolites [32, 33], pillared clays [34, 35], on which iron or copper ions are immobilised, are also used as efficient catalysts for total phenol oxidation.

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium). They have a particular crystal structure of a tectosilicate-type, characterised by pores with larger size than those of the ions (molecules) that pass through. Mono- and divalent cations such as Na^+, K^+, Ca^{2+} or Mg^{2+} compensate the negative charge that exist in the zeolite crystalline network due to isomorph replacement of silicon (IV) with alumina (III). These counter ions are mobile and can be total or partial exchanged during ionic exchange processes [36-38].

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Zeolites - both natural and synthetic, may be used as ionic or molecular filters due to this particular micro-porous structure.

Zeolitic volcanic tuff is the main rock-type containing zeolites. These volcanoclastic deposits contain the largest concentrations of zeolites, which result from the transformation of magmatic products such as volcanic glass and primary aluminosilicate minerals [39].

Clinoptilolite is a hydrated aluminosilicate member of the heulandite group and it is one of the more useful natural zeolites. Applications for clinoptilolite-bearing rocks include use as additives to cement, deodorization of ammonia-polluted environments [40], treatment of municipal and industrial wastewaters [41], and preparation of lightweight aggregates [42]. Clinoptilolite is well suited for these applications because of its large amount of pore space and ionic exchange capacity, and because of its high resistance to extreme temperatures and its chemically neutral basic structure.

The best represented zeolite species in altered volcanic tuffs from Romania are clinoptilolite; besides mordenite, natrolite, phillipsite, laumontite, stilbite, and analcime were also identified, but in lower quantities.

The aim of this work was to modify a zeolitic volcanic tuff from Aluniş (Cluj County), by ionic exchange with iron ions in order to test it as catalysts for phenol catalytic wet air oxidation (CWAO). We used two samples from the area mentioned before, labelled A1 and A8. Preliminary tests performed on both samples showed that the results are quite similar. Therefore this paper presents the results obtain for the A8 zeolitic volcanic tuff sample, a fine-pelitic tuff, with a relative homogeneous composition and structure.

EXPERIMENTAL SECTION

Zeolitic volcanic tuff compositional investigations

Natural zeolitized volcanic tuffs were collected from Alunis area (Cluj County). The pyroclastic rocks belong to the Dej Tuff Complex, of a Lower Badenian age. The main petrographical component of this complex is represented by white and grey volcanic tuff that may be interlayered with clays, marls and clayey sandstones [43]. Most of the tuffs from the studied area have a vitric texture and are extensively altered. The intensive alteration processes – mainly represented by zeolitization, silicification, bentonitization, and calcification – that affected these tuffs, locally led to the formation of economically valuable accumulations.

At Aluniş, the Dej Tuff is present as polysequential sedimentary rhythms characterized by several granulometric types building up a normal succession that point up to a pulsating volcanic activity. The rocks are white in colour and the texture is either compact or vacuolar.

Representative samples from Aluniş (Cluj County) were investigated by using optical microscopy, scanning electron microscopy (SEM), X ray diffraction (XRD), chemical analysis and Fourier transformed infrared spectroscopy (FTIR).

The petrographic observations were made using an optical microscope (Zeiss AxioLab) on thin sections. The study was focussed on the identification of the different mineralogical phases, on their quantification, and on the structural description of the material. The micromorphological features of the zeolitic tuffs were examined in silver-coated, fresh surfaces of the selected samples with a JEOL JSM 5510LV scanning electron microscope (SEM).

The chemical analyses on bulk rocks were performed at ICEI Cluj-Napoca using usual analytical methods for silicate materials [44].

The X-ray diffraction analyses were performed on a Siemens Bruker, with Cu Kα anticathode. The diffractograms were recorded from 10°to 70°2 θ. The analytic conditions were 40 A, 40 kV, step of 2 degrees.

Fourier transformed infrared spectra were realised on a JASCO-615 apparatus on 400-4000 cm^{-1} domain, resolution 2 cm^{-1}.

Catalyst preparation

A zeolitic volcanic tuff sample from Aluniş (Cluj County), A-ZVT, granulation d < 0.2 mm, brought in –Na form was contacted with a solution containing iron ions in order to obtain the desired catalyst – Fe/ZVT.

The stages involved in the zeolitic volcanic tuff preparation are as follows: crushing, grinding, size separation, washing with distilled water, drying at 105°C for 6 hours, treatment with 1M HCl in a stirring reactor with a zeolite : acid solution ratio of 1:10, washing with distilled water to pH = 7 and finally drying at 105°C for 6 hours. At the end of this sequence we obtained the zeolite in -H form (Z-H). Also, during the treatment with HCl, zeolite channels are cleaned and pores opened [45]. To bring the zeolite in -Na form which proved to be more efficient in the ionic exchange process [45-48], the zeolititic volcanic tuff sample was subjected subsequently to an alkaline treatment with a strong Na^+ solution (1M NaCl solution brought to pH = 10 with a 1M NaOH solution) according to equation (1). After the alkaline treatment the zeolitic volcanic tuff sample was washed again with distilled water to pH = 7 and dried for 6 hours at 105°C.

$$\text{Z-H} + \text{NaCl} \rightleftharpoons \text{Z-Na} + \text{HCl} \tag{1}$$

The zeolite prepared as described before was subsequently brought in Z-Fe form using a $FeSO_4{\cdot}7H_2O$ 0.5N solution. The ionic exchange process, equation (2), was realised in a batch reactor in static regime using 35 g zeolitic volcanic tuff in –Na form and 70 ml solution containing iron ions. Solid and solution were kept in contact for 24 hours. After impregnation, iron modified zeolitic volcanic tuff sample was separated by filtration, dried for 6 hours at 105°C and then calcinated at 400°C for 4 hours. We obtained in this way the wet air oxidation catalyst, containing 0.33 mg Fe/g solid, labelled Fe/A-ZVT. The initial and final concentration of iron ions in the solution was determined using $KMnO_4$ volumetric method.

$$2\text{Z-Na} + \text{Fe}^{2+} \rightleftharpoons \text{Z}_2\text{-Fe} + 2\text{Na}^+ \tag{2}$$

Catalytic wet air oxidation – operating conditions

Phenol total oxidation, catalytic wet air oxidation (CWAO), was carried out in a thermostated stirred batch reactor (magnetic stirrer) at atmospheric pressure, using different air flows (20, 40 and 60 L/h) and temperatures of 20, 40 and 60°C. In the reactor were introduced 4 g of Fe/ZVT catalyst and 100 cm^3 phenol solution, containing approximately 1 g phenol/dm^3. Phenol was measured with $KBrO_3$-KBr in excess of KI in acidic medium (bromate-bromide method). The initial concentration of phenol was determined to be 1.05 g/dm^3. During the experiment phenol determination was carried out every 1 hour. Also, we determined the chemical oxygen demand using CCO-Mn method. The experiment was carried out for 360 minutes.

The evolution of phenol oxidation process was followed by means of phenol conversion (calculated from values of phenol concentration at a moment *t* and initial concentration of phenol, equation 3) and overall oxidation process efficiency calculated using chemical oxygen demand values (as CCO-Mn).

$$X_{phenol} = \frac{C_i - C_t}{C_i} \cdot 100 \qquad (3)$$

where,

C_i is the phenol initial concentration, in mg/L
C_t is the phenol final concentration, in mg/L.

RESULTS AND DISCUSSIONS

Petrographic results

The volcanic tuffs from all the beds cropping out in the study area have mostly a vitric and vitric crystal texture and they are zeolitized.

The rocks consist of 70-85% volcanic glass, 15-25% crystals, and lithic fragments in subordinate amounts (2-3%). Petrographically the samples can be defined as rhyodacitic tuffs.

The main component is represented by volcanic glass as fragments with angular edges (glass shards). Pyrogenic crystal fragments include quartz, K-feldspar, acid plagioclases, biotite, hornblende and opaque minerals (figure 1). The quantitative composition is as follows: zeolites 65%, quartz 7%, phyllosilicates 5%, feldspars 8%.

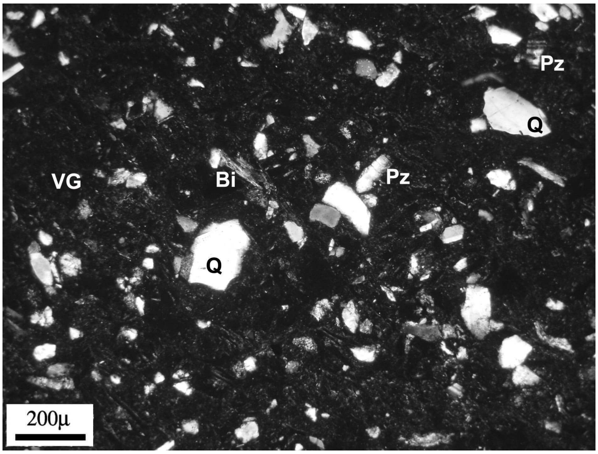

Figure 1. Details of the vitric crystal tuff from Aluniş (Cluj County), N+, optic microscope, polarized light; Q = quartz, Pz = plagioclase, Bi = biotite, VG = volcanic glass.

Significant amounts of volcanic glass in the pyroclastic sequence from Aluniş have been replaced by zeolites (between 60-70%), which consist mainly of clinoptilolite (figure 2).

These alterations are attributed to the diagenesis of the volcanic glass (vitreous matrix and glass shards) into zeolite minerals, opal-CT and probably clay minerals.

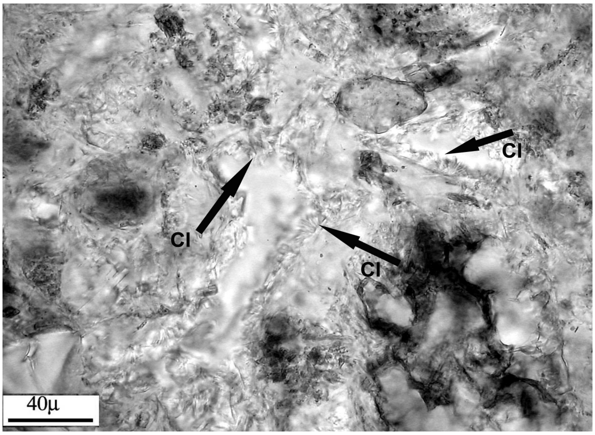

Figure 2. Pseudomorphic replacement of a glass shard by zeolites (clinoptilolite); vitric crystal tuff, Aluniş (Cluj County), 1N; optic microscope, polarized light Cl = clinoptilolite.

Scanning electronic microscopy (SEM) shows that the tuff commonly contains crystals of clinoptilolite of micron- and submicron- size or as larger crystals in the pores or voids (figures 3, 4). The zeolite crystals are about 2-10 microns in size; rarely do they reach 40-50 microns. Subordinately fibrous crystals of mordenite and opal-CT spheres occur (figure 3).

Opal-CT forms thin bladed crystals that aggregate locally into small lepispheres and commonly coexist with clinoptilolite.

Some clusters of a fibrous mineral are present with clinoptilolite and opal-CT. There is no specific evidence in the XRD pattern, probably due to the low quantities, but the fibrous habit suggests that the mineral is most likely mordenite.

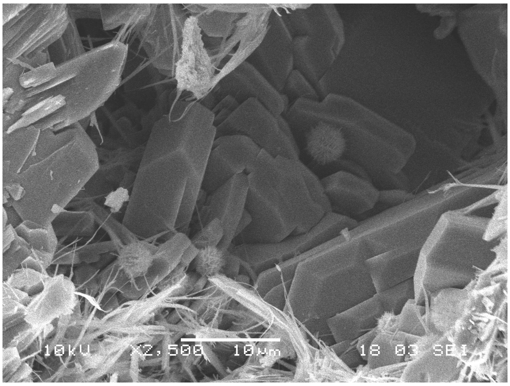

Figure 3. SEM image of a tuff sample from Aluniş (Cluj County). Tabular clinoptilolite crystals with minor amounts of fibrous crystals (most likely mordenite); Opal-CT lepispheres rarely occur (central, down left).

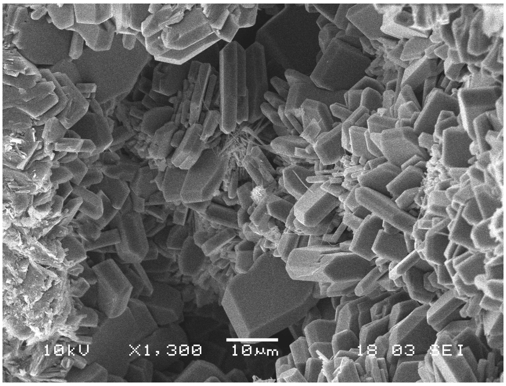

Figure 4. SEM image of a tuff sample from Aluniş (Cluj County). Clinoptilolite euhedral tabular crystals.

The X-ray diffraction patterns obtained on random powders of the whole material show the massive presence of clinoptilolite as the main zeolite species (figure 5). The semi-quantitative estimation from the X-ray diffractograms indicates that the zeolites reach between 60% and 70% from the crystallized fractions of the tuff from Aluniş. According to the microscopic observations, other minerals identified are quartz, feldspar, and clay minerals.

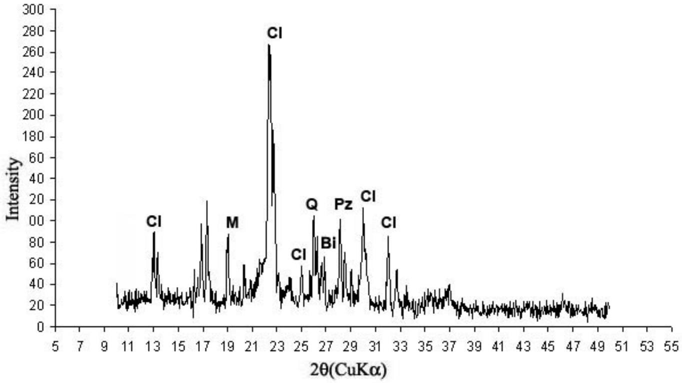

Figure 5. Powder X-ray diffractogram of a volcanic tuff sample from Aluniş (Cluj County); Cl = clinoptilolite, Pz = plagioclase, Q = quartz, Bi = biotite, M = montmorillonite.

The bulk chemical analyses performed on tuff samples are presented in table 1. The chemical composition is very similar with that of samples of volcanic tuffs from other occurrences that belong to the Dej Tuff Complex in Cluj County. The high concentration of secondary and hydrated material (zeolite and clay minerals) is indicated by the high values of L.O.I (loss of ignition), 14.23%. Considering an average 15% L.O.I., attributed mainly to the zeolitic minerals, the amount of clinoptilolite in the samples from Aluniş may be estimated around 60%.

Table 1.

Chemical composition of the zeolitic tuff from Aluniş (Cluj County).

Oxides, [%]	**SiO_2**	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**L.O.I.**
Aluniş	62.06	0.34	14.07	1.61	5.72	0.96	0.35	0.86	14.23

FTIR spectra of the zeolitic volcanic tuff sample, figure 6, indicates the presence of specific zeolite peaks [49, 50]. Were identified peaks corresponding to O-H bond stretching (3446.17 cm^{-1}), angular deformation of H-O-H

(1635.34 cm^{-1}), an intense band of T-O asymmetric stretching (1064.51 cm^{-1}), three weaker bands of T-O external symmetric stretching (794.53, 721.26 and 669.18 cm^{-1}), a medium intense band (605.54 cm^{-1}) corresponding to external vibrations of tetrahedrical units coupled in rings and a peak corresponding to O-T-O angular deformation (464.76 cm^{-1}); T indicates the tetrahedrical position of Si and Al.

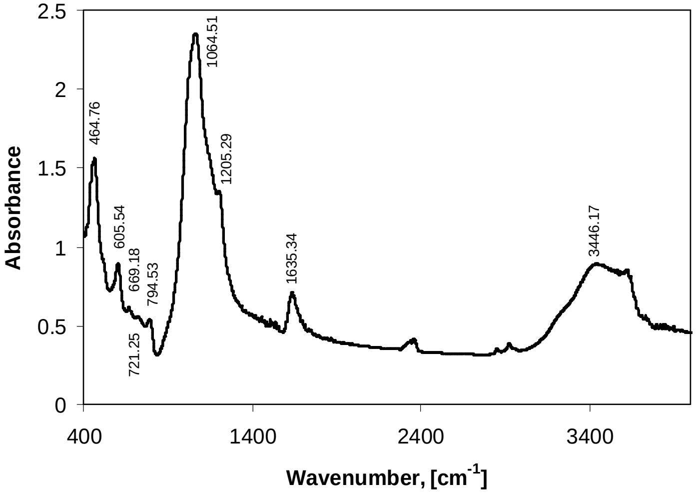

Figure 6. FTIR spectra of a tuff sample from Aluniş (Cluj County).

The volcanic tuffs from Aluniş formed due to the cementation of the explosive products of acidic and subordinately intermediary character, during the explosive stage of the Tertiary volcanism [43].

The process of zeolitization, of a sin- and diagenetic nature (halmyrolysis), took place in a marine, alkaline environment at a pH > 7, and it was a one-way process: primary material (glass, crystalloclasts) → zeolites [51]. It was mainly the volcanic glass that was substituted by zeolites, due to its high instability in the marine environment. The resulted zeolitic species were dependent on temperature, pressure and the variable chemical parameters, such as Si:Al ratio, Ca^{2+}, Na^+ and K^+ ratios and the pressure-dependent H_2O (P_{H2O}) and CO_2 (P_{CO2}) activities [51].

The amount of zeolite is directly correlated to the original amount of volcanic glass. Based on mineralogical (XRD and SEM) analyses, the studied volcanic tuffs from Alunis contain exclusively the zeolite clinoptilolite (heulandite group).

The petrographic and chemical analyses of the vitric tuff from Alunis suggest that zeolite may reach up to 65% of the whole rock. Glass shards have been leached and the resulting molds are partly filled by clinoptilolite crystals (figures 3, 4). This suggests that the processes of zeolitization involved direct dissolution of glass and precipitation of clinoptilolite. The opal-CT represents, probably, the silica that was left over after the formation of zeolite from the glass shards, which being of acid composition, are silica rich (> 60% SiO_2).

Catalytic wet air oxidation results

Phenol catalytic wet air oxidation was conducted at: (a) a constant oxygen flow rate of 20 L/h and different temperatures of 20, 40, 60℃, and (b) a constant temperature of 20℃ and different air flows of 20, 40, 60 L/h.

The influence of operating temperature over the phenol concentration variation in time is presented in figure 7. As expected, phenol concentration decreases significantly with the increasing of the temperature. In case of the operation at 20 and 40℃ phenol concentration drops from the initial 1.05 g/dm^3 to 0.7 and 0.5 g/dm^3, while in case of the higher temperature (60℃) a steep drop down to 0.06 g/dm^3 was recorded. The presented values are calculated after a reaction time of 360 minutes. Maximum values for phenol conversion for the three temperature used in the phenol oxidation process are presented in figure 8. The highest phenol conversion value was 94.03%, obtained at 60℃.

