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BASALT TUFA AS A BACTERICIDE FILLER FOR SOME PACKAGING MATERIALS

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Abstract: *A dependence of the catalytic and antibacterial activity of some basalt tufa samples on their qualitative and quantitative composition, preliminary thermal and/or chemical treatment conditions were investigated. As seen from the chemical X-ray phase and atom adsorption analyses, the tufa is a highly siliceous (Si/Al mass ratio is about 4.7÷5.9) zeolite-like mineral with comparatively high content of iron (68÷74 g/kg), some bioelements (Mg, Ca, K, Na) and microelements (Ti, Mn, Zn, Cu). The positive* $(\equiv Si^{+})_s$ *and negative* $(\equiv SiO^{-})_s$ *surface active centers were determined by IR spectroscopy. These points ensure high catalytic and bactericide activity of the material. The influence of preliminary thermal and chemical treatment of basalt tufa on its bactericide activity against pathogenic Staphylococcus aureus and Escherichia coli was also investigated. Possible utilization of natural basalt tufa as an antibacterial filler for the packaging materials is discussed.*

Keywords: *basalt tufa, catalytic and antibacterial activity, packaging materials, Staphylococcus aureus, Escherichia coli.*

1. Introduction

Quality of packaging materials is an important factor influencing consumer acceptance, competitive potential, storage time and safe transportation of various goods. As a result, the modern packaging materials industry shows strong extension, new technologies are developing and new materials are coming to the market. Construction of the packaging materials consisting of some bioactive, bactericide agents, enzymes and genuine films is one of promising directions in this branch. Such materials can effectively preserve biologically and nutritionally valuable components and keep high overall quality of the foodstuff.

The potential usability of the composites based on the natural alumosilicate basalt tufa (BT) in construction of such bactericide materials is comparatively high. BT can be obtained in the form of magmatic rock (volcanic glass, basalt, slag) or as a mineral (plagioclase, pyroxene) [1]. BT tufa is one of the waste materials formed massively at modern industrial basalt production. Many efforts are being made to elaborate effective solutions for its utilization. Depending on the chemical composition, BT can be used as highly effective pigments [2], sorbents for drinking water and wastewaters treatment [1], as a substrate for the toxic waste and exhaust gas decontamination [3] and so on. Since this mineral is easily available and ecologically safe, it can potentially be proposed as a

filler for the composite antibacterial materials.

It is known that the adsorption, antibacterial and catalytic parameters of BT can vary depending on its chemical composition, structure, porosity, dispersability and preliminary thermal and/or chemical treatment [1, 4]. Therefore, it is possible to govern the catalytic and antibacterial activity of BT by changes in the above characteristics that can be through thermal or chemical modification of the material. This way, either highly active catalysts and bactericide compositions or low active passive materials can be obtained. Both solutions seem promising in the context of construction and development the mineral fillers for modern packaging.

This paper deals with the investigation of dependence of catalytic and bactericide characteristics of BT on its qualitative and quantitative composition and conditions of its thermal and chemical modification. A possibility of developing bactericide packaging filler using various modified and treated BT samples is also discussed.

2. Experimental

The tufa samples obtained from Polytske-2 (Ukraine) deposit (see chemical composition data in Table 1) and products of their thermotreatment at 250–1000 ^{0}C or chemical treatment with H_2SO_4, HCl, HNO_3, H_3PO_4 were used in this experimental series.

Chemical composition of the samples was determined by classical chemical methods (for Si, Al, Fe, Mg, Ca, P and S) and AAS (for Na, K, Zn, Ni, Cu, Co) at KAC-120 M1 spectrometer in the acetylene/air flame [5].

The powder surface was analyzed with X-ray Photoelectron Spectroscopy (XPS) also referred to as Electron Spectroscopy for Chemical Analysis (ESCA) using ESCALA™ XI$^+$ X-ray Photoelectron Spectrometer Microprobe. XPS is an elemental analysis technique, which is capable of detecting all elements except for H and He and has a nominal detection limit of ~0.1 atom %. Spectral interferences may prohibit the detection of some elements in relatively low concentrations. Samples were measured at a 90° take-off-angle yielding a sampling depth of ~10 nm. The analysis area was ~500 µm in diameter. Analyses were performed with a monochromatic Al kα x-ray source. The powder particle size analysis was performed with a Field Emission Scanning Electron Microscopy (FESEM) using Hitachi SU70 Electron microscope. FESEM images depict topographic features of the sample surface. FESEM imaging was performed at 2 keV. One hundred particles of each powder were measured to provide an average particle size. Both powders were coated with ~100 Å of gold to facilitate analysis [6].