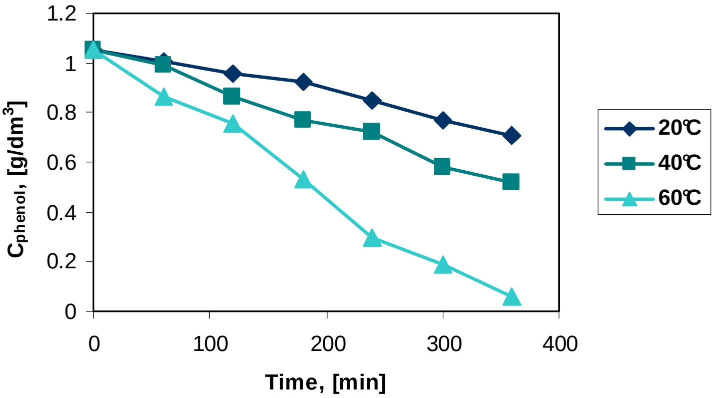

Figure 7. Concentration of phenol as a function of time at different temperatures and constant air flow rate, 20 L/h.

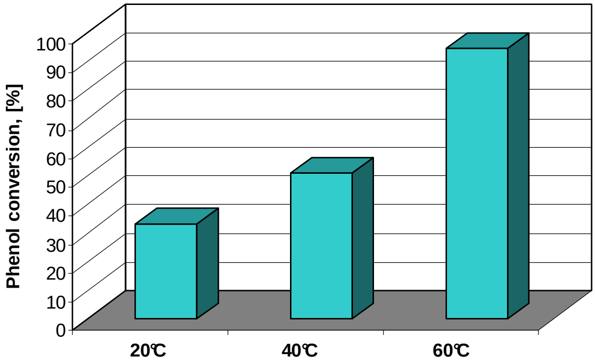

Figure 8. Maximum conversions for phenol CWAO at different temperatures and constant air flow rate, 20L/h.

Variation of phenol concentration in time, when different air flows were used is presented in figure 9. The decrease of phenol concentration is not as steep as in the case of temperature variation. After 360 minutes the final concentration reached for the three air flows are as follows: 0.7, 0.6 and 0.4 g/dm^3, respectively for 20, 40 and 60 L/h faced to the initial

1.05 g/dm^3 concentration. The maximum value obtained for phenol conversion in this case was 56.72%, figure 10, therefore we can conclude that an increase of the flow rate will lead to a small increase in the phenol oxidation process efficiency.

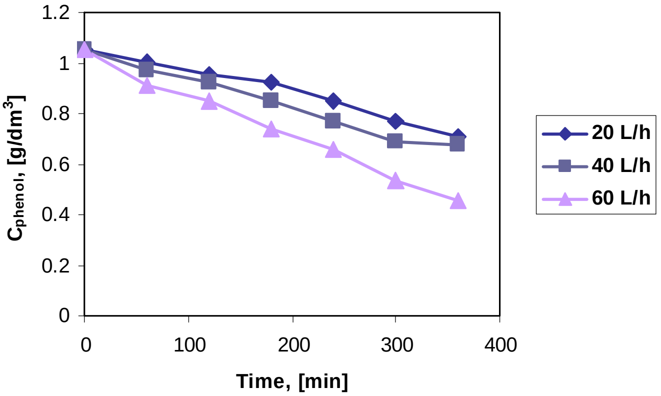

Figure 9. Concentration of phenol as a function of time at different air flow rates and constant temperature, 20℃.

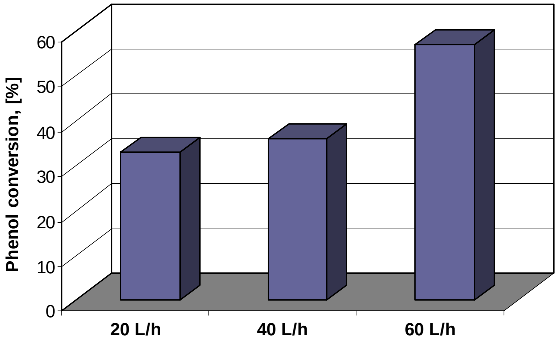

Figure 10. Maximum conversions for phenol CWAO at different air flow rates and constant temperature, 20℃.

During the oxidation process we also determined the chemical oxygen demand as CCO-Mn and we calculated the overall efficiency of the oxidation process using the CCO-Mn values, as mg $KMnO_4/dm^3$, calculated during the process. If we compare phenol conversion values with overall efficiencies, figure 11, we can conclude that phenol oxidation took place with formation of oxidation secondary products. This effect is more important at lower temperatures, 20 and 40℃, where phenol conversion is higher that overall efficiencies. At 60℃, phenol and other oxidation products are removed in proportion of 94, respectively 93%.

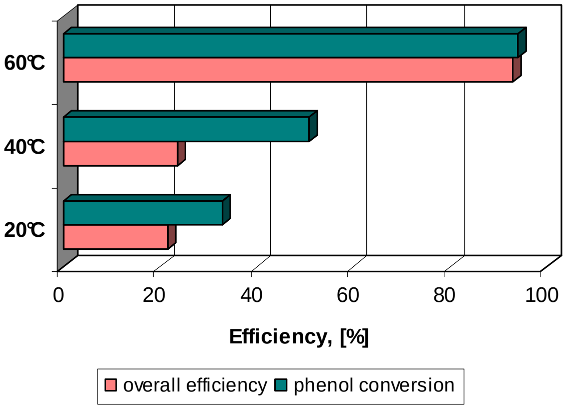

Figure 11. Maximum values for overall efficiency of the oxidation process, after 360 minutes at different temperatures and constant air flow rate, 20L/h.

Assuming a first order kinetic for the phenol removal, we used these results to calculate rate constants and activation energy. From the slopes of the kinetic curves for phenol catalytic wet air oxidation, figure 12, log[1/(1-X_{phenol})]=f(t), we calculated the rate constants for phenol removal. Results are presented in table 2.

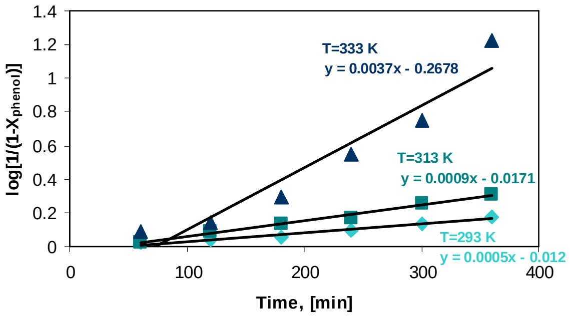

Figure 12. Kinetic curves for phenol catalytic wet air oxidation on Fe/A-ZVT.

Table 2.

Rate constants for phenol removal on a Fe/ZVT catalyst.

T, K	k, min^{-1}	1000/T, K^{-1}	lnk
293	0.5×10^{-3}	3.4129	-7.6009
313	0.9×10^{-3}	3.1949	-7.0131
333	3.7×10^{-3}	3.0030	-5.5994

Using rate constant values and Arrhenius equation we represented lnk=f(1000/T), effect of the temperature on the rate constant for phenol removal (figure 13). From the slope of this plot we calculated the activation energy to be E_A=40.19 kJ/mol.

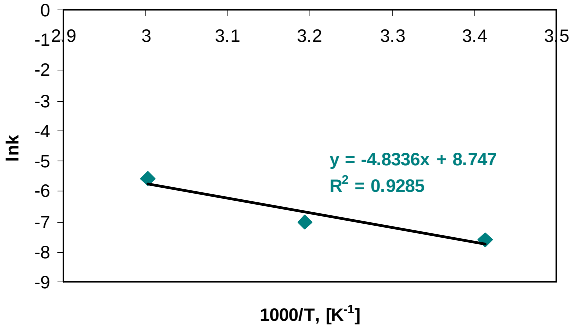

Figure 13. Arrhenius plot for phenol wet air oxidation on Fe/A-ZVT.

For the wet hydrogen peroxide oxidation of phenol [24] on a CuY-5 catalyst, E_A was calculated to be 90.32 kJ/mol, while E_A values from literature varied from 55 to 175 kJ/mol. The lower values are considered to be more characteristic for total oxidation, while the higher ones probably resulted from polymerisation to tars rather than from true oxidation [24]. Using a crude bentonite sample Barrault and co-workers [35] prepared samples of Al-Cu pillared clays using different techniques. They found that the rate of phenol oxidation into carbon dioxide using hydrogen peroxide as oxidation agent, increased after the addition of copper mainly due to a heterogeneous oxidation rather than to a homogeneous Fenton-like oxidation.

CONCLUSIONS

We prepared a catalyst containing iron using a natural zeolitic volcanic tuff from Aluniş (Cluj County), Fe/ZVT. This type of catalyst can be used in catalytic wet air oxidation process for wastewaters treatment at lower temperatures by comparison with non-catalytic processes [27].

The influence of temperature and air flow rate over the phenol conversion and overall process efficiency was studied. An increase of the operating temperature led to an increase in phenol conversion and overall process efficiency. Phenol conversions up to 94.03% were reached. The maximum value for process efficiency was calculated to be 93% using CCO-Mn values. An increase of the air flow rate led to a small increase in the phenol oxidation process efficiency.

Further studies will be performed in order to establish the catalyst reproducibility and lifetime, the influence of the catalyst quantity over the process efficiency. Other catalysts using different type of natural supports and different metal ions will be also prepared and studied.

ACKNOWLEDGMENTS

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REFERENCES

1. A. Santos, P. Yustos, B. Durban, F. Garcia-Ochoa, *Ind. Eng. Chem. Res.*, **2001**, *40*, 2773.
2. A. Santos, P. Yustos, B. Durban, F. Garcia-Ochoa, *Catal. Today*, **2001**, *66*, 511.
3. C. Catrinescu, C. Teodosiu, M. Macoveanu, J. Miehe-Brendle, R. Le Dred, *Water Res.*, **2003**, *37*, 1154.

4. A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, J. A. Casas, J. J. Rodriguez, *Environ. Sci. Technol.*, **2004**, *38*, 133.
5. M. A. Barrou, L. Haber, A. Maier, J. Zhao, M. Burron, EPA/635/R-02/006, **2002**.
6. http://www.inchem.org/documents/ehc/ehc/ehc161.htm
7. http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/phenol/phenol.html
8. A. Alejandre, F. Medina, A. Fortuny, P. Salagre, J. E. Sueiras, *Appl. Catal. B: Environ.*, **1998**, *16*, 53.
9. Y-H. Shen, *Water Res.*, **2002**, *36*,1107.
10. S. Al-Asheh, F. Banat, L. Abu-Aitah, *Sep. Purif. Technol.*, **2003**, *33*, 1.
11. E. Fernandez, D. Hugi-Cleary, M. V. Lopez-Ramon, F. Stoeckli, *Langmuir*, **2003**, *19*, 9719.
12. Z. Lazarova, S. Boyadzhieva, *Chem. Eng. J*, **2004**, *100*, 129.
13. W. Kujawski, A. Warszawski, W. ratajczak, T. Porebski, W. Capala, I. Ostrowska, *Desalination*, **2004**, *163*, 287.
14. D. Fino, C. Carlasi Jara, G. Saracco, V. Specchia, P. Spinelli, *J. Appl. Electrochem.*, **2005**, *35*, 405.
15. A. M. Polcaro, A. Vacca, S. Palmas, M. Marcia, *J. Appl. Electrochem.*, **2003**, *33*, 885.
16. Y. G. Adewuyi, *Ind. Eng. Chem. Res.*, **2001**, *40*, 4681.
17. G. Collins, C. Foy, S. McHugh, T. Mahony, V. O'Flaherty, *Water Res.*, **2005**, *39*, 1614.
18. A. Nuhoglu, B. Yalciu, *Proc. Biochem.*, **2005**, *40*, 1233.
19. J-M. Herrmann, *Catal. Today*, **1999**, *53*, 115.
20. U. Bali, E.C. Catalkaya, F. Sengul, *J. Env. Sci. Health*, **2003**, *A38*, 2259.
21. F. Luck, *Catal. Today*, **1999**, *53*, 81.
22. R. Andreozzi, V. Caprio, A. Insola, R. Marrota, *Catal. Today*, **1999**, *53*, 51.
23. B. Legube, N. Karpel Vel Leitner, *Catal. Today*, **1999**, *53*, 61.
24. S. Zrncevic, Z. Gomzi, *Ind. Eng. Chem. Res.*, **2005**, 44, 6110.
25. I. V. Perez, S. Rogak, R. Branion, *J. Supercrit. Fluids*, **2004**, *30*, 71.
26. V. Mishraef, V. Mahajani, J. Joshi, *Ind. Eng. Chem. Res.*, **1995**, *34*, 2.
27. Y. I. Matattov-Meytal, M. Sheintuch, *Ind. Eng. Chem. Res.*, **1999**, *37*, 309.
28. A. Cybulski, J. Trawczynski, *Appl. Catal. B: Environ*, **2004**, *47*, 1.
29. L. Chang, I-P. Chen, S-S. Lin, *Chemosphere*, **2005**, *58*, 485.
30. P. M. Alvarez, D. Mclurgh, P. Plucinski, *Ind. Eng. Chem. Res*, **2001**, *41*, 2153.

31. A. Santos, P. Yustos, S. Gomis, G. Ruiz, F. Garcia-Ochoa, *Ind. Eng. Chem. Res.*, **2005**, *44*, 3869.

32. M. Noorjahan, V. D. Kumari, M. Subrahmanyam, L. Panda, *Appl. Catal. B: Environ*, **2005**, *57*, 291.

33. N. H. Phu, T. T. K. Hoa, N. V. Tan, H. V. Thang, P. L. Ha, *Appl. Catal. B: Environ*, **2001**, *34*, 267.

34. J. Barrault, J-M. Tatibouet, N. Papayannakos, *C.R. Acad. Sci. Paris, Serie IIc Chimie*, **2000**, *3*, 777.

35. J. Barrault, C. Bouchoule, K. Echachoui, N. Frini-Srasra, M. Trabelsi, F. Bergaya, *Appl. Catal. B: Environ.*, **1998**, *15*, 269.

36. F. Cakicioglu-Ozkan, S. Ulku, *Microporous Mesoporous Mater.*, **2005**, *77*, 47.

37. M. Macoveanu, D. Bîlba, N. Bîlba, M. Gavrilescu, G. Soreanu, “Procese de schimb ionic în protectia mediului”, Matrixrom, Bucuresti, **2002**, chapter 1, 2.

38. V. Badillo-Almaraz, P. Trocellier, I. Davila-Rangel, *Nuclear Instruments and Methods in Physics Research*, **2003**, *B 210*, 424.

39. L. R. Hay and A. R. Sheppard, *Reviews in Mineralogy and Geochemistry, Natural Zeolites, Occurrence, Properties, Applications*, Ed. D.L.Bish, D.W.Ming, **2001**, *45*, 217.

40. F. A. Mumpton, *Proceedings of the 3rd National Congress - AIMAT*, omaggio scientifico a Riccardo Sersale, Ed C. Colella, De Frede, Napoli, Italy, **1996**, 31-64.

41. M. Pansini, *Mineralium Deposita*, **1996**, *31*, 563.

42. L. K. Kazantseva, I.A. Belitsky, B. A. Fursenko, *Natural Zeolites - Sofia ’95*, Ed. G. Kirov, L. Filizova, Petrov, Pensoft Publishers, Sofia, Bulgaria, **1997**, 33.

43. I. Marza, Fl. Codoreanu, Al. Hosu, M. L. Placeanu, D. Marian, R. Pop, D. Tamas, “The Volcanic Tuffs from the Transylvanian Basin, Romania”, Cluj-Napoca, **1991**, chapter 5.

44. *** “Minereuri Nemetalifere. Metode de analiza si incercari. Colectie STAS”, Editura Technica, Bucuresti, **1978**.

45. A. Iovi, G. Burtica, R. Pode, *Chem. Bull. Tech. Univ. (Timisoara)*, **1993**, *52*, 29.

46. K. D. Mondale, R. M. Carland, F. F. Aplan, *Minerals Eng.*, **1995**, *8*, 535.

47. C. Cobzaru, S. Oprea, T. Hulea, V. Hulea, E. Dumitriu, *Rev. Chim.*, **2002**, *53*, 674.

48. M. Panayotova, B. Velikov, *J. Env. Sci. Health Part A*, **2003**, *A38*, 545.

49. F. D. Iacomi, “Zeoliti Naturali. Structura, Proprietati, Utilizare”, Editura Universitatii Aurel Vlaicu, Arad, **2001**, chapter 3 .

50. A. T. Balaban, M. Banciu, I. Pogany, “Aplicatii ale metodelor fizice in chimia organica”, Editura Stiintifica si Enciclopedica, Bucuresti, **1983**, chapter 3 .

51. I. Bedelean, S. Stoici S., “Zeoliti”, Editura Tehnica, Bucuresti, 1984, chapter 4.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

THE WASTE RUBBER USED TO IMPROVE THE PROPERTIES OF COMPOSITE MATERIALS

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ABSTRACT. Recycling of rubber dust finds an interesting application in the field of composite materials. Incorporation of rubber aggregates in a matrix, confers to the composite material remarkable physico-mechanical and thermo-hydrous properties. In this work we presented a green technology for the waste rubber conditioning, sources and a possibility of use in composite materials parts.

Keywords: *rubber waste, composite materials, recycling*

INTRODUCTION

Mixtures of rubber, steel and textiles, used tires are not dangerous waste [1]. However, they present a danger to the environment and health in the event of fire or incineration (pollutant emissions of gas and possibly of an oily liquid).

The composite materials have unquestionable advantages compared with metallic materials (low mass for a high rigidity). However, some of their properties remain weak (tolerance at damage, for example).

With the aim of modifying these properties, we propose, in this study, doping during manufacture of certain types of laminated composites. The doping process consists in the addition of some specific particles during the molding process of the composites, figure 1.

In this study, we used recycled rubber particles from worn tires; these particles were obtained by cryogenic crushing. The goal is the improvement of the properties in the case of the shocks and vibrations. This study presents firstly, the technique of composite materials doping. Secondly we showed that it is possible to inject resin on a dry reinforcement starting from all Liquid Composite Molding (LCM) processes without deteriorating the installation of these elastomeric particles within material. Finally certain results of mechanical tests will be presented.

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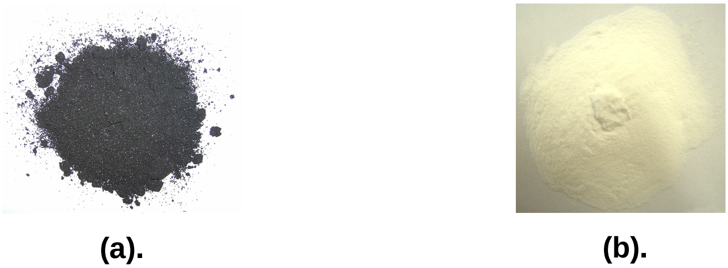


Figure 1. Doping material. (a) rubber particles; (b) bonding agent.

A first series of quasi-static experiments carried out on doped glass/ epoxy specimens showed that for a rate of well defined doping ratio, the mechanical characteristics values are between 10 % and 20 %. These values were confirmed by damages under shock tests [2].

Taking in account the fact that this study proposes a new way for recycling of used tires we consider that the work we done can contribute to environmental protection. Moreover, it appears that beside used tires many structural parts, in small or great quantities, can be considered for processing by this technique (elements of automobile such as body, bumpers, etc). The obtained plates can also be used in new adhesive bonded assemblies with single or double lap.

RESULTS AND DISCUSSION

In order to evaluate the influence of the rubber particles in the laminate, on the mechanical behavior, several types of mechanical tests were carried out: inter laminar shear test, tensile tests under transversal direction, tree point bending test and delamination propagation in mode I and II [4].

The un-doped epoxy/glass plate and the manually doped plates with rubber particles were tested to determine the mechanical properties. The results are presented in tables 1 and 2.

Table 1.

Mechanical properties of the composite plates
(Young Modulus, Poisson ratio and fracture stress).

	Un-doped	**10% doping**	**20% doping**	**30% doping**
E_{11}^{T} **(MPa)**	14680	14260	13850	13500
ν_{12}	0.12	0.12	0.12	0.12
σ_{11}^{R} **(MPa)**	347	319	295	275
$E_{flexion}$ **(MPa)**	14206	12002	10650	8202
σ_{12}^{R} **(MPa)**	92	65	40	35

Concerning the results in tensile load, the most significant modifications are those with fracture. The fracture stress decreases with the mass rate of particles. However, this type of material, having a nonlinear behavior, relieves only a small influence on the yield stress.

Some important modifications of the mechanical characteristics are also raised on the results in bending and inter laminar shearing. The particles were placed in the composite without any particular surface chemical treatment. A suitable surface chemical treatment will support the adherence of the matrix on the rubber particles, which should improve the composite behavior in shear.

Table 2.

Critical energy release rate in mode **I** and **II** (Shear Modulus).

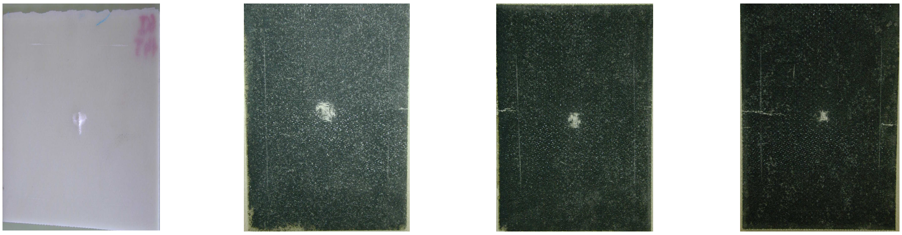
	Without doping	**10 % doping**	**20 % doping**	**30 % doping**
G_{Ic} **(J/m^2)**	850 - 1200	800 - 1100	-	-
G_{IIc} **(J/m^2)**	3000	2400	1500	1000

Some breaking tests were also realized in order to determine the influence of these particles presence on the delamination propagation (DCB for mode I and ENF for mode II) [4]. The values of the refund rates of the critical energy in mode I and II are given in table 2. The rubber particles insertion modifies the energy in mode I but on the other hand the energies values in mode II are strongly decreased as soon as we exceed a 10 % particles mass rate.

However, it was established during the tests, that the presence of the particles in the material stabilize the propagation of the delamination in mode II (the propagation of the delamination in mode II is often unstable for the ENF test and the delamination propagates as soon as it is initiated under the central support).

The final objective of this study, with recycled rubber particles, was to improve the impact behavior. For that, we made some plates of 150 mm × 100 mm in size, which were tested in a falling weight machine. The plates are positioned (simple plane support) on a plate base of the assembly revealing a free window of 125 mm x 75 mm.

In figure 2, we presented evolution of the damage on the opposed face to the impact for various particle percentages. Concerning the presence of 20 % of particle in laminate mass, any fracture of fibers is observed.



Un-doped 20 % 30 % 40 %

Figure 2. Visualization of defect after impact.

The process used to obtain doped plates, with 10 %, 20 %, 30 % or 40 % mass rubber particles, using the procedure described in the experimental section, are illustrated in figures 3 and 4.

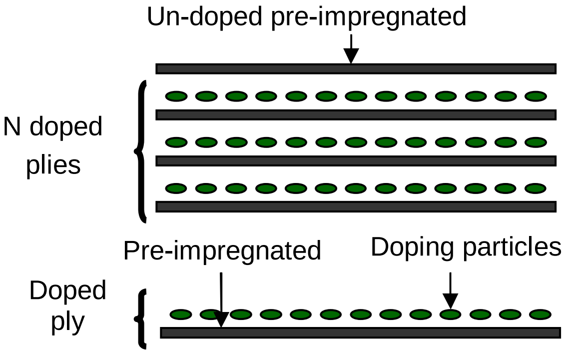


Figure 3. Impregnation process scheme.

We consider that the epoxy resin is sufficiently viscous to maintain in place the doping particles during the various phases of handling.

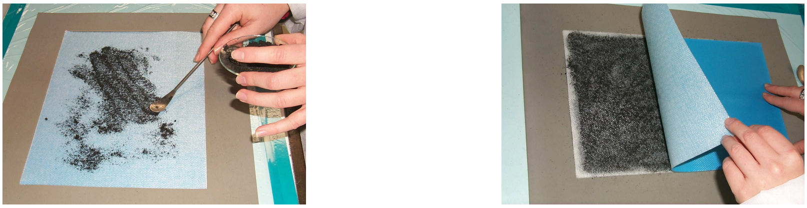


Figure 4. Manual doping of impregnated laminates.

The infusion technique belongs to the family of Liquid Composite Molding (LCM) as well as Resin Transfer Molding. The resin transfer through the dry immobilized reinforcement in the mold is ensured, in this case, by a vacuum pump and does not require an additional pressure. This technique, not very expensive, makes possible the usage of flexible mold (polyamide or PVC) ensuring the compaction of the fabric folds that are infused and maintained in place on the rigid mold by the same vacuum network. The principle of infusion is schematized in figure 5.

The infusion process was retained because the development of composite-made parts, in small series, makes possible the visualization of the polymer flows, see figure 6, (against transparent flexible mold), in the second time to show the immobilization of the elastomeric particles during the injection phase and finally is applicable as well for structural and for "large diffusion" parts.

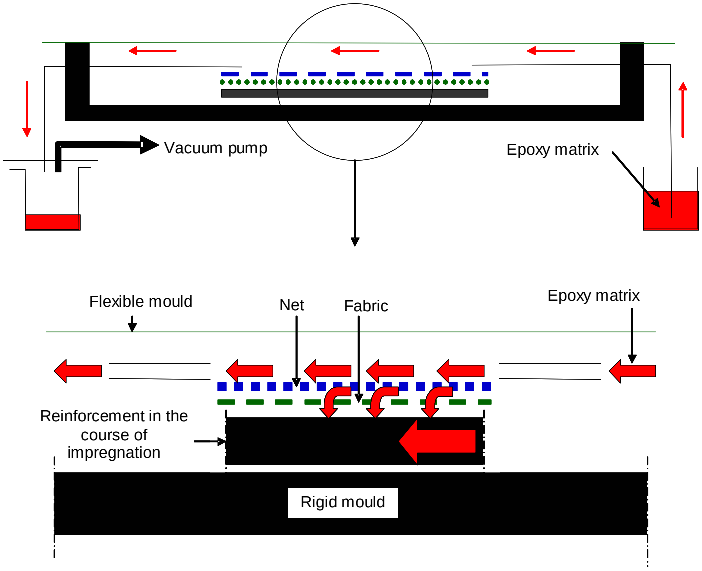


Figure 5. Infusion process scheme.

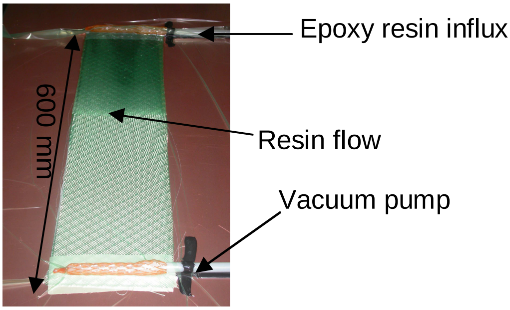


Figure 6. The infusion process.

For this molding process, a series of un-doped specimens is also carried out in order to be used as reference.

CONCLUSIONS

This study made possible the development of two manufacture techniques of composite materials doped with rubber particles. The objective was to validate the manufacture procedures and to raise the influence of the elastomeric particles presence on the mechanical behavior.

This study proposes the possibility of worn tires recycling, which currently creates a large concern with regard to environmental protection. It is well highlighted that the composites doping can allow a strongly improvement of certain characteristics (held with the shock shown in this study).

Also some more important tests regarding the particles influence on the mechanical behavior of the composites were performed.

The incorporation of rubber aggregates in a matrix, confers remarkable physico-mechanical and thermo-hydrous properties to the composite material. Thus, for example the presence of rubber particles improves the composite resistance in particular climatic conditions like cycles of freezing and also appreciably reduces the material density.

EXPERIMENTAL SECTION

Two families of specimens were carried out: the first, made from un-doped and doped glass/epoxy starting from a twill 2 fabric, pre-impregnated, ref. 5492 1808 42/120 provided by CTMI company and the second made from satin 5 glass fiber, un-doped and doped, impregnated with epoxy resin by the infusion method.

For the two specimens families, doping via elastomeric particles (rubber coming from worn tires) was carried out in an artisanal way (powdering by hand).

The polymerization of the epoxy polymer was realized by curing in an oven at 120 °C.

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REFERENCES

1. R. K. Dhir, M. C. Limbachiya, K. A. Paine, “Recycling and reuse of used tyres”, Thomas Telford Publishing, **2001**.
2. F. Lachaud, R. Piquet, *$15^{ème}$ Journées Nationales sur les Composites, Compiègne*, France, mars, **2005**.
3. J. Aboissière, *Propagation de dommages d'impact dans un matériau composite stratifié à fibres de carbone et résine époxyde*, Thèse de l'Université Paul Sabatier, **2003**.
4. R. H. Martin, *Journal of Composites Technology & Research*, **1997**, *19*, 20.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

Cd^{2+} REMOVAL FROM SYNTHETIC WASTEWATERS USING *SCENEDESMUS OPOLIENSIS* GREEN ALGAE

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ABSTRACT. The main purpose of this research paper was to study the Cd^{2+} adsorption capacity of green algae from solutions of heavy metal in different concentrations. In this respect, experimental determinations were carried out using *Scenedesmus opoliensis* species to investigate the power of retention of green algae when it is used as natural biological filter. The adsorption processes was studied using three different concentrations, regime, at normal temperature and pH = 5.2. Heavy metal ion was namely 4.36 mg Cd^{2+}/L, 12.70 mgCd^{2+}/L and 20.49 mg Cd^{2+}/L, in dynamic adsorbed up to a yield of 50-52% over an interval of no more than 120 minutes, with an important increase in the first 10 minutes. The retention capacity, Q_s, of algal material adsorbent grows from 0.67 mg Cd^{2+}/g adsorbent for C_1=4.36 mgCd/L to 3.28 mg Cd^{2+}/g adsorbent for C_3=20.49 mgCd^{2+}/L. The analytical method employed in this study is atomic absorption.

Keywords: *biosorption, heavy metal, Scenedesmus opoliensis* green algae, *adsorption capacity, atomic absorption method*

INTRODUCTION

The rapid industrial development, various wastes containing different metal ions are directly or indirectly discharged into the environment, rising serious environmental pollution problems and threatening marine life [1].

There are many processes that can be used for the removal of metals from wastewaters including chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption [2].

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Microorganisms can remove heavy metal ions by a large variety of processes such as cell walls biosorption, entrapment in extracellular capsules and uptake by membrane transport of the metal ions into cell cytoplasm, microprecipitation and oxidation-reduction reactions. Some or all of these processes could take place in living microorganisms [3].

Metal ions are adsorbed first on the cells surface by the interactions between the metal ions and the metal-functional groups such as carboxyl, phoshate, hydroxyl, amino, sulphur, sulphyde, thiol, etc., present in the cell wall and then they penetrate the cell membrane and enter the cells [4].

Cadmium is one of most toxic heavy metals whose toxicity is attributed in part to its ability to accumulate in tissues. There are some reports on the destruction of the chloroplast by heavy metal ions at higher concentrations [5]. In fact, cadmium ions disorganize chloroplasts and cause the damage of photosynthetic pigments [6]. As a consequence of this, the photosynthetic activity could severely be affected, causing growth inhibition or complete death of the cells [7, 8].

The purpose of this study is to evaluate the biosorption capacity of the *Scenedesmus opoliensis* algae for Cd^{2+} from aqueous solutions.

RESULTS AND DISCUSSION

As biosorbent we used *Scenedesmus opoliensis* green algae, figure 1. Heavy metal ions removal was tested using synthetic Cd^{2+} solutions (C_1=4.36 mg Cd^{2+}/L, C_2=12.70 mgCd^{2+}/L and C_3=20.49 mgCd^{2+}/L), in dynamic regime (under magnetic, continuous stirring at 200 rot/min for 2 h), at room temperature and pH = 5.2.

The biomass of live algae (*Scenedesmus op.*) was added to the synthetic solutions of heavy metal ions. In order to determine residual Cd^{2+} concentration in the solution, 2 ml samples were taken out at specific time intervals.

Figure 1. *Scenedesmus op.* [9].

The difference between the initial and remaining metal concentration was assumed to be taken up by the biosorbent.

Evolution of Cd^{2+} concentration in time as a function of initial concentration is presented in figure 2. We found that in all three cases (three solution containing different quantities of cadmium ions) the concentration of Cd^{2+} significantly decreases, faster in the first 10 minutes from the beginning of the experiment, while the equilibrium was reached after 60 minutes for solution with initial concentration C_1, 70-80 minutes for C_2 and approximately 120 minutes for the most concentrated initial solution C_3 (figure 2).

For adsorption yields, calculated values were placed around 50%, with small differences between the three initial concentrations, increasing from 50.90% for C_1=4.36 mg Cd^{2+}/L to 52.84% for C_3=20.49 mg Cd^{2+}/L (figure 3).

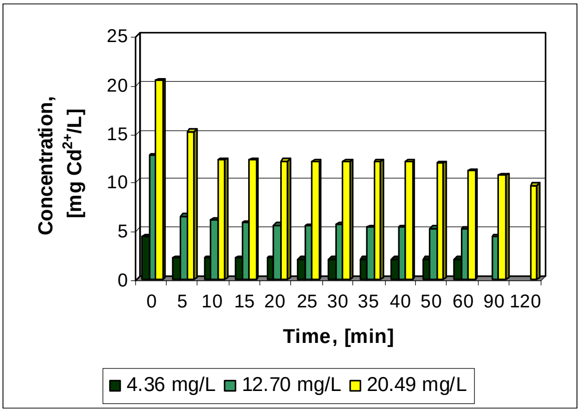

Figure 2. Evolution of Cd^{2+} concentrations in time for initial solutions containing different quantities of cadmium ions; 0.66 g dry mass biosorbent/15 ml solution.

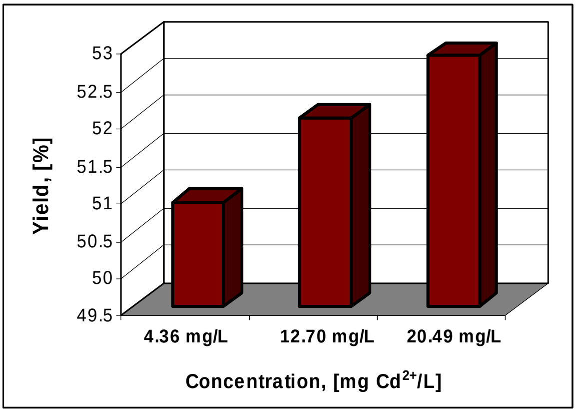

Figure 3. Maximum yield (%) values for Cd^{2+} adsorption on algae biosorbent; influence of the initial concentration of cadmium ions.

The retention capacity, Q_s of algal material adsorbent increases from 0.67 mg Cd^{2+}/g adsorbent for C_1=4.36 mg Cd^{2+}/L to 3.28 mg Cd^{2+} /g adsorbent for C_3=20.49 mg Cd^{2+}/L (figure 4).

Some of our previous studies [10] using dead algae as biosorbents (destroyed through thermal exposure) showed that the biosorption results were comparable with those from present paper (with live algae), or are even better. One possible explanation could be the metabolic extracellular products, which may form complexes with metals to retain them in solution [11].

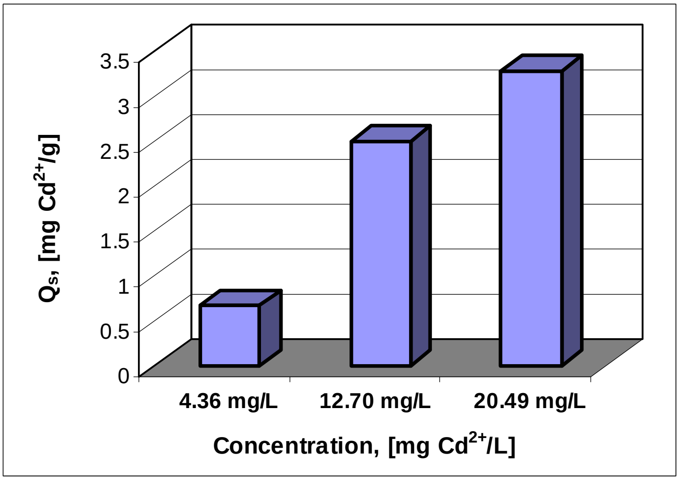

Figure 4. Maximum absorption capacity values for algae biosorbent; influence of the initial concentration of cadmium ions.

CONCLUSIONS

The present study proves that *Scenedesmus oppoliensis* could be an effective biosorbent for the removal Cd^{2+} from wastewaters. In this respect, three quality parameters were investigated: (1) heavy metal ions concentration in solution after contact with algae, (2) the yield calculated for the biosorption process, and (3) heavy metal ions retention capacity of algae.

Residual cadmium in the aqueous solutions, measured after 2 hours exposure periods, showed that the concentrations of Cd^{2+} significantly decrease, faster in initial 10 minutes, achieving the equilibrium after 60 minutes for solution with initial concentration C_1=4.36 mg Cd^{2+}/L, 70-80 minutes for C_2=12.7 mg Cd^{2+}/L and approximately 120 minutes for the most concentrated initial solution, C_3=20.48 mg Cd^{2+}/L.

In conclusion, for the three initial concentrations used in our experiment, cadmium was adsorbed up to yields of 50-52%, with retention capacity values comprised between 0.67 and 3.28 mg Cd^{2+}/g biosorbent.

Hence, it is possible to remove cadmium in a simple treatment using *Scenedesmus oppoliensis* green algae.