Surface area of the samples has been determined using BET method by the low-temperature argon adsorption while all IR spectra were recorded with Avatar 320 FT-1R spectrophotometer.

Antibacterial activity of the samples was investigated using the diffusion method (also known as the disks method) [7]. The bacterial colonies were cultivated from the ATCC standard strains *Escherichia coli* and *Staphylococcus aureus*, while a paper disk impregnated with antibiotic novobiocin was used as a control experiment.

3. Results and Discussion

Following components were identified in natural tufa samples: zeolites (35–40 %), montmorillonite (30–40 %), feldspars (10–15 %), silica materials (4–5 %) and hematites (3–5 %) [1]. Averaged data of the tufa composition are shown in Table 1 as mass percents of the corresponding oxides.

Table 1.

Chemical composition of the basalt tufa from Polytske-2 deposit

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3
67.44	1.75	12.82	10.14	0.09	5.02	0.46	0.94	1.06	0.12	0.11

The data in Table 1 prove that BT is in fact an alumosilicate having the mass ratio Si/Al=4.7÷5.9, which also contains 68÷74 g/kg of Fe. Besides that, the mineral also consists of detectable amounts of micro-elements Mn, Zn, Cu, Ni, Co ranged from 0.71 to 0.08 g/kg [1].

It was also found that many physico-chemical parameters of the tufa, which are responsible for its adsorption, catalytic and antibacterial properties, can be sufficiently altered after its thermal treatment. In this context, an influence of the treatment temperature of the tufa grains porosity and specific surface area was carried out for the four hours long modification at 105, 250, 400, 500, 750 and 1000 °C in air.

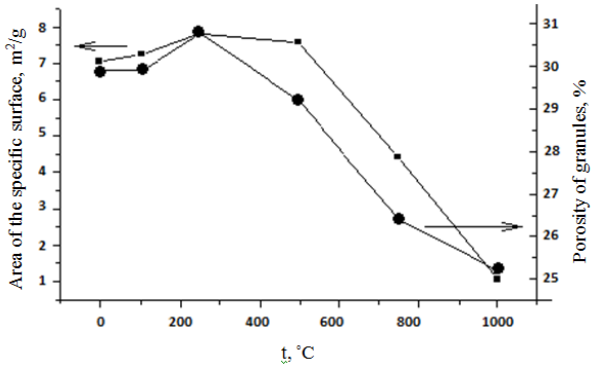
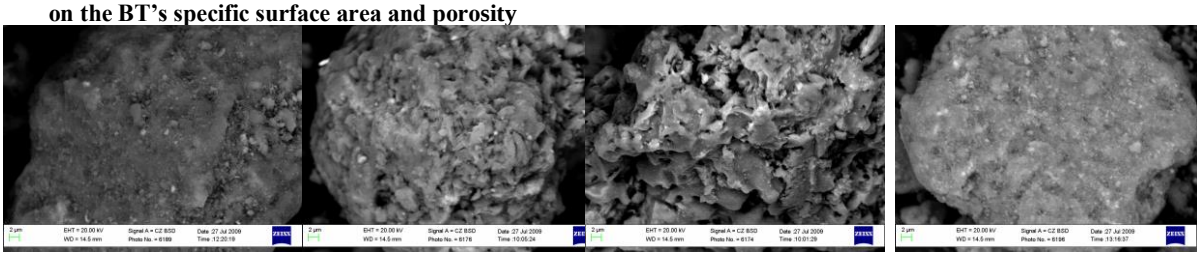


Figure 1. Influence of the modification temperature on the BT's specific surface area and porosity

As seen from Fig. 1, the area of specific surface and porosity of the grains sized from 1 to 2 mm depend on the thermo-treatment conditions. Both dependencies look similarly – reach their maximum values for 200–400 ^{0}C and then decrease for the higher modification temperatures. Such a pattern may be caused by losses of the hygroscopic and zeolite's water that occurs at this temperature [8]. Adsorption capacity of the tufa also increases for the temperatures 105–400 ^{0}C followed by the decrease for the higher temperature values.

Pores, surface holes and channels can be seen in the electron microscope images taken with zoom x10000 (see Fig. 2). Porosity of the grains is rising for temperatures 250–400 ^{0}C and then drops at further increase of temperature. This effect is caused by sintering of the powdery particles ended by melting of the mineral at 1050 ^{0}C.

Mechanic strength of a material is one of important parameters outlining its possible utilization as a catalyst or bactericide agent. This parameter is linearly growing with the thermal modification temperature.