EXPERIMENTAL SECTION

The cadmium solution was prepared by dissolving $Cd(NO_3)_2 \times 4H_2O$ (analytically reagent) in deionized water.

Axenic monoalgal cultures of *Scenedesmus opoliensis* P. Richter, obtained from the culture collection of Cluj Biological Research Institute [12], were grown in Kuhl-Lorenzen (KL) nutrient media supplemented [13].

The biosorption process was conducted in batch conditions in a Berzelius flask (beaker) where we poured 15 ml of concentrated algae solution over 150 ml solution of Cd^{2+} of different concentrations (4.35, 12.7 or 20.49 mg Cd^{2+}/L). The solutions thus formed were placed on a magnetic stirrer and there were continuously mixed, at 25ºC. In order to determine residual Cd^{2+} concentration in the solution, 2 ml samples were taken out at specific time intervals with a syringe and filtered using M.E. Cellulose filter with the pore dimension of 0.45 µm. The analytical method employed in the Cd^{2+} concentration measurements was atomic absorption carried out with a Senso AA Spectrometer. Calibration was performed within a linear calibration range of cadmium.

To determine the dry mass of algae 15 ml of initial green solution were dried to constant mass, in a drying oven, at 105ºC. The weighted dried biomass was 0.66 g.

REFERENCES

1. P. L. Bishop, "Pollution Prevention: Fundamentals and Practice", Tsinghua University Press, Beijing, **2002**, chapter 1.
2. A. T. Al-Fawwaz, W. O. Wan Maznah, *International Conference on Environment Research and Technology* (ICERT 2008), abstract book.
3. M. Vidali, *Pure App. Chem.,* **2001,** *73*, 1163.
4. K. K. I. U. Arunakumara, Z. Xuecheng, *J. Ocean Univ. Chin.*, **2008**, *7*, 60.
5. Y. Sag, T. Kutsal, *Process Biochemistry,* **1996**, *31*, 573.
6. C. Lamaia, M. Kruatrachuea, P. Pokethitiyooka, E. S. Upathamb, V. Soonthornsarathoola, *Sci. Asia*, **2005,** *31*, 121.
7. G. F. Leborans, A. Novillo, *Water Res.*, **1996**, *30*, 57.
8. N. Atri, L. C. Rai, *J. Microbiol. Biotech.*, **2003**, *13*, 544.

9. *Scenedesmus op.* in http://videnskab.dk/content/dk/teknologi/intelligent, Foto: G. Fahnenstiel.
10. C. Majdik, C. Indolean, T. Pernyeszi, *13-th International Conference of Chemistry,* Cluj-Napoca, 8-11 Nov, **2007**.
11. S. K Mehata, *Progress and Prospects, Critical Reviews in Biotechnology*, **2005**, *25*, 113.
12. N. Dragos, L. S. Peterfi, L. Momeu, C. Popescu, “An Introduction to the Algae and the Culture Collecton Of Algae”, Presa Universitară Clujeană, Cluj-Napoca, **1997**, chapter 2.
13. L. Fodorpataki, A. L. Marton, T. L. Csorba, *Contribuții Botanice*, **2001**, *34*, 101.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

COPPER BIOSORPTION ON A STRAIN OF SACCHAROMYCES CEREVISIAE ISOTHERM EQUILIBRIUM AND KINETIC STUDY

ADINA GHIRIŞAN[a], SIMION DRĂGAN[a], VASILE MICLĂUŞ[a]

ABSTRACT. In the present work, biosorption of copper ions from aqueous solutions on a strain of *Saccharomyces cerevisiae*, collected from the waste of a brewing industry, was studied in batch system for a better understanding of biosorption isotherm equilibrium, as well as biosorption kinetics. The influence of different sorbent dosages on the sorption of copper ions was investigated. Freundlich and Langmuir isotherm models were used for interpreting the copper biosorption equilibrium and the isotherm constants (i.e., for Freundlich isotherm model, $k = 10.454$ and $n = 3.017$) were determined by experimental data. Freundlich adsorption isotherm ($R^2 = 0.9642$) was found to be more suitable than the Langmuir isotherm ($R^2 = 0.8709$) for correlation of equilibrium biosorption data. Kinetics of biosorption for copper ions was investigated using the first- and second-order models. The kinetic constants were also determined. Second-order kinetics ($R^2 = 0.9937 – 0.9996$) was found to fit the experimental data better than the first-order model ($R^2 = 0.743$).

Keywords: *copper, biosoption, Saccharomyces cerevisiae, Freundlich and Langmuir models*

INTRODUCTION

Water pollution with heavy metals due to industrial activities such as mining, metal processing, electroplating and dyeing is an issue of great environmental concern [1]. Traditional treatments for these wastewaters include chemical precipitation, membrane processes, ion exchange, adsorption and reverse osmosis. Many of these approaches can be less cost effective or difficult for practical use. In an earlier work we have shown the possibility of heavy metals removal from acid mine wastewater using apatite, a calcium-phosphate mineral [2]. Minerals are being commonly applied in environment treatment, based on their properties, such as surface adsorption, high ionic exchange capacity, dissolution, hydration, and mineralogical-biological interactions [3, 4].

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In the last decade more studies referring to the removal of heavy metals from groundwater and wastewater researched natural products adsorption capacity, due to their availability in large quantities as waste or by-products from agricultural and biological processes [5, 6].

The adsorptive studies using treated and untreated waste baker's beer yeast have shown that yeast could be a promising adsorbent for ions such as Zn^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} [7-10]. The advantages of *Saccharomyces cerevisiae* as biosorbent are: *S. cerevisiae* as a by-product is easier to get from fermentation industry, in comparison with other types of waste microbial biomass; is easy to cultivate at large scale; is generally regarded as safe; and is an ideal model organism to identify the mechanism of biosorption in metal ion removal.

Copper ion was chosen for the present study with the regard to its wide presence in the mine wastewaters [2]. In the same time copper is widely used as metal in our daily life, and as any other heavy metals it is potentially toxic for living organisms. The concentration limit of copper in wastewaters for discharge in aquatic media according to Romanian legislation is 0.1 mg/L [11].

The objectives of the present study were: to investigate the biosorption of Cu^{+2} from aqueous solutions on a strain of *Saccharomyces cerevisiae* yeast collected from the waste of a Romanian brewing industry – URSUS at different biosorbent yeast dosages (from 0.1 to 0.4 g dry yeast/100 ml copper solution), and then to apply the isotherm equilibrium models and the kinetics of biosorption to experimental data for a better understanding of biosorption mechanism of copper ions on *Saccharomyces cerevisiae* yeast.

EXPERIMENTAL SECTION

Materials

Biosorbent yeast waste *Saccharomyces cerevisiae* was collected from the Romanian brewery URSUS Cluj-Napoca (fermentation unit) and transported to the laboratory in plastic containers. The yeast was then washed several times with distillated water and separated by filtration using filter paper, dried in a hot air oven at 80℃ for 24 hours and stored for further use.

Stock artificial copper solutions of 1000 mg/L Cu^{+2} were prepared from $CuSO_4 \times 5H_2O$ of analytical grade and double distillated water. The solutions were diluted as required to obtain working solutions.

The pH of copper solutions was adjusted at 2.2, value which reproduces the pH of an acid mine wastewater, by addition of H_2SO_4 0.1 M. The pH values were measured using a digital pH-meter, (Thermo Electronic Corporation). Fresh dilutions were used for each biosorption study.

Methods

Batch adsorption experiments were carried out by shaking Erlenmeyer flasks on a rotary shaker at 150 rpm and at room temperature (20℃) for biosorptive experiments. The samples were then filtered using filter paper and the concentration of metal ions in the filtrate was analyzed using Varian Atomic Absorption Spectrophotometer SpectrAA-880 type with deuterium background correlation. Each determination was repeated three times and the results were given as average values. The standard deviation is less than 7%.

RESULTS AND DISCUSSION

Biosorptive isotherm of copper

The effect of contact time on copper biosorption at different *Saccharomyces cerevisiae* yeast dosages was studied and the results were shown in figure 1. As seen in figure 1, the equilibrium concentration was reached in about 120 minutes at lower concentration of yeast, but at higher concentration of yeast the biosorption took about 60 minutes.

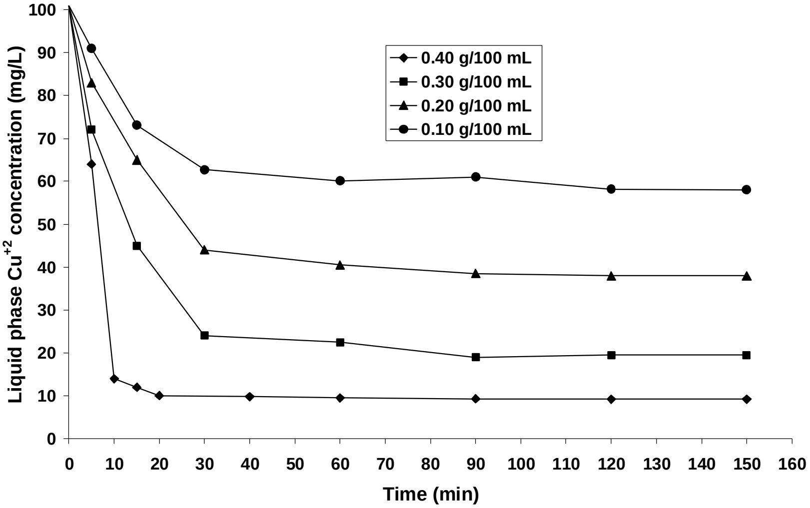


Figure 1. Biosorption of Cu^{+2} by *Saccharomyces cerevisiae* yeast at different dosages of yeast at pH = 2.2.

To determine the copper sorption mechanism on *Saccharomyces cerevisiae* yeast, experimental measurements were conducted using an initial copper concentration C_i = 100 mg/L and different concentrations of biosorbent (0.1 – 0.4 g/100 mL). The results of biosorption were plotted as figure 2 shown, where C_{eq} (mg/L) is the final equilibrium concentration of copper remaining in the solution and q (mg/g) is the metal uptake (equation 1).

$$q = V \cdot \left(C_i - C_{eq}\right) / S \tag{1}$$

The sorption isotherm relationship was than mathematically expressed using Freundlich model (equation 2) and Langmuir model (equation 3).

$$q = k \cdot C_{eq}^{(1/n)} \tag{2}$$

$$q = \left(q_{\max} \cdot b \cdot C_{eq}\right) \cdot \left(1 + b \cdot C_{eq}\right)^{-1} \tag{3}$$

where, k and n are Freundlich constants, q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), interpreted as the total number of binding sites available for biosorption, and b (L/mg) is the Langmuir constant related to the affinity between the sorbent and sorbate [12].

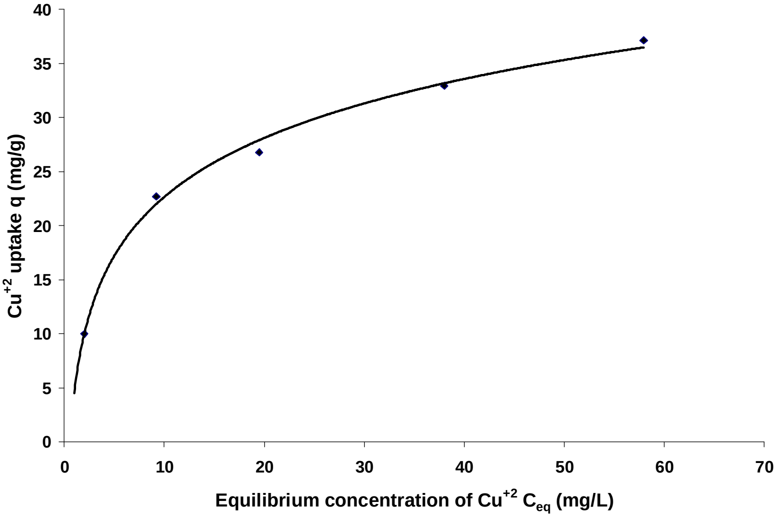


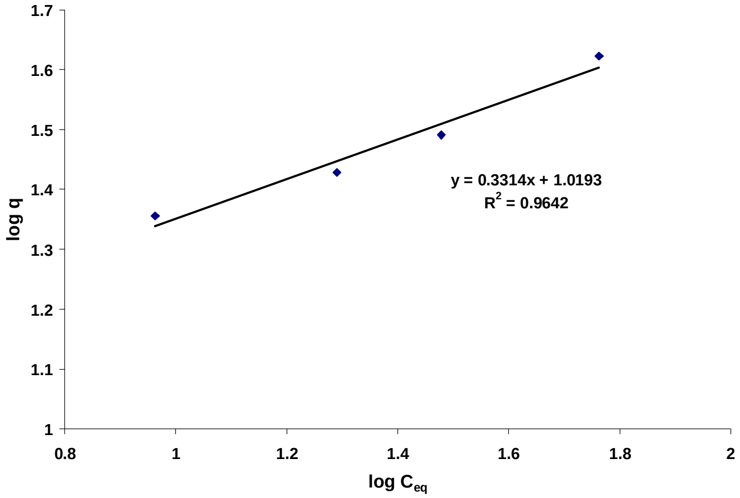
Figure 2. Adsorption isotherm of Cu^{+2} by *Saccharomyces cerevisiae* yeast at pH = 2.2.

The Freundlich equation which deals with heterogeneous surface adsorption can be linearized by plotting it in a log-log format (equation 4, figure 3a).

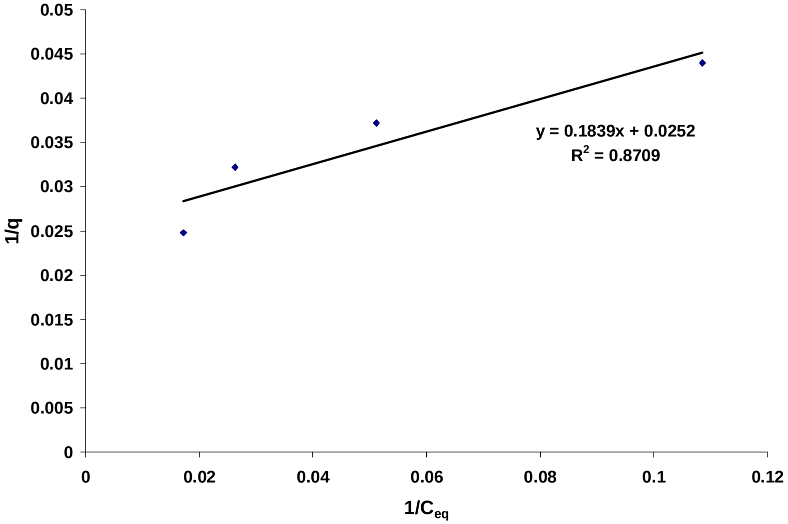
$$\log q = \log k + n^{-1} \cdot \log C_{eq} \qquad (4)$$

The Langmuir model was linearized as equation 5 shows (figure 3b):

$$1/q = (q_{\max} \cdot b)^{-1} \cdot (C_{eq})^{-1} + (q_{\max})^{-1} \qquad (5)$$



(a).



(b).

Figure 3. Application of adsorption models to experimental data: (a). Freundlich model, (b). Langmuir model.

The correlation coefficients obtained from Freundlich and Langmuir models were 0.9642, respetively 0.8709. The better correlation of Freundlich model with experimental data suggests heterogeneous surface adsorption. Freundlich and Langmuir parameters were estimated from the fitting of experimental points of copper biosorption (table 1).

Table 1.

Freundlich and Langmuir parameters estimated from experimental data.

FREUNDLICH	**LANGMUIR**
k (L/g) = 10.454	q_{max} (mg/g) = 40
n = 3.017	b (L/mg) = 0.137
S.D. = 0.07	S.D. = 0.06

Maximum biosorption capacity was calculated to be q_{max} = 40 mg Cu^{+2}/g yeast. From the Langmuir model a value of K = 1/b = 7.3 (mg/L) was determined for the affinity constant, comparable with literature data [9].

Kinetic models

Kinetic models can be helpful to better understand the mechanisms of metal biosorption and to evaluate performance of biosorbents for metal removal. Generally, the study of adsorption dynamics describes the solute uptake rate. The kinetics of copper sorption on the *S. cerevisiae* yeast was analyzed using pseudo-first-order and pseudo-second-order [13, 14] models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

The pseudo-first-order equation is generally expressed as follows:

$$\frac{d\,q_t}{d\,t} = k_1 \cdot (q_e - q_t) \tag{6}$$

where,

q_e and q_t are the adsorption capacity at equilibrium and at time t, (mg/g),

k_1 is the rate constant of pseudo first-order adsorption.

After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (6) becomes:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \tag{7}$$

The plot of log (q_e - q_t) versus time should give a linear relationship from which k_1 (1/min) and q_e can be determined from the slope and intercept of the plot, respectively. The correlation coefficient obtained was R^2 = 0.743.

The pseudo-second-order adsorption kinetic rate equation is expressed as equation 8 shows:

$$\frac{d\,q_t}{d\,t} = k_2 \cdot (q_e - q_t)^2 \tag{8}$$

where,

k_2 is the rate constant of pseudo second-order adsorption (g/mg·min).

For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation 8 becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^{\,2}} + \frac{1}{q_e} \tag{9}$$

The correlation of experimental data using pseudo-second-order model for different sorbent dosages (0.1 – 0.4 g) is shown in figure 4. The high values of correlation coefficients (R^2 = 0.9937 – 0.9996) have shown that the biosorption of copper using as biosorbent *S. cerevisiae* yeast has followed a pseudo-second-order kinetic.

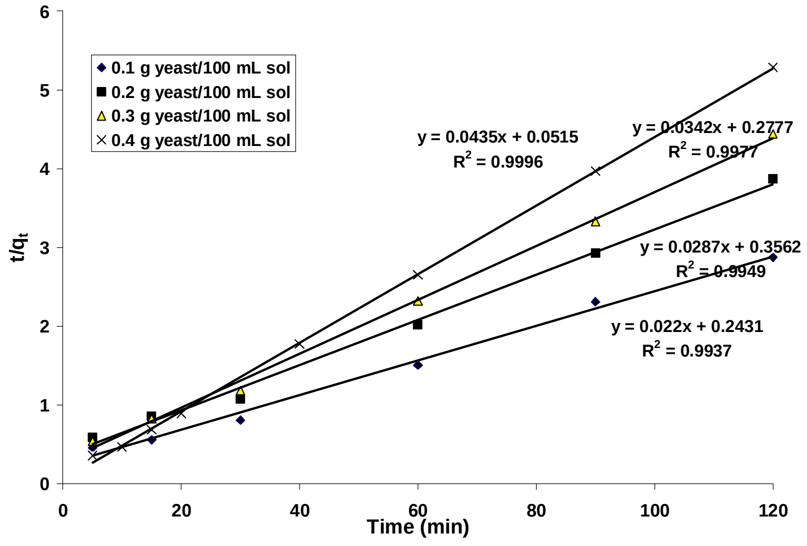


Figure 4. Correlation of experimental data using the pseudo-second-order model.

Sorption parameters and the correlation coefficients obtained from experimental data analyzed in terms of pseudo-second-order equation are given in table 2.

It easy to see that q_e was inversely related to the added yeast mass (S). While k_2 increased from 0.0019 to 0.036 (g/mg·min), h, increased from 2.790 to 19.04, as the yeast dosage increased from 0.1 to 0.4 g/100 mL solution. A similar behavior was reported by Vasudevan et al. in the case of biosorption of cadmium on Baker's yeast [8].

Table 2.

The effect of yeast dosages on copper sorption parameters

S (g/100 mL)	**R^2**	**q_e (mg/g)**	**k_2 (g/mg·min)**	**h (mg/g·min)**
0.1	0.9937	45.45	0.0019	3.925
0.2	0.9949	34.84	0.0023	2.790
0.3	0.9977	29.24	0.0042	3.590
0.4	0.9996	23.00	0.0360	19.04

where S is the yeast dosage; q_e - copper ion uptake capacity at equilibrium; k_2 – rate constant and $h = k_2.\ q_e^2$ – initial adsorption rate.

CONCLUSIONS

Saccharomyces cerevisiae yeast collected from the waste of URSUS brewery has been successfully used as a potential biosorbent to treat wastewater contaminated with copper ions. The amount of sorbed copper ions at equilibrium was related to yeast ratio.

The biosorption was mathematical described using Freundlich and Langmuir models. The better correlation of Freundlich model with experimental data suggests a heterogeneous surface adsorption. Freundlich and Langmuir parameters were estimated from the fitting of experimental points of copper biosorption. The maximum biosorption capacity was q_{max} = 40 mg Cu^{+2}/g yeast. From the Langmuir model a value of K = 7.3 (mg/L) for the affinity constant was determined.

Kinetics of biosorption of copper ions was investigated by using the pseudo-first- and pseudo-second-order models and the kinetic parameters were determined. Second-order kinetics (R^2 = 0.9937 – 0.9996) was found to fit the experimental data better than the first-order model (R^2 = 0.727).

REFERENCES

1. N. Goyal, S.C. Jain, U.C. Banerjee, *Advances in Environmental Research*, **2003**, *7*, 311.
2. A. Ghirişan, S. Drăgan, A. Pop, M. Simihăian, V. Miclăuş, *Can. J. Chem. Eng.*, **2007**, *85*, 900.

3. D. J. Vaughan and R. A. Wogelius, *Environmental Mineralogy*, **2000**, *2*, 3.
4. S. P. Singh, L. Q. Ma, W. G. Harris, *Journal Environ. Qual.,* **2001**, *30*, 1961.
5. C. R. Teixeira Tarley, M. A. Zezzi Arruda, *Chemosphere*, **2004**, *54*, 987.
6. N. Basci, E. Kocadagistan, B. Kocadagistan, *Desalination*, **2004**, 164, 135.
7. P. A. Marques, H. M. Pinheiro, J. A. Teixeira, M. F. Rosa, *Desalination*, **1999**, *124*, 137.
8. P. Vasudevan, V. Padmavathy, S. C. Dhingra, *Bioresource Technology*, **2003**, *89*, 281.
9. Y. Goksungur, S. Uren, U. Guvenc, *Turk. J. Biol*., **2003**, *27*, 23.
10. P. Vasudevan, V. Padmavathy, S. C. Dhingra, *Bioresource Technology*, **2003**, *89*, 281.
11. *** Norma Tehnică privind condițiile de descărcare în mediul acvatic a apelor uzate NTPA-001/2002 aprobată prin HG 188/2002 şi HG 352/2005 pentru modificarea şi completarea HG 188/2002.
12. B. Volesky, “Sorption and Biosorption”, BV-Sorbex, Inc., St. Lambert, Quebec, **2004**, chapter 6.
13. Y. S. Ho, G. McKay, *Process Biochem*., **1999**, *34*, 451.
14. K. A. Krishnan, A. Sheela, T. S. Anirudhan, *J. Chem. Tech. Biotech*., **2003**, *78*, 642.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

CARBON DIOXIDE HIDRATION: MECHANISTIC LESSONS FROM ENZYMATIC SYSTEMS

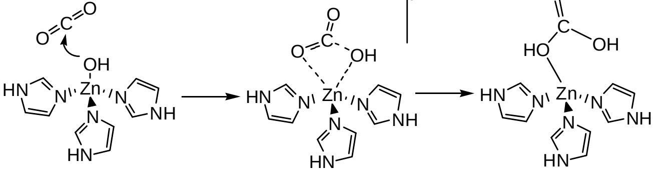
RADU SILAGHI-DUMITRESCU[a], **ANDRAS KALLAY**[a]

ABSTRACT. Carbon dioxide is arguably one of the most significant challenges for bioremediation, given its involvement in global warming. One reaction that would remove CO_2 from the atmosphere is hydration to bicarbonate. Living organisms have found a way to efficiently catalyze this reaction, employing the enzyme carbonic anhydrase, which employs a tetrahedral zinc active site. Here, we employ density functional (DFT) calculations in order to understand why nature has chosen this particular metal and this particular coordination geometry for CO_2 hydration. We ask the question whether other metals, such as iron or cooper, would be able to catalyze the same reaction in coordination environments such as seen in other metalloproteins. We find that the key of the carbonic anhydrase reaction lies not so much in the choice of metal, as in geometrical elements which allow the metal-bound carbonate to become a proper product.

Keywords: *carbon dioxide, carbonic anhydrase, density functional, hydration*

INTRODUCTION

Hydration of CO_2, a major metabolite in vivo as well as a major pollutant from an environmental point of view, is catalyzed in vivo by carbonic anhydrases (CANH) to produce bicarbonate, employing a tetrahedral zinc active site whose ligands are three endogenous histidine ligands and a hydroxide/aqua ligand. The active form of this site is the hydroxo one, and the metal-bound OH group is responsible for a nucleophylic attack on the CO_2 in the key step of the catalytic mechanism, wherein the nascent bicarbonate ligand becomes bidentate to the zinc (cf. scheme 1) [1, 2].



Scheme 1

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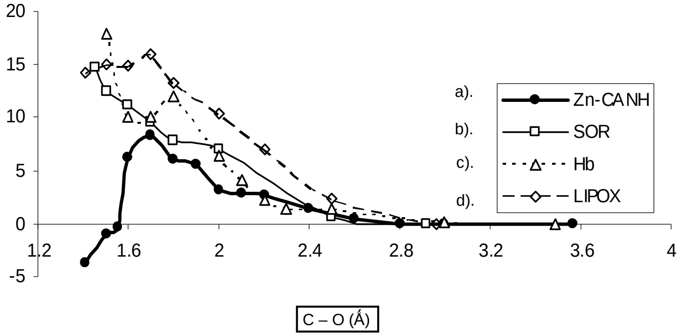
The choice of a tetrahedral zinc site for the CANH reaction is typically discussed in the general terms of the choice of zinc for non-redox, hydration/hydrolysis reaction. Here, we employ density functional theory (DFT) methods to explore the advantages of employing a tetrahedral zinc active site for the hydration of carbon dioxide. We find that zinc appears to be preferred by living organisms for the CANH active site due to its preference for tetrahedral coordination geometry (as opposed to the more sterically-demanding octahedral geometry preferred with other metals such as Fe). Other factors favoring zinc (such as redox activity of some metals, or intrinsic nucleophilicity of the metal-bound OH group) may also be at play but are seen to be mere side-benefits compared to the sterical argument.

RESULTS AND DISCUSSION

Scheme 2 shows the calculated potential energy surface for CO_2 hydration by the carbonic anhydrase active (CANH) site. The very low activation barrier is in good agreement with experiment and with previous computational results [2]. There is a rearrangement of the OH ligand throughout the reaction (with the transition state featuring the nascent bicarbonate ligand as bidentate): it is ligated to zinc in the reactants but is no longer a zinc ligand in the product (it is substituted by an oxygen atom originating from CO_2). Also shown are similar reaction curves for three other metalloprotein active sites which, like CANH, feature a metal bound-hydroxide at least under some conditions: lipoxygenase (LIPOX) [3], hemoglobin (Hb) [4] and superoxide reductase (SOR) [5]. With all three models the attack of the iron-bound hydroxide onto the carbon atom in carbon dioxide is extremely facile, implying that Zn-CANH is not unique in its ability to catalyze CO_2 hydration. However, the iron systems (Hb, SOR, LIPOX) do not feature a product stable enough to make the reaction feasible. This latter shortcoming is NOT due to the metal: it is rather due to the octahedral environment around the iron, which is more sterically demanding than the tetrahedral environment around the Zn in CANH, and therefore does not allow facile reorientation of the OH group away from the metal, as required by the mechanism presented schematically in scheme 1. Consistent with this, we also find (results not shown) that (1) water or ammonia instead of imidazole as ligands to the zinc model do not raise the reaction barrier to any significant extent, and (2) placing Co, Fe or Cu instead of Zn in the carbonic anhydrase model does not lower the reaction barrier to any significant extent.



Scheme 2

CONCLUSIONS

The key of the carbonic anhydrase reaction is not so much the choice of metal or ligand, as in geometrical elements which allow the metal-bound carbonate to become a proper product.

EXPERIMENTAL SECTION

The BP86 functional, which uses the gradient-corrected exchange functional proposed by Becke [6], the correlation functional by Perdew [7], 6-31G** were used as implemented in Spartan [8].

ACKNOWLEDGMENTS

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REFERENCES

1. S. Schenk, J. Notni, U. Kohn, K. Wermann, E. Anders, *Dalton Trans.*, **2006**, 4191.
2. G. Parkin, *Chem. Rev.*, **2004**, *104*, 699.
3. N. Lehnert, E. I. Solomon, *J. Biol. Inorg. Chem.*, **2003**, *8*, 294.
4. J. Dunne, D. A. Svistunenko, A. I. Alayash, M. T. Wilson, C. E. Cooper, *Adv. Exp. Med .Biol.*, **1999**, *471*, 9.
5. R. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, E. D. Coulter, D. M. Kurtz, Jr., *Inorg. Chem.*, **2003**, *42*, 446.
6. A. D. Becke, *Phys. Rev.*, **1988**, 3098.

7. J. P. Perdew, *Phys. Rev.*, **1986**, *B33*, 8822.

8. SPARTAN '04 for Windows, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

ASSESSMENT OF *AQUA REGIA* EXTRACTABLE AND PLANT-AVAILABLE Pb CONTENT IN POLLUTED SOIL

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ABSTRACT. In this study for monitoring the soil contamination with Pb in the industrially polluted area of Baia Mare, the *aqua regia* extractable Pb content as well as the plant-available fraction were determined by inductively coupled plasma atomic emission spectrometry, after extraction in $HCl-NHO_3$ mixture and in buffered DTPA, respectively. The *aqua regia* extractable Pb content was in the range of 88-2200 mg/kg, exceeding in all cases the alert level (50 mg/kg) and in most cases the intervention level (100 mg/kg) for sensitive soils. The plant-available Pb ranged between 10-292 mg/kg, exceeding in most soil samples the concentration limit of 20 mg/kg DTPA-extractable Pb considered to be the maximum level to avoid human risk. The average percentage of plant-available Pb was 21% showing that considerable amounts of Pb could be absorbed from soil by plants and propagated through the food chain in human organism.

Keywords*: soil contamination, aqua regia extractable Pb content, plant-available Pb*

INTRODUCTION

Lead is naturally found in the Earth's crust at about 15–20 mg/kg rarely occurring in its elemental state, but rather in its +2 oxidation state in various ores. However, the highest levels found in the environment come from human activities [1].

Pollution with lead is of major concern due to its high toxicity and potential to accumulate. The Environmental Protection Agency (EPA) has determined that lead is a probable human carcinogen. The International Agency for Research on Cancer (IARC) has determined that inorganic lead compounds are probably carcinogenic to humans, but the organics are not classifiable as to their carcinogenicity in humans based on inadequate evidence from studies in humans and in animals [2].

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Data obtained following the *aqua regia* extraction can be regarded as an approximation of the total contents, which is of concern especially for soils affected by anthropogenic contamination, but does not provide information regarding availability [3].

To assess the plant-available fraction, a great variety of single or sequential extraction schemes have been developed [4, 5]. The extraction with diethylenetriaminepentaacetic acid (DTPA) was initially designed to predict micronutrient deficiencies in soil, but it has also been employed for the estimation of metal availability for plants [6, 7].

This paper presents the *aqua regia* extractable Pb content as well as the plant-available Pb fraction determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after extraction in *aqua regia* and in buffered DTPA, respectively, in Baia Mare.

EXPERIMENTAL SECTION

Situated in North West Romania, Baia Mare is one of the pollution hot spots of the region [8]. There is a long mining history in the surrounding area but the pollution becomes severe in the recent decades as a result of industrial development.

In a study for monitoring the soil contamination with Pb in the industrially polluted area of Baia Mare, 30 soil samples were collected in the summer of 2007 [9-11].

In each case the soil samples were collected from 0-20 cm depth using a stainless steel shovel, air dried to constant weight, sieved through a 2 mm diameter sieve. The fraction below 2 mm was split in two parts. One part was stored in polyethylene bags for the determination of plant-available Pb content. The other part was ground to a fine powder in a tungsten-carbide swing mill for 3 min and sieved through a 250 μm sieve. The fraction below 250 μm was homogenized and stored in polyethylene bags until the *aqua regia* extraction.

In order to determine the *aqua regia* extractable Pb contents, samples were processed according to ISO 11466:1995. An amount of 1 g soil sample (<250 μm) was weighed, introduced into the reaction flask and maintained at room temperature for 16 h with 21 ml of 12 M HCl and 7 ml of 15.8 M HNO_3. The mixture was then heated under reflux conditions for 2 h. The solution was filtered and diluted to 100 ml with 0.5 M HNO_3.

The plant-available Pb contents of soils were extracted in DTPA according to ISO 14870:2001. An amount of 10 g of soil sample (<2 mm) was weighed into a 125 mL Erlenmeyer flask, then 20 mL of DTPA extracting solution was added. Each flask was covered with a stretchable parafilm and shaken for 2 h at room temperature using a magnetic shaker.

Aqua regia extractable and plant-available Pb concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using the scanning spectrometer SPECTROFLAME (Spectro Analytical Instruments, Kleve, Germany).

RESULTS AND DISSCUSION

The range, lower and upper quartile and median of *aqua regia* extractable and plant-available Pb are presented in figure 1.

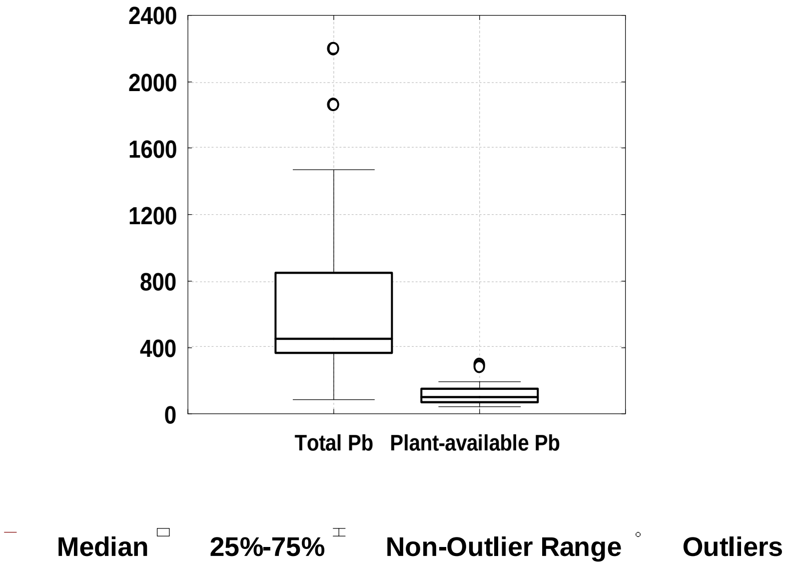

Figure 1. The range, lower and upper quartile and median of *aqua regia* extractable (total) and plant-available Pb.

The *aqua regia* extractable Pb content was in the range of 88-2200 mg/kg with an average of 680 mg/kg, exceeding in all cases the alert level (50 mg/kg) and in most cases the intervention level (100 mg/kg) for sensitive soils.

The averages of *aqua regia* extractable and plant-available Pb contents are presented in figure 2.

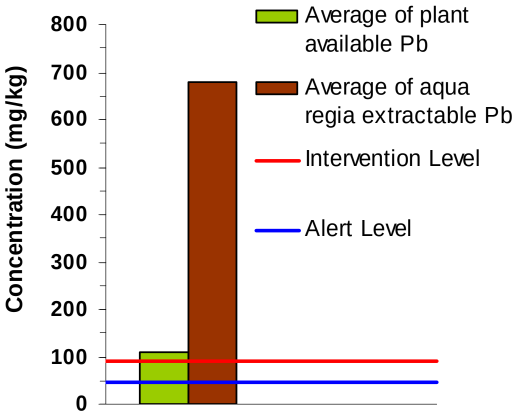

Figure 2. The average of *aqua regia* extractable and plant-available Pb contents.

The plant-available Pb ranged between 10-292 mg/kg with an average of 110 mg/kg, exceeding in most soil samples the concentration limit of 20 mg/kg DTPA-extractable Pb [12] considered to be the maximum level to avoid human risk.

The average percentage of plant-available Pb was 21% showing that considerable amounts of Pb could be absorbed from soil by plants and propagated through the food chain in human organism.

CONCLUSIONS

The high contents of *aqua regia* extractable and plant available Pb found in soil show a severe pollution in the studied area. Considering the environmental mobility and the toxicity of lead a global initiative aimed to monitor and minimize human and environmental consequences of the ongoing lead emissions is mandatory.

REFERENCES

1. I. Thornton, R. Rautiu, S. Brush, "Lead - the facts", Imperial College Consultants Ltd, London, UK, **2001**, chapter 6.
2. Agency for Toxic Substances and Disease Registry, Draft Toxicological Profile for Lead, U.S. Department of Health and Human Services, Atlanta, Georgia, **2005**.

3. B. E. Davies, C. Bifano, K. M. Phillips, J. L. Mogollon, M. Torres, *Environ. Geochem. Health*, **1999**, *21*, 227.

4. A. Sahuquillo, A. Rigol, G. Rauret, *Trends Anal. Chem.*, **2003**, *22*, 152.

5. S. Perez-Santana, M.Pomares Alfonso, M. Villanueva Tagle, M. Pena Icart, C. Brunori, R. Morabito, *Chemosphere*, **2007**, *66*, 1545.