A B C D

Fig. 2. Electronic microscope images of the BT disperse particles during the thermomodification process: A – natural source material; B–D – after thermomodification at 250 ^{0}C, 400 ^{0}C and 1000 ^{0}C respectively.

No evidence of the new phases formation was found in the X-ray structure analysis data embracing the range 105–1000 ^{0}C. Therefore, a rise in the mechanical strength can be caused by a deeper structuring of the granules because of the constitution water losses.

An acidic modification of the tufa samples was performed using the 3 mole/l solutions

of H_2SO_4, HCl, HNO_3 and H_3PO_4 during 3 hours at the room temperature for the ratio solid phase/solution 1:1.5. Following conclusions can be drawn from analysis of the acidic modification results shown in Table 2.

- The acids can be placed in the sequence $HCl > H_2SO_4 > H_3PO_4 > HNO_3$ according to their activity in elution of calcium;
- Similar sequence based on the magnesium elution efficiency would be $H_2SO_4 > HC1 > H_3PO_4 > HNO_3$;
- Total amount of eluted aluminum and iron in the form of their oxides M_2O_3 decreases in the row $H_2SO_4 > HC1 > H_3PO_4 > HNO_3$ [9].

As seen from Table 2, H_2SO_4 and HCl are the most effective acidic modifiers of the BT materials.

Table 2. Concentrations of Ca^{2+}, Mg^{2+} and (Al^{3+}+ Fe^{3+}) found in the acidic extracts (C) and their elution degrees (α)

Modifying acid	Ca^{2+}		Mg^{2+}		Al^{3+}+ Fe^{3+} as Me_2O_3	
	C (g/l)	α, %	C (g/l)	α, %	C (g/l)	α, %
H_2SO_4	0.3360	68.08	0.1345	0.97	4.9280	14.30
HCl	0.5605	93.57	0.0895	1.97	4.3900	12.74
H_3PO_4	0.4485	90.88	0.0560	1.23	4.5280	13.14
HNO_3	0.0745	15.09	0.0220	0.49	2.4680	7.16

The acidic-soluble phases are being eluted from the surface of BT in course of its acidic modification, which results changes in the chemical composition, increase of the tufa's defect ratio, specific surface area and concentration of the active centers. IR-spectroscopy data prove that the Bronsted-type (≡Si–OH) and Lewis-type ($\equiv Si....O(H^+)H)^-$ surface singular points act like catalytic and antibacterial centers of BT [1].

These conclusions were alternatively verified by chemical analysis, which evidenced rise in SiO_2 content after acidic modification of the tufa samples.

A comparative study of catalytic activity (CA) of the source and modified tufa was realized using a model reaction of hydrogen peroxide decomposition. An experimental mixture contained H_2O_2 – NaOH – H_2O (pH=10) and BT powder (weight ratio was 1:20) at 20 ^{0}C. Permanganate titration was used to determine concentration of peroxide. As a result, CA of the thermally modified BT was found 1.6–3 times higher than that for the natural untreated material. Catalytic activity of tufa depends on the thermotreatment temperature and increases for the sequence: untreated tufa < modification at 250 ^{0}C < 400 ^{0}C < 1000 ^{0}C. This result proves that chemical composition of the tufa surface that changes in course of the modification is the crucial factor governing its catalytic activity.

As mentioned above, adsorption and catalytic activity of natural alumosilicates can sufficiently influence their adsorption and catalytic properties. This kind of treatment causes changes in qualitative and quantitative composition of the material and generates new surface active centres [10]. Detailed results of the catalytic activity values are shown in Fig. 3 for various modification conditions and concentrations of H_2O_2.

It has been found that CA of the chemically modified samples increases for 1.2–4.5 times if the pH of the medium is alkaline comparing to the activity values of untreated tufa. Besides, the type of the modifying agent also influences the tufa activity and the following sequence can be built according to increase of the agents' efficien-

cy: untreated tufe < modified by NaOH < HNO_3 < H_3PO_4 < H_2SO_4 < HCl.

Next stage of the investigation was aimed onto determination of antibacterial activity of various tufa samples. It was found that antibacterial activity of both thermally and chemically modified examples against *Escherichia coli* is higher than that against *Staphylococcus aureus* (see Table 3).

Further elaboration of practical aspects related to possible utilization of these materials as antibacterial components leads to the concept of the tufa-containing packaging materials that should be developed, constructed and then compared with other packaging materials exhibiting or not exhibiting some antibacterial properties.