6. W.L. Lindsay, W.A. Norwell, *Soil Sci. Soc. Am. J*, **1978**, *42*, 421.

7. I. Maiz, I. Arambarri, R. Garcia, E. Mollan, *Environ. Pollut.*, **2000**, *110*, 3.

8. E. Cordos, T. Frentiu, A. Rusu, G. Vatca, *Analyst*, **1995**, *120*, 725.

9. E. A. Konradi, M. Ponta, T. Frentiu, M. Senila, E. Cordos, *Environment and Progress*, **2006**, *8*, 199.

10. E. A. Konradi, M. Ponta, T. Frentiu, M. Senila, C. Roman, A. Mihaly Cozmuta, E. Cordos, *“Preliminary study on soil lead pollution around the Bozanta Mare tailing pond using Tessier’s extraction scheme”*, Optoelectronical Techniques for Environmental Monitoring and Risk Assessment Summer School, OTEM 2006, July 31 – August 09, **2006**, Baia Mare, Romania.

11. E. A. Levei, M. Senila, C. Tanaselia, T. Frentiu, L. David, E. Cordos, *Metal fractionation in particles emmited by nonferrous metallurgical plant from Baia Mare, Romania*, 41 st IUPAC World Chemistry Congress, 5-11 august, **2007**, Torino, Italia.

12. Q. W. Yang, W. S. Shu, J. W. Qiu, H. B. Wang, C. Y. Lan, *Environ. Int.,* **2004**, *30*, 883.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

HEAVY METAL CONTAMINATION OF SOIL IN BAIA MARE MINING AREA

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ABSTRACT. In the Baia Mare area, located in North-Western Romania, around an industrial complex involved in mining, metallurgical and chemical activities, the environment and particularly the soils are polluted due to the acid rains and heavy metals. The soils in this area are affected by the emissions from these industrial activities. From environmental point of view, all heavy metals are very important because they cannot be biodegraded in soils, so they tend to accumulate and persist in urban soils for decades. Lead, cadmium, copper, zinc and nickel are metals frequently reported to have a high impact on organisms. Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity. In Baia Mare, 35 soil samples were collected covering the whole area (industrial and residential). The concentrations of heavy metals were determined by inductively coupled plasma atomic emission spectrometry after *aqua regia* digestion. The obtained results showed that the concentrations of Pb exceeded the intervention level for all samples; for Cu and Zn concentrations, the half of samples exceeded the intervention level; for Cd concentrations, one third of samples exceeded intervention level; for As concentrations, the majority of samples exceeded alert level; Cr concentrations exceeded alert level for two samples; and the alert level for Ni has not been exceeded.

Keywords: *heavy metals, pollution, Baia Mare, ICP-AES*

INTRODUCTION

Heavy metals in soils continue to receive increasing attention due to the growing scientific and public awareness of environmental issues and the development of analytical techniques to measure their concentrations accurately [1].

The soils are both a source of metals and also a sink for metal contaminants. The factors controlling the total and bioavailable concentrations of heavy metals in soils are of great importance with regard to human toxicology and agricultural productivity [2].

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Some heavy metals such as Cu, Mn, Co, Cr, Mo and Zn are essential in small but critical concentrations for the normal healthy growth of plants, animal or both, although they are toxic at high concentrations [3, 4].

The heavy metals of greatest concern with regard to the human health, agriculture and ecotoxicology are: Cd, Pb, Ni, As. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals are dangerous because they tend to bioaccumulate [5].

Studies of heavy metals in ecosystems have indicated that many areas near urban complexes, metalliferous mines or major road systems contain anomalously high concentrations of these elements. In particular, the soils in such regions have been polluted from a wide range of sources with Pb, Cd, As [6].

The mining, manufacture and disposal of metals and metal-containing materials inevitably cause environmental pollution [7].

EXPERIMENTAL SECTION

The ecological role of soil in urban ecosystems is very important. The state of the urban environment is affected by different sources of contamination, being a complex problem, especially when pollution is considered [8].

Mining and nonferrous ore processing activities are the leading cause of metal emissions, often associated with elevated soil concentrations in adjacent regions.

The industrial activities in this area have lead to contamination of air, soil and vegetation for decades. The winds and residual water infiltration have a serious contribution to the pollutant dispersion in soil and ground waters, reaching also the food chain since the residents from rural adjacent areas cultivate the vegetables and the animals feed in their own gardens. Considering all these aspects, it is important to monitor the heavy metal pollution in soils from this area [9].

This paper reports the determination of heavy metals in soil samples for the pollution assessment of the Baia Mare area. Lead, copper, cadmium, zinc, chromium, nickel and arsenic contents have been chosen as indicators of the pollution degree for the studied area.

In our study, the soil samples were collected to cover the whole area (industrial and residential) and to reflect both industrial and traffic pollution. The sampling sites of soils are represented in figure 1.

A number of 35 soil samples were collected in Baia Mare, in March 2007. Soil samples were collected at 0-20 cm depth and were stored in polyethylene bags for transport to laboratory. The soil samples were air-dried, mechanically ground and sieved to obtain the fraction below 2 mm. To determine the total content of heavy metals, the soil samples were digested in *aqua regia* (HCl 37.5% and HNO_3 65%), during 16 hours at room temperature and then, 2 hours, at reflux conditions.

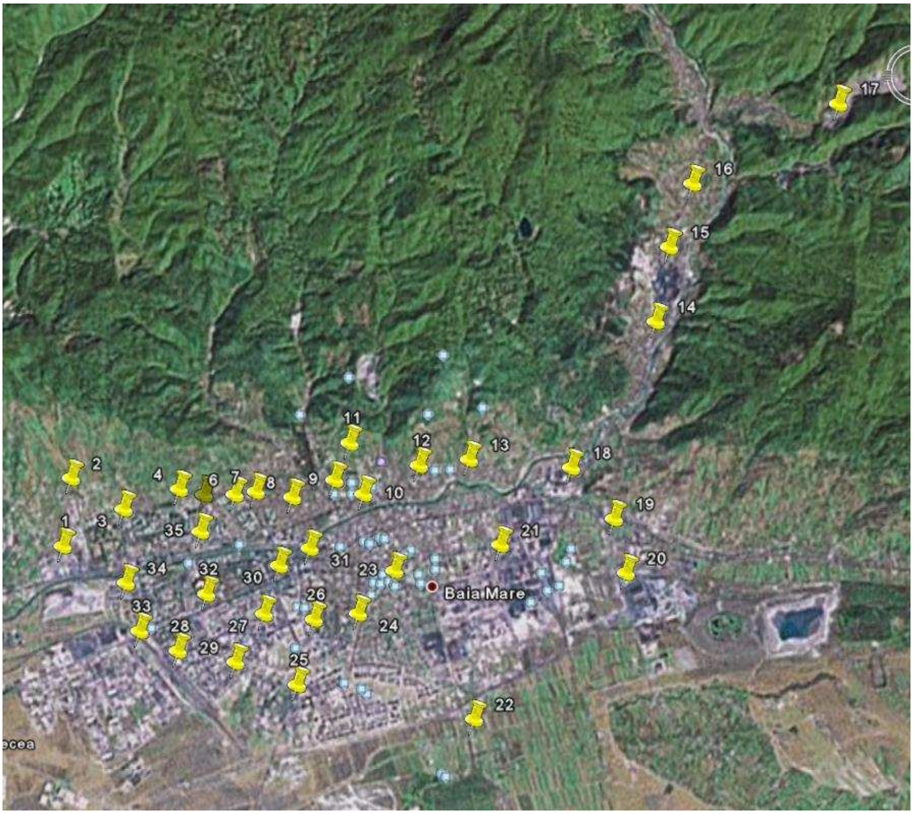

Figure 1. The sampling sites in Baia Mare.

The extract was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) using a SPECTRO FLAME (SPECTRO, Kleve, Germany). The quantification was performed using an external calibration with multielemental Merck standard solution.

The method detection limits and the uncertainties used in ICP-AES analyses for each metal are given in table 1.

In table 2 are shown the variation ranges, mean concentrations in soil and alert levels for sensitive soils, for Pb, Cu, Cd, Zn, Ni, Cr and Mn.

Table 1.

Detection limits and uncertainties of ICP-AES.

Element	Detection limit (DL), mg/kg	Uncertainty, %
Pb	2.2	8.9
Cu	0.25	7.9
Cd	0.25	9.2
Zn	0.5	7.8
Ni	0.7	8.2
Cr	2.1	9.0
Mn	0.1	7.6

Table 2.

Variation ranges, mean concentrations in soil, alert and intervention levels for sensitive soils.

Element	*Aqua regia*		Alert level (mg/kg)	Intervention level (mg/kg)
	Variation range (mg/kg)	Mean concentration (mg/kg)		
Cr	37,3-169	63,7	100	300
Ni	5,9-16,7	10,3	75	150
Cu	38,1-1770	314	100	200
Zn	109-11500	1830	300	600
Pb	87,8-23300	1792	50	100
Cd	1,9-29,9	7,9	3	5
As	22,6- 1910	166	15	25

RESULTS AND DISCUTIONS

The distribution of Cd, Ni, Cr contents, extracted in *aqua regia*, in Baia Mare area is represented in figure 2, and the distribution of Pb, Cu, Zn, As in figure 3, respectively.

The figures show that the obtained values are homogenous for Cd, Ni, Cu and As and varies in larger ranges for Pb, Cr and Zn.

The mean values of the determined concentrations are shown in figures 4 and 5, respectively.

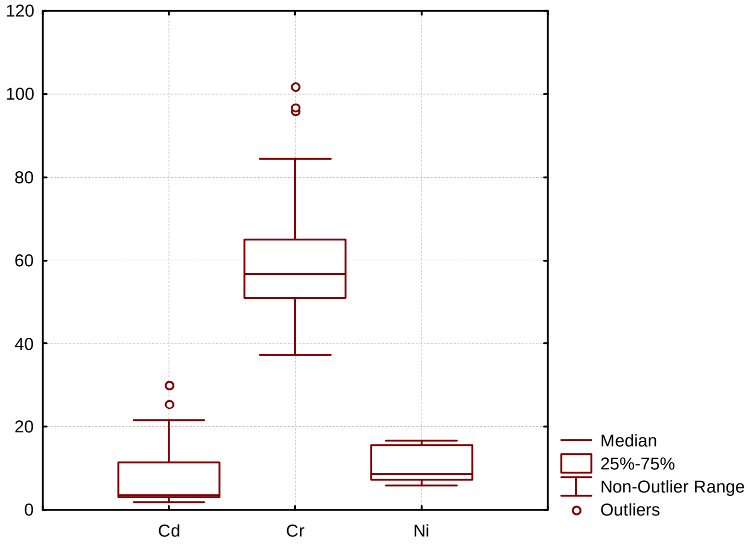

Figure 2. The distribution of Cd, Cr, Ni concentrations.

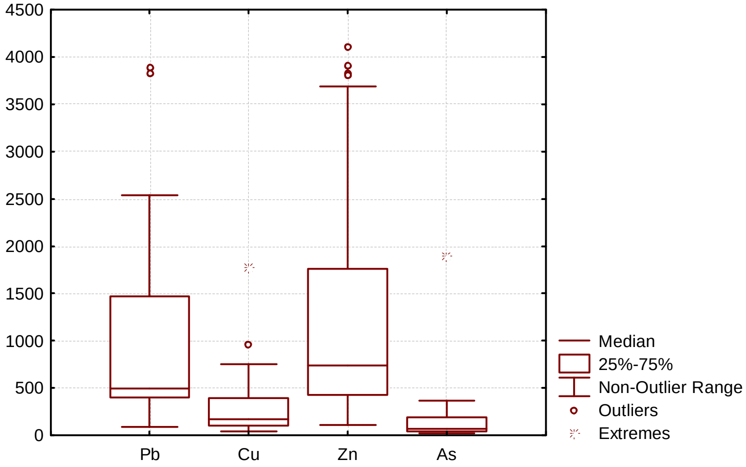

Figure 3. The distribution of Pb, Cu, Zn, As concentrations.

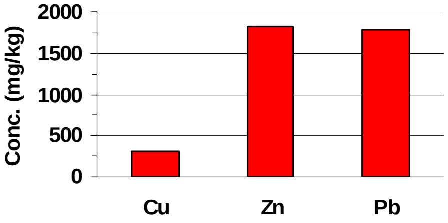

Figure 4. Mean concentrations of Cu, Zn, Pb in Baia Mare area.

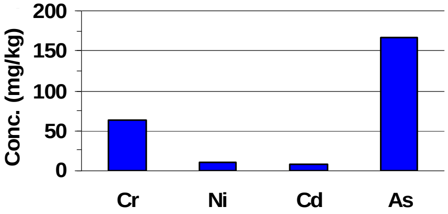

Figure 5. Mean concentrations of Cr, Ni, Cd, As in Baia Mare area.

The obtained results showed that the concentrations of Pb exceeded the intervention level for all samples; for Cu and Zn concentrations, the half of samples for Cd and third of samples for As exceeded the intervention level; and for booth metals the majority of samples exceeded alert level. The Cr concentrations exceeded alert level for two samples, and the alert level for Ni has not been exceeded.

CONCLUSIONS

The results showed that heavy metals contamination of soil in Baia Mare area is significant, indicating a severe situation, needing urgent measurements of pollution stopping and applying soil decontamination solutions, especially they cannot be degraded or destroyed.

Due to the high metal content from both areas the metal accumulation in vegetables grown in the vicinity of industrial sites represents a potential risk for public health.

The determined concentrations represent a tool for human health risk assessment and urban soil quality evaluation for planning and soil management practices [10].

REFERENCES

1. R. Lacatusu, M. Dumitru, I. Risnoveanu, C. Ciobanu, M. Lungu, S. Carstea, B. Kovacsovics, C. Baciu, Soil pollution by acid rains and heavy metals in Zlatna region, Romania, p. 817-821, In D. E. Stott, R. H. Mohtar and G. C. Steinhardt (eds.), **2001**. Sustaining the Global Farm. Selected papers from the 10th International Soil Conservation Organisation Meeting, May 24-29, 1999 at Purdue University and the USA-ARS National Soil Erosion Research Laboratory.
2. A. Kabata-Pendias, S. Dudka, *Environmental Geochemistry and Health*, **1991**, *13*,108.
3. J. B. Diatta, W. Grzebisz, K. Apolinarska, *Electronic Journal of Polish Agricultural Universities, Environmental Development*, **2003**, *6*(2), #1; Available Online http://www.ejpau.media.pl.
4. M. Tuzen, *Microchemical Journal*, **2003**, *74*, 289.
5. D. A., Cataldo, R. E., Wildung, *Environmental Health Perpectives*, **1978**, *27*, 149.
6. B. J., Alloway, "Heavy Metals in Soils", Blakie, Glasgow, **1995**.
7. C. Roman, E. Cordos, M. Ponta, V. Viman, A. Vogt, "Gold Extraction in Central and Eastern Europe and Commonwalth of Independent States", Jagiellonian University Press, Krakovia, **2005**.
8. J. M., Pope, M. E. Farago, I. Thornton, E. Cordos, *Water, Air and Soil Pollution*, **2005**, *162*, 1.
9. A. Mihaly-Cozmuta, L. Mihaly-Cozmuta, V. Viman, G. Vatca, C. Varga, *American Journal of Applied Sciences*, **2005**, *2*, 358.
10. E. A. Cordos, T. Frentiu, M. Ponta, I. Marginean, B. Abraham, C. Roman, *Chemical Speciation and Bioavailability*, **2006**, *1*, 11.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

ESTIMATION OF METALS BIOAVAILABILITY IN RIVER WATERS BY IN SITU SPECIATION USING THE TECHNIQUE OF DIFFUSION GRADIENTS IN THIN FILMS (DGT)

MARIN ŞENILĂ[a], ERIKA-ANDREA LEVEI[a], CECILIA ROMAN[a], LĂCRIMIOARA ŞENILĂ[b], BELA ABRAHAM[a], CORDOŞ EMIL[a,b]

ABSTRACT. Trace metals such as Cu, Zn, Mn and Ni play an important role as essential elements in aquatic systems. Elevated concentrations of these elements and of non-essential elements such as Cd, however, may be toxic. Investigation of the speciation of trace metals is a prerequisite to evaluating their bioavailability and mobility. Biological responses of organisms often have been shown to be related to the free-ion activity of a metal ion or to the concentration of labile metal species in solution. We evaluated the application of DGT as a tool to determine Cu, Zn, Ni, Cd and Mn concentrations and speciation in Crisul Alb River. Total metals, dissolved metals and labile-DGT metals concentration were determined. The DGT-labile species of Cu and Zn amounted to 15–30% of the total dissolved concentrations, Cd and Ni to 40-50% and Mn to 70-80%.

Keywords: *DGT, metals bioavailability, speciation, ICP-MS*

INTRODUCTION

The developed technique of Diffusive Gradients in Thin-films (DGT) is used to measure in situ concentrations and fluxes of trace substances in sediments and natural waters. It operates by introducing a localized sink which induces a diffusional flux to the DGT device [1].

DGT can be used for many different purposes, including: in situ measurements, monitoring (time averaged concentrations), speciation (labile inorganic and/or organic species), bioavailability (effective concentration), fluxes in sediments and soils, kinetic and thermodynamic constants, high spatial resolution measurements (sub-mm), 2D concentration images.

Reliable measurements of trace metal speciation in the aquatic environment are essential for studies of trace metal cycling and metal bioavailability [2].

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DGT - diffusive gradients in thin-film technique comprises a layer of hydrogel overlying a layer of immobilised binding agent (ion-exchange resin) [3-6]. The DGT technique is based on Fick's first law of diffusion. By ensuring that transport of metal ions to an exchange resin is solely by free diffusion through a gel layer of known thickness, the concentration in the bulk solution can be calculated from the metal mass measured in the resin. If a sufficiently thick diffusion layer is selected, the flux of metal to the resin is independent of the hydrodynamics in solution above a threshold level of convection [7-9].

The response of DGT devices depends on a variety of factors, including reaction and transport parameters, DGT assembly design, and sediment characteristics. In an effort to quantify the influence of some of these on DGT response, Harper et al. developed the DIFS (DGT Induced Fluxes in Sediments and Soils) model, which they used principally to investigate the effect of different resupply regimes on DGT measurements. As a result they were able to derive in situ estimates for solute resupply kinetics and capacities of solid phase reservoirs [10].

We evaluated the application of DGT as a tool to determine Cu, Zn, Fe, Co and Mn concentrations and speciation in Crisul Alb and Certej River. Total metals, dissolved metals and labile metal species concentration were determined.

EXPERIMENTAL SECTION

The *in situ* measurements were performed in June 2007, by placing the DGT devices for two days in Certej and Crişul Alb river water. The locations of the two selected catchments are presented in figure 1.

Unfiltered, filtered and DGT water samples were collected from five sampling points in Crişul Alb and three sampling points in Certej. Sampling points description are presented in table 1.

All reagent used were of analytical grade (suprapure nitric acid). Ultrapure water was used obtained using a Millipore system. DGT deployment units from DGT Research Ltd Lanchester, UK were used for deployment on the domain. An OI Analytical Microwave digestion unit was used for samples digestion. All instrumental determinations were done using an ICP-MS ELAN DRC II, Perkin-Elmer with reaction cell for reducing interferences.

Clean bottles (washed with nitric acid 0.2 M) were used to collect water samples. For total metals determinations, unfiltered water was sampled and acidulated immediately on the field (pH<2) using 2-3 drops of concentrate nitric acid suprapure. The collected samples were then digested in laboratory using the digestion unit.

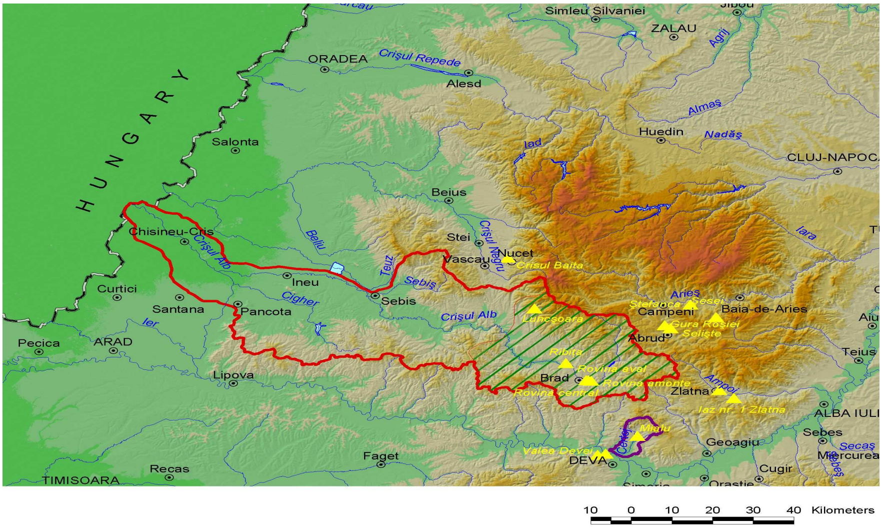

Figure 1. Crişul Alb and Certej catchments.

Table 1.

Sampling points in Crişul Alb and Certej.

Sampling Points	**Locations**	**Comments**	**Water pH values (measured on the field)**
CA1	Crişul Alb, Varsand, near to Hungarian boundary	Slightly polluted	7.47
CA2	Crişul Alb, Ineu	Slightly polluted	7.90
CA3	Crişul Alb, Gurahont	Slightly polluted	8.30
CA4	Crişul Alb, Brad, downstream Rovina dam	Slightly polluted	7.82
CA5	Crişul Alb, Criscior, backgroud	Natural background for Crisul Alb	8.17
C1	Certej, Harau	Polluted	4.92
C2	Certej, near Mialu dam	Polluted	2.54
C3	Certej, near acid mine stream	Polluted	2.98

For total dissolved metals determinations, the water samples were filtered on the field using syringes with filter holder (0.45 micron) and acidulated to pH<2.

DGT labile metal species were measured by deploying the DGT devices in the river water for metals accumulation. After two days, the devices were retrieved and the resins containing the retained metals were placed into plastic tubs and 10 ml nitric acid 1 M was added for metals elution.

RESULTS AND DISCUSSIONS

Total, total dissolved and labile DGT concentrations of Cu, Zn, Fe, Co and Mn were measured simultaneously by ICP-MS. The total and total dissolved concentrations were measured directly by ICP-MS. Calculations of the DGT measured concentration are based on the Fick's first law of diffusion:

$$F = D\, dC/dx \qquad (1)$$

where,

F - steady state flux of an ion
D - diffusion coefficient
dC/dx - concentration gradient

Each metal has a specific diffusion coefficient trough the diffusive gel. After measurement of metals in elution solution, we calculated the mass of metal accumulated in the resin gel layer (M) using equation (2):

$$M = Ce\,(V_{HNO3} + Vgel)/fe \qquad (2)$$

where,

Ce is the concentration of metals in the 1M HNO_3 elution solution (in µg/l)
V_{HNO3} is the volume of HNO3 added to the resin gel
V_{gel} is the volume of the resin gel, typically 0.15 ml
fe is the elution factor for each metal, typically 0.8

The concentration of metal measured by DGT (C_{DGT}) can be calculated using equation (3).

$$C_{DGT} = M\Delta g/(DtA) \qquad (3)$$

where,

Δg is the thickness of the diffusive gel (0.8mm) plus the thickness of the filter membrane (typically 0.14 mm)
D is the diffusion coefficient of metal in the gel
t is deployment time
A is exposure area ($A=3.14\ cm^2$)

The obtained results for measured concentrations of Cu, Zn, Fe, Co and Mn are presented in figure 2.

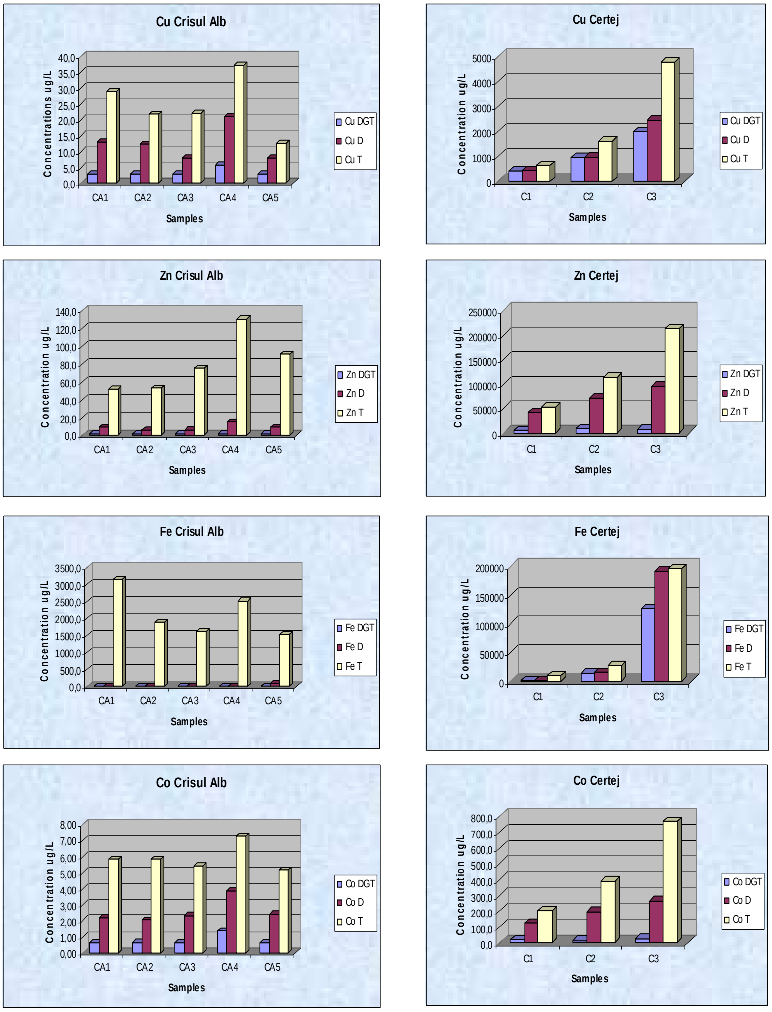

Figure 2. Total, total dissolved and DGT labile metals in Crişul Alb and Certej.

CONCLUSIONS

The DGT-labile species of Cu and Zn amounted to 15–30% of the total dissolved concentrations, Cd and Ni to 40-50% and Mn to 70-80%.

A slight pollution of Crisul Alb River with heavy metals can be observed. The pH values ranged between 7.47 – 8.30 and the higher concentrations of heavy metals were founded in particulate matter. Also, from total dissolved concentration only a low part is in labile forms.

In the sampling stations from Certej the pH values ranged between 2.54 and 4.92 indicating a strong impact of acid mining drainages. High concentrations of heavy metals were founded, a high proportion in dissolved form and most then that, bioavailable.

REFERENCES

1. W. Davison, H. Zhang, G.W. Grime, *Environ. Sci. Technol*. **1994**, *28*, 1623.
2. N. Odzak, D. Kistler, H. Xue, L. Sigg, *Aquat. Sci.,* **2002**, *64*, 292.
3. H. Zhang, W. Davison, *Anal. Chem*.**1995**, *67*, 3391.
4. W. Davison, H. Zhang, *Nature,* **1994**, 367, 546.
5. H. Zhang, W. Davison, *Anal. Chem*., **2000**, 72, 4447.
6. H. Zhang, W. Davison, *Pure Appl. Chem*., **2001**, 73, 9.
7. M. R. Twiss, J. W. Moffett, *Environ. Sci. Technol*., **2002**, 36**,** 1061.
8. H. Zhang, W. Davison, *Analytica Chimica Acta*, **1999**, *398*, 329.
9. B. A. Westrin, A. Axelsson, G. Zacchi, *J. Controlled Release* **1994**, *30*, 189.
10. M. P. Harper, W. Davison, W. Tych, H. Zhang, *Geochim. Cosmochim. Acta,* **1998**, *62*, 2757.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

REMOVAL OF Zn^{2+} FROM SOME SYNTHETIC WASTEWATERS BY IMMOBILIZED SACCHAROMYCES CEREVISIAE CELLS

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ABSTRACT. Biosorption of heavy metal ion (Zn^{2+}) by immobilized *Saccharomyces cerevisiae* cells was studied. The biosorbent that we studied was made from fresh Bakers' yeast commercially available under beads form. We used three different initial concentrations of Zn^{2+} in solution, 129.60 mg Zn^{2+}/L, 213.41 mg Zn^{2+}/L and 304.88 mg Zn^{2+}/L, for biosorption study in dynamic regime, at 25℃ and neutral pH. Adsorption yields, η, and retention capacity, Q_s, were calculated and compared. From all the experimental data it can be concluded that using yeast as a biological filter the concentration of Zn^{2+} from synthetic samples was considerably reduced. UV/VIS spectroscopy was used for determination of the adsorption degree of Zn^{2+} from synthetic wastewater samples.

Keywords: *Saccharomyces cerevisiae, heavy metals, biosorption, immobilization, molecular adsorption method.*

INTRODUCTION

Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for recovery of heavy metals from industrial waste streams [1]. Most studies of biosorption for metal removal involved the use of either laboratory-grown microorganism or biomass generated by the pharmacology and food processing industries or wastewater treatment units. The biosorption of heavy metal ions using microorganisms is affected by several factors. These factors include the specific surface

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properties of the organism (biosorbent) and the physicochemical parameters of the solution such as temperature, pH, initial metal ion concentration and biomass concentration [2]. Non-living biomass appears to present specific advantages in comparison to the use of living microorganisms. Killed cells may be stored or used for extended periods at room temperature, they are not subject to metal toxicity and nutrient supply is not necessary. Moreover, the pretreatment and killing of biomass either by physical or chemical treatments [3, 4] or crosslinking [5] are known to improve the biosorption capacity of biomass. For example, the immobilization of biomass has the advantages of using an adsorption column in a multi-cycle biosorption process.

Saccharomyces cerevisiae is an inexpensive, readily available source of biomass for heavy metal removal from wastewaters and possesses good metal-binding potential [6-8]. Yeasts are a growth form of eukaryotic microorganisms classified in the kingdom Fungi, with about 1,500 species described [9]. Investigations conducted by several researchers demonstrated that *S. cerevisiae* is capable of accumulating heavy metals such as Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+},Cr^{2+} and Ni^{2+} [10-14].

The main application of zinc is as a coating for the protection of steel against corrosion. Zinc itself forms an impervious coating of its oxide on exposure to the atmosphere, and, hence, the metal is more resistant to ordinary atmospheres than iron, and it corrodes at a much lower rate.

The toxicity of the metals increases sharply in the order Zn < Cd < Hg. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. The free zinc ion is also a powerful Lewis acid up to the point of being corrosive [15].

Metal uptake by microorganisms occurs in two stages: first stage consisting in passive adsorption of metal ions to the external cell surface, and second stage in which metal ions are subsequently transported through the cell membrane into the cell itself [16, 17].

The aim of this study was to test and compare immobilized *Saccharomyces cerevisiae* cells for their capacity to adsorb Zn^{2+}, which is a widely distributed heavy metal in water. Although calcium alginate is a cheap, non-toxic, and abundantly available immobilization matrix, insufficient literature was found about Zn^{2+} removal by alginate immobilized biosorbents.

RESULTS AND DISCUSSION

In order to investigate the effects of different Zn^{2+} concentration on metal uptake of immobilized *S. cerevisiae* cells, the biosorption experiments were conducted increasing the heavy metal ion initial concentration (129.60 mg/L; 213.41 mg/L; 304.88 mg/L). Figure 1 shows the variation of Zn^{2+} concentrations during the biosorption process.

As it can be seen in figure 1, the initial Zn^{2+} concentration decreases in every biosorption experiment. In the first 25 minutes from the beginning of the experiment, Zn^{2+} concentration drops significantly (exponential decrease). This trend is followed, in all cases, by a slowly decrease until a constant value (equilibrium concentration) was reached. For the initial concentration C_1=129.60 mg Zn^{2+}/L, after approximately 55 – 60 minutes the heavy metal ion content from analyzed samples goes to zero, which means that Zn^{2+} ions are totally retained on the immobilized *S. cerevisiae.*

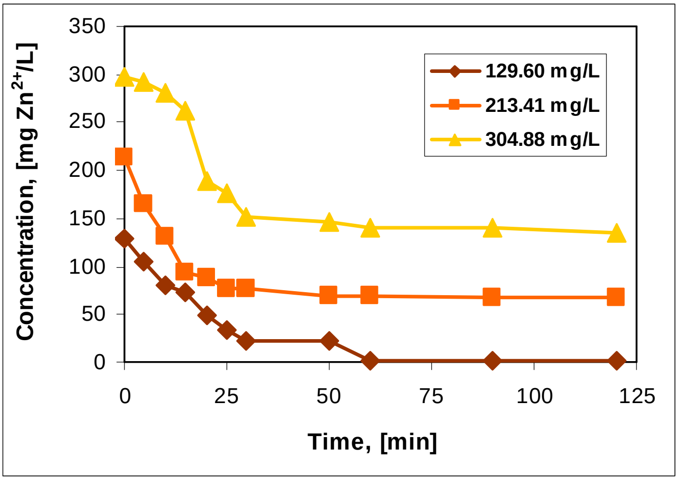

Figure 1. The biosorption of Zn^{2+} dependence of time for immobilized *S. cerevisiae* cells, at different initial Zn^{2+} concentrations. The biosorbent concentration was 2.75 g/150 ml (dry mass/volume).

Our results are in agreement with literature data regarding biosorption mechanism that is considered to take place in two stages [18]. In a first stage (dynamic regime) a pseudo-equilibrium is reached, while in a second stage (that takes place in some cases in static regime, on longer time intervals) a slowly decrease of metal concentration takes place. This decrease may be explained as a metal crossing through the cell wall, when intracellular accumulation takes place [18].

The adsorption yield, η [%], was calculated as follows:

$$\eta = \frac{C_i - C_f}{C_i} \times 100$$

where,

C_i is the initial concentration of solution (C_1, C_2, C_3), mg/L
C_f is the final concentration of Zn^{2+} in solution, mg/L.

For this parameter, the calculated values are ranging between 98.80% (for C_1 = 129.60 mg Zn^{2+}/L) and 56% (for C_3 = 304.88 mg Zn^{2+} /L).

The metal uptake is influenced by the initial Zn^{2+} concentration. The retention capacity, Q_s, of yeast adsorbent increases from 5.1 mg Zn^{2+}/g adsorbent for C_1=129.60 mg Zn^{2+}/L to 7.1 mg Zn^{2+}/g adsorbent for C_3=304.88 mg Zn^{2+}/L (figure 2).

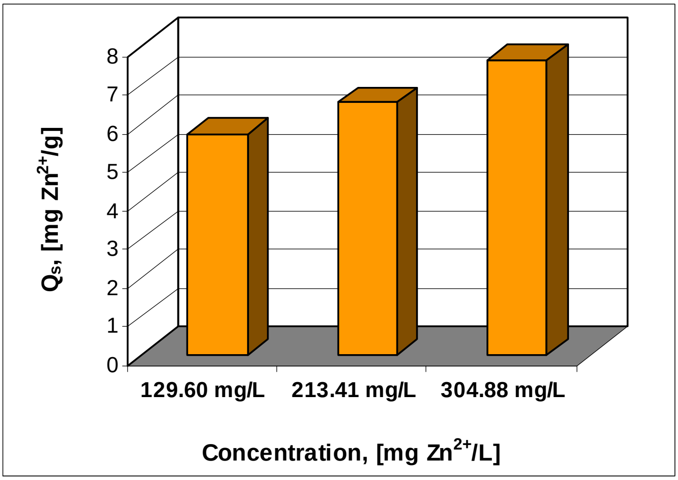

Figure 2. The influence of the initial concentration over the Zn^{2+} uptake, Q_s, by the immobilized *S. cerevisiae*. The biosorbent concentration was 2.75 g/150 ml (dry mass/volume).

CONCLUSIONS

In this study, immobilized *S. cerevisiae* cells have been successfully used as a biosorbent for the removal of Zn^{2+} ions from synthetic wastewaters.

For the successful application of biosorption, biomass needs to be immobilized to increase its mechanical strength, density, reusability and resistance to mechanical environments. In this study, Calcium alginate gel was chosen for the immobilization experiments as it is cheaply and abundantly available, nontoxic and highly selective for certain ion species. Calcium alginate proved to be a suitable material for immobilization of *Saccharomyces cerevisiae* cells.

The initial Zn^{2+} concentration decreases in every biosorption experiment. For the initial concentration C_1 = 129.60 mg Zn^{2+}/L, after approximately 55 – 60 minutes the heavy metal ion content from analyzed samples goes to zero, which means that Zn^{2+} ions are totally removed from the water sample. The maximum retention capacity, Q_s, was calculated to be 7.1 mg Zn^{2+}/ g adsorbent for the biggest initial concentration (C_3=304.88 mg Zn^{2+}/L).

As a general conclusion we can say that using yeast as a biological filter it's a good method in reducing the concentration of heavy metals ions from wastewaters.

EXPERIMENTAL SECTION

Microorganism. The microorganisms were obtained from commercial type *Saccharomyces cerevisiae* cells (Pakmaya).

Biosorbent immobilization. For calcium alginate immobilization of yeast, 2.5 g biosorbent (baker yeast's) was suspended in 30 ml alginate solution (3g Na-alginate mixed with 1 ml ethanol was added to 100 ml distillated water and incubate for 30 minutes). A 100 ml aliquot of alginate - biosorbent suspension containing 2% Na-alginate was added drop by drop to 1000 ml of 2% $CaCl_2$ solution with a peristaltic pump. Alginate drops solidified upon contact with $CaCl_2$, forming beads and thus entrapping biosorbent particles. The beads were allowed to harden for 30 min and then were washed with distillated water in order to remove excess of calcium ions.

Metal uptake. The retention capacity of biosorbent, Q_s, was calculated as follows:

$$Q_s = \frac{m_i - m_f}{g}$$

where,

m_i is the initial mass of metal from ion solution, mg
m_f is the final mass of metal in the solution after biosorption, mg.
g is the mass of the dry *S. cerevisiaie,* mg

Biosorption experiments. The stock solution of Zn^{2+} was prepared by dissolving a weighed quantity of $ZnSO_4 \times 7H_2O$ in deionized water. The immobilized biosorbent, 2.75 g, was added in a flask over 150 ml Zn^{2+} solution (129.60 mg Zn^{2+} /L, 213.41 mg Zn^{2+}/L and 304.88 mg Zn^{2+}/L) under continuous magnetic stirring at 200 rot/min for 2 h. The experiment was continued until a constant Zn^{2+} ion concentration was obtained. 1 ml samples were taken at different intervals of time and analyzed in order to determine Zn^{2+} concentration.