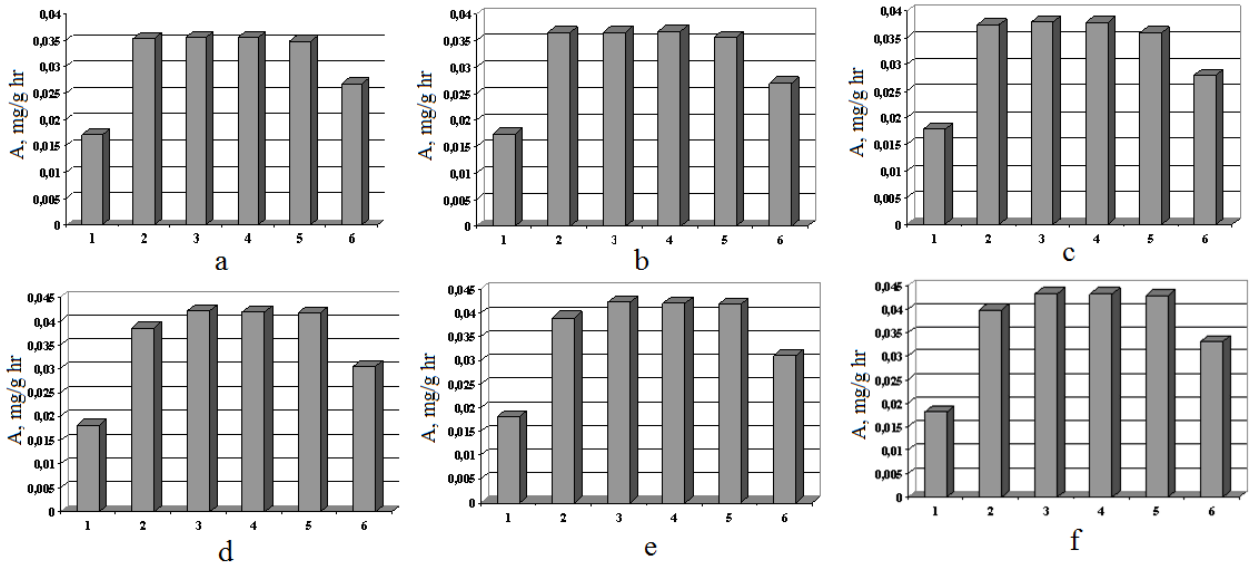


Figure 3. Catalytic activity of the chemically modified tufa samples in the system H_2O_2 – NaOH – H_2O $C_0(H_2O_2)$ = 0.05 (a); 0.1 (b); 0.2 (c); 0.4 (d); 0.8 (e); 1.6 (f) M/l: 1 – untreated BT; 2–6 – after modification with HNO_3, HCl, H_2SO_4, H_3PO_4, NaOH correspondingly.

Table 3.

Antibacterial activity of thermally and chemically modified tufa samples against *Escherichia coli* and *Staphylococcus aureus*

Sample	Number of *Escherichia coli* (*Staphylococcus aureus*) after treatment with tufa and % of remaining microbes				
	Initial	after 4 h	%	after 8 h	%
BT after thermotreatment at 250 ºC	$7.8\cdot10^4$ ($6.7\cdot10^4$)	$2.8\cdot10^3$ ($1.6\cdot10^3$)	96 (98)	0 0	100 (100)
BT after chemical treatment with solution of HCl	$7.3\cdot10^5$ ($9.7\cdot10^5$)	$2.2\cdot10^4$ ($1.4\cdot10^4$)	97 (99)	0 0	100 (100)

In this context, the tufa-containing samples of packaging paper with 10 wt % of the basalt tufa modified at 250 ^{0}C were made and then used for the ISO 27447:2009(E) antibacterial activity tests [6]. Rather high antibacterial activity of both samples has been detected since even 4 hours long test ensured elimination of 95.7 and 92.3 % of *Escherichia coli* and *Staphylococcus aureus* respectively while complete disinfection was registered after 8 hours long treatment No antibacterial activity has been detected in the similar experiments carried out with no tufa containing paper packaging. This gives us ground to envisage good prospects for construction and further development

of the non-toxic tufa-containing food packaging materials.

4. Conclusion

High antibacterial activity against the standard strains of *Escherichia coli* and *Staphylococcus aureus* has been established for the composite materials containing some thermal or chemically modified basalt tufa. This activity remains at sufficient level for the paper packaging materials containing such composites. Therefore, they can be considered as antibacterial fillers for the foodstuff packaging manufacturing.

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