Zn determination. Zn^{2+} ions concentration was determined in the supernatant according to STAS 6327-81 using spectrophotometric method (potassium ferricyanide, λ = 420 nm, UV/VIS JENWAY 6305 spectrophotometer).

REFERENCES

1. B. Volesky, *Tibtech.*, **1987**, *5*, 96.
2. A. I Zouboulis, E. G. Rousou, K. A. Matis, I. C. Hancock, *Chem. Technol. Biot.,* **1999**, *74*, 429.
3. D. Brady, A. Stoll, J. R. Duncan, *Environmental Technology*, **1994**, *15*, 229.
4. C. P. Huang, A. Morehart, *Water Res.*, **1990**, *4*, 433.
5. A. Leusch, Z.R. Holan, B. Volesky, *J. Chem. Technol. Biot.,* **1995**, *62*, 279.
6. G. M. Gadd, “Fungi in Bioremediation”, Cambridge University Press, Cambridge, **2001**, chapter 5.
7. C. P. Kurtzman, J. W. Fell, “The Yeast Handbook”, Germany: Springer - Verlag Berlin Heidelberg, **2006**, chapter 1.
8. P. R. Norris, D. P. Kelly, *J. Gen. Microbiol.*, **1977,** *99*, 317.
9. B. Volesky, H. May, Z. R. Holan, *Biotechnol. Bioeng.,* **1993**, *41*, 826.
10. D. Brady, J. R. Duncan, *Appl. Microbiol. Biotechnol.,* **1994**, *34*, 149.
11. A. Engl, B. Kunz, *J. Chem. Technol. Biot.*, **1995**, *63*, 257.
12. Y. Lu, E. Wilkins, *J. Hazardous Materials*, **1996**, *49*, 165.
13. B. A. Volensky, H. A. Mayphillips, *Appl. Microbiol. Biotechnol.,* **1995**, *42*, 165.
14. B. S. Wilhelmi, J. R. Duncan, *Biotech. Lett.*, **1995**, *42*, 1007.
15. C. White, G. M. Gadd, *FEMS Microbiol. Ecol.,* **1986**, *38*, 277.
16. G. M Gadd, J. A. Sayer, “Environmental Microbe–Metal Interactions”, ASM Press, Washington DC, **2000**, chapter 3.
17. K. J. Blackwell, I. Singleton, J. M. Tobin, *Appl. Microbiol. Biotechnol.,* **1995**, *43*, 579.
18. S. Li, J-I. Xia, H. Huan, N. Zhen-Yoan, *J. Central South University of Technology*, **2007**, *14*, 41.

STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIII, 3, 2008

ECOLOGICAL SYSTEM FOR WASTE FORMING SANDS IN FOUNDRIES RECYCLING

VIOREL DAN[a], OVIDIU NEMEŞ[a], VASILE-FILIP SOPORAN[a]

ABSTRACT. This work presents results regarding the thermal regeneration of waste forming sands. The following aspects were considered: process thermal and hydro-dynamical conditions, constructive elements specifically for calcinations in fluidized bed, recommended parameters for the technological process of thermal regeneration, constructive solutions for the fluidized bed calcinations module and specifically parameters for the calcinations module.

Keywords: *waste forming sands, thermal regeneration, fluidized bed*

INTRODUCTION

Foundry sands wastes utilization represent a priority direction at global [1, 2] and national level [3] from at least two points of view: firstly because there are great quantities of waste sands to be deposited and secondly to protect the natural reserves of sand.

Regeneration of sands forming mixtures [4] involves removing the damaged components, the sand obtained after regeneration having comparable properties with those of new sand, while its cost is lower than that of the new one (reaching often up to about 25 % of the price of the new sand).

In this paper we present a thermal regeneration process of the forming sand wastes.

RESULTS AND DISCUSSION

In the process of the forming sand mixtures manufacture with chemical binders, bonding of the sand granules takes place in two ways: the first is the physical way and is related to the binders distribution on the sand grain during mixing process when a number of “bridges” between the sand grain during the compression were formed, and the second refers to the physical and chemical processes during which the system and cohesive forces appearance are strengthened. In this case, the refractory granular material participates in the chemical interaction with the binders and presents importance, especially for the existence, in the sand, of some active chemical ingredients.

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In case of organic binders, after the knock-out of mould, a heterogeneous product forms, as a result of the temperature gradient presence in the mould: around solidified alloy, resin is completely burnt (CO and CO_2); in the next region of the mould, a multitude of products, more or less volatile were generated, and also a damaged layer of resin that is stuck on the sand grain; the external mould parts are subject to lower temperatures and the building materials are almost undamaged.

The thermal regeneration consists in bringing the sand to a sufficiently high temperature for a certain period of time in order to ensure that the chemical binders (synthetic resin) from the surface of the sand grain were burnt. It is important that the heat unit and the air temperature to be adequate, otherwise the synthetic resin could be transformed in volatile organic carbonates which might lead to an increase of the air emissions over the allowable limit.

The heat transfer, that takes place between the fluidized bed and the solid particles, is made according to the following relation:

$$Q = A \cdot \alpha \cdot \Delta T = A \cdot \alpha \cdot (T_f - T_p), \quad [W] \tag{1}$$

where,

A is the surface area participating in the thermal exchange, m^2
α is the heat transfer coefficient between the two parts, $W/m^2 \cdot K$
T_f is the fluid temperature, K
T_p is the particles temperature, K.

Due to the large heat exchange area (the entry temperatures of the gas under the grid layer are 950 ÷ 1000 ℃) the fluidized layer of granular material with a thickness of 0.40 ÷ 0.45 m is maintained at a temperature high enough to remove the binder film from the sand granules surface.

To maintain the sand layer fluidized, it is necessary to fulfill the following condition:

$$\Delta p = H \cdot (1 - \varepsilon) \cdot (y_p - y_f), \quad [N/m^2] \tag{2}$$

where,

Δp is the hydraulic resistance of the fluidized layer (v = 0.4 ÷ 1.0 m/s)
H is the fluidized layer height, m
γ_p is the volumetric weight of solid particles, N/m^3
γ_f is the volumetric weight of the fluid in N/m^3
ε is the rarefaction index.

In the proposed technology, the heat treatment module must meet, under the regeneration process of the waste mixture, the following functions: bring the mixture at a sufficient high temperature, in order to ensure that the binders burning process starts (pre-heat stage); burn the chemical binders from the sand granules (burning stage); recover the heat from the combustion process and from the regenerated sand cooling; cool the waste sand to an acceptable temperature for the technological preparation process of the forming mixture; collect toxic gases resulted from the heat treatment, in order to filtrate them.

Figure 1 schematically presents the thermal treatment module under the environmental regeneration of waste sand mixtures.

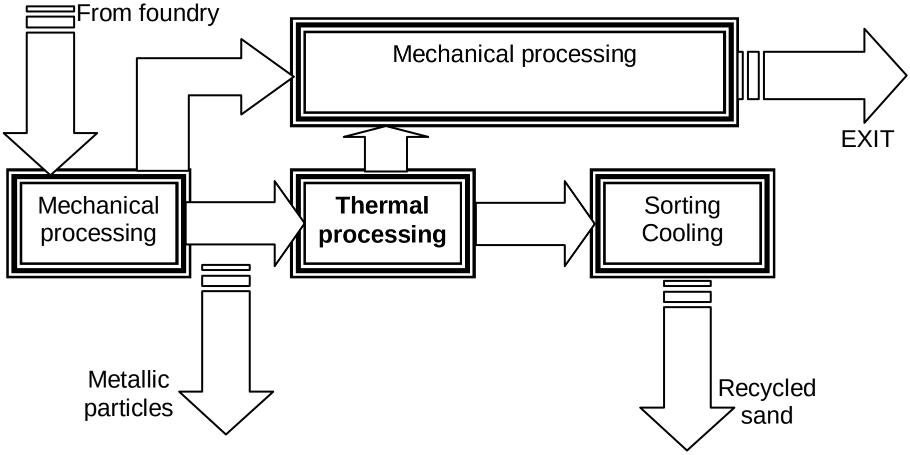

Figure 1. The thermal processing module in the ecological system.

CONCLUSIONS

The regenerative thermal process can be applied successfully in the case of wastes with organic binders, which are destroyed by burning.

To achieve a good efficiency of the process is mandatory to recover the heat from the combustion gases and from the cooling system of the recycled sand.

For the thermal regeneration process in fluidized bed, the used forming mixture must be subjected, before the regeneration process, to a separation operation of the metallic impurities, grinding and individualization of the granules.

After the regeneration process, the resulted gases must undergo a purification process before their discharge into the atmosphere.

REFERENCES

1. O. Pretet, *Fonderie Fondeur d`aujourd`hui*, **2004**, 233.
2. M. Zatkoff, "ASM Handbook, vol.15, Casting", ASM International, **1996**.
3. V. Dan, *Studii şi cercetări privind utilizarea energiei microundelor în procesele din turnătorii*, Cluj-Napoca, Teză de doctorat, **2000**.
4. G. Clements, *The Engineer*, **1991**, 23.

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TOWARD NEW COMPOSITE MATERIALS STARTING FROM MULTI-LAYER WASTES

ANCA MARIA GOMBOŞ[a], OVIDIU NEMEŞ[a],
VASILE FILIP SOPORAN[a], ALEXANDRA VESCAN[a]

ABSTRACT. Starting from multi-layer wastes new composite materials have been obtained. Physical properties of these materials and the hygroscopic behavior were established.

Keywords: *waste, multi-layer packages, plastic materials, composite materials*

INTRODUCTION

Wrapped products and merchandise represent a part of the modern world and facilitate our lives in various ways. However, the volume of wastes from packages dramatically increased in the recent times. This problem is more and more acute due to the diversity and the large number of these types of packages, which through their constitution demand a selective collection. Due to the non biodegradable nature of the packages waste, finding solution in order to put good use of them is absolutely necessary.

As a result of the problems caused by wastes, a series of researches are carried out. As far as the multi-layer packages are concerned, they are being studied not only from the point of view of materials recuperation [1-3] but also of obtaining new materials [4]. Due to the fact that the polyethylene terephthalate packages together with multi-layered ones are preponderant in the food industry, there are some researches concerning valorization through cracking [5].

Obtaining new composite materials from wastes represent a remarkable interest as far as there are some preoccupations in recycling paper, wood and plastic wastes. In their studies, Cui et al. [6], Caroll et al [7], Ichazo et al. [8], Selke and Wichman [9] pay a special attention to composite materials from wooden and plastic waste. Also, other researches regarding new composite materials, based on paper and polymeric resin, have been carried out [10, 11].

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RESULTS AND DISCUSSION

In this paper we propose a study on the properties of some composite materials obtained from multi-layer packaging wastes, containing aluminum, paper and polyethylene terephthalate (ex. juice packs). The multi-layer packages have been carefully washed and cut into small pieces so they could be shredded using a laboratory knives mill, GRINDOMIX GM 200**.** The obtained material was compressed at high temperature without any kind of bonding materials addition.

There have been carried trials at various grinding, pressure and temperature levels. In addition, the plate composition was also diversified. There have been produced plates from aseptic ground packages and plates with addition of recovered polyethylene from multi-layer packages with paper and plastic material content.

The composite material plates have been produced in a mould presented in figure 1. To ensure the heating of the material, the mould was endowed with an electrical resistance, which guarantees the required forming temperature.

Figure 1. The plates fabrication mould.

To obtain different plates we firstly vary only the pressure (between 2 - 20 MPa) and the temperature (maximums between 120 - 170°C) figure 2), and afterwards we have varied the composition by developing some mixing formula: shredded multi-layer packages and recovered polyethylene from packages which do not contain aluminum in ratios of 6.5:1 and 1:1.02, multi-layer package and PET flakes in ratio of 1.02:1 (figure 3).

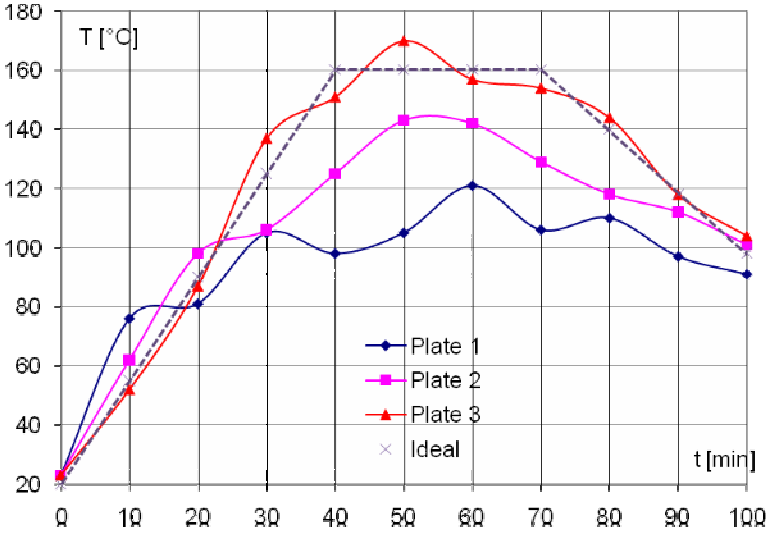

Figure 2. The temperature variation during the forming process.

Varying the composition of the initial mixture we obtained new composite materials with different porosity and permeability. In order to achieve this, we used polyethylene from multi-layer packages containing only paper and plastic material. The recovery of the polyethylene was made possible by stirring the mixture at 100℃.

a.
75 g multi-layer packages.

1:1

b.
65 g multi-layer packages
10 g polyethylene.
6.5:1

c.
38 g multi-layer packages;
37g PET flake.
1.02:1

Figure 3. Plates obtained with various ratio formulas.

From all the obtained plates only those with polyethylene terephthalate addition had a brittle structure because of the PET flakes which remain unmodified in their structure.

The plates behavior in humid environments

The experiments performed to establish the hygroscopic behavior consists in dropping 2 ml of water on the plate surface and measuring the total absorption time (table 1).

It was observed that water does not penetrate in the areas covered with aluminum foil and the water front does not advance in that area (figure 4a. and 4b.).

Table 1.

The absorption behavior of the plates.

Test	Water quantity [ml]	Absorption time [min]	Dispersion front $[d_i - d_0]$ * [mm]	Spot diameter at the total water absorption [mm]
1	2	t_0=0	0	60
		t_1=10	10 – 15	
		t_2=15	10 – 25	
		t_3=20	20 – 35	
2	2	t_0=0	0	85
		t_1=10	10 – 15	
		t_2=15	20 – 25	
		t_3=27	30 – 45	

* d_o - the diameter at the time t_o; d_i - the diameter at the time t_i; i = 1 ... 3.

The experimental data showed that we have a 3.5 mm penetration depth after 20 minutes, see figure 4c (the plate thickness is 6 mm).

After the total absorption of the water, the plate showed a form alteration consisting in a slight growth of the material (figure 4b and 4c).

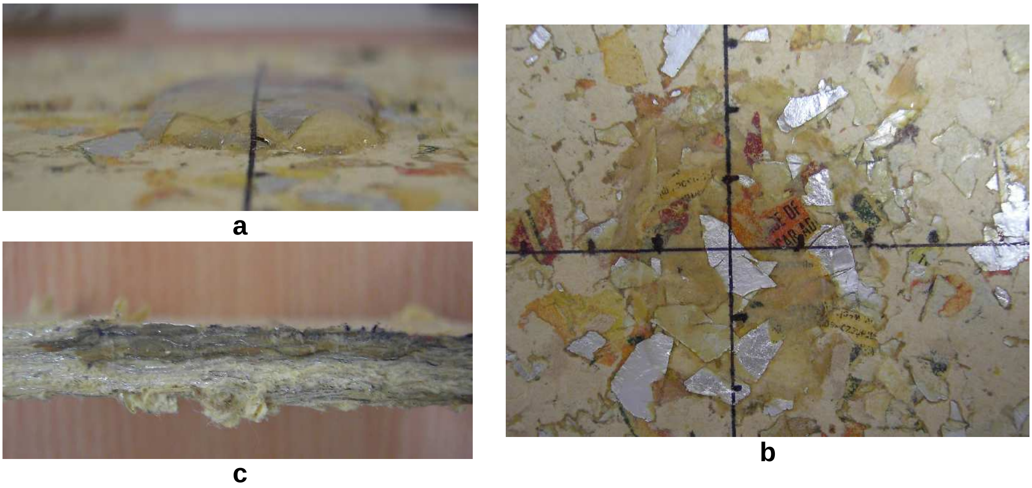

Figure 4. Water behavior of the plates. **a**. water drop on the plate surface; **b**. water dispersion on the surface, **c**. water penetration in the plate.

CONCLUSIONS

Taking in account the fact that we observed that the new composite materials we obtained, absorbed water, we can concluded that there cannot be used in humid environment like exterior building plating.

It was noticed the fact that an increased polyethylene ratio can improve the hygroscopic behavior, leading even to impermeable surfaces.

In the same time this plates can be used in the study of adhesive bonded joint assemblies.

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REFERENCES

1. C. Ludlow-Palafox, H. A. Chase, *The Chemical Engineer*, **2001**, 28.
2. C. Ludlow-Palafox, H. A. Chase, *Industrial & Engineering Chemistry Research*, **2001**, *40,* 4749.
3. C. Ludlow-Palafox, H. A. Chase, *Proceedings of the 6th World Congress of Chemical Engineering.* Melbourne, Australia, **2001**.

4. A. Murathan, A.S Murathan, M. Gürü, M. Balbas, *Materials and Design,* **2007**, *28*, 2215.
5. D. Stanică–Ezeanu, *Materiale Plastice*, **2007**, *44*, 3.
6. Y. Cui, S. Lee, B. Noruziaan, M. Cheung, J. Tao, *Composites: Part A*, **2008**, *39,* 655.
7. D.R. Carroll, R.B. Stone, A.M. Sirignano, R.M. Saindon, S.C. Gose; M.A. Friedman, Resources, *Conservation and Recycling*, **2001**, *31*, 241.
8. M.N. Ichazo, C. Albano, J. Gonzalez, R. Perera, M.V. Candal, *Compos Struct*, **2001**, *54*, 207.
9. S.E. Selke, I. Wichman, *Composites: Part A*, **2004**, *35*, 321.
10. I. Baroulaki, G. Pappa, P.A. Tarantili, D. Economides, K. Magoulas*, Proceeding of the 8th Polymers for Advanced Technologies International Symposium*, Budapest, Hungary, **2005**, 13.
11. P. Yadav, A. Nema, S. Varghese, S.K. Nema, *Polymer Engineering and Science*, **1999**, *39*, 1550.