STUDY ON FIBROUS COMPOSITES BEHAVIOUR IN HYDRODYNAMIC PROCESS OF WINE FILTRATION

Petronela Nechita,[a*] Elena Bobu,[b] Florin Ciolacu,[b] and Armand Kontek [c]

This study concerns the implementation and performance evaluation of fibrous composites in sterile filtration of wine. Conditions of preparation were established having in view that the separation of particulate contaminants from liquids by depth filtration is occurring by mechanical entrapment into structural pores and by electrokinetic adsorption, and both retention mechanisms are influenced by various factors. Functional characteristics and behaviour of the filtering composite in industrial filtration of wine were evaluated. It was found that the effectiveness with which micro-organisms were retained was substantially improved by a porous structure characterized by small pores, and respectively by high resistance to air filtration, as well as by a higher content of cationic charges in the system.

Keywords: Filtering composites; Alimentary liquids; Depth filtration; Porous structure; Yeasts; Bacteria; Colloids

*Contact information: a: Pulp and Paper Research and Development Institute – SC Ceprohart SA Braila, RO-810019; b: Gheorghe Asachi Technical University of Iasi, RO-700050; c: ICDVV Valea Calugareasca, Romania; *Corresponding author: E-mail:petronela.nechita@ceprohart.ro*

INTRODUCTION

Filtration can be performed based on two principles, surface or absolute filtration and depth filtration. In surface filtration, which also is known as membrane filtration or cartridge filtration, the particles are removed at the surface of the filter, which consists of a membrane with holes of a determined size. This type of filtration requires extra care and training because the membrane can get blocked very quickly; therefore, it should be used only in the final stages of wine filtration, prior to bottling.

Depth filtration involves gradient density filter sheets that are a composite of modified cellulose pulps and filter aids, enabling the efficient clarification and sterile filtration of wine, beer, distilled spirits, and allied beverages. In the process of filtering through fibrous composites, retention of contaminants could be achieved through one or both mechanisms: mechanical filtration and electrokinetic adsorption. In mechanical filtration, contaminating particles are retained by the entrapment into structural pores of the sheet, which have a smaller diameter than those of contaminants. The electrokinetic adsorption in depth fibrous filter could occur when there are attractive forces between contaminant particles and internal surface of porous structure (Cotea 1985).

An important development in the process of depth filtration it is the understanding that many particles, occurring in wine in the suspension and colloidal state, are carrying an electrostatic negative charge, which is evident from measurements of zeta potential. Thus, it is possible to incorporate compounds in the structure of the filter medium that carry positive electrostatic charges. These compounds will produce a positive charge at pore surfaces that will attract particles of opposite charge, which will be retained even in pores of higher diameter than contaminant particle size. It must be mentioned that zeta potential-type sheets do not trap colloids, but these could be precipitated by interactions with cationic charged polymers.

One can conclude that filter sheets (fibrous composites) with superior throughput capacity and excellent retention capabilities have to be produced with a controlled porosity (mechanical retention), positive charge (electrokinetic retention), and need a high wet strength. They can be relied on to remove micron and sub-micron particulates, such as gross solids, haze constituents, yeasts, bacteria, and colloids on a consistent basis, yet preserve color, aromas, and flavors in wine, beer, and other beverages.

STUDY BACKGROUND

The porous filtering composites known in the filtration of alimentary liquids as appropriate retention media for fine particulate contaminants are obtained from mixtures of cellulose fibres and mineral particles with different additives. The sheets are formed under dynamic conditions by free and vacuum dewatering and then are dried and finished.

The scheme in Fig. 1 gives an overview of how the properties of a filtering fibrous composite are related to the requirements of field application and how the manufacturing process variables may interact to produce a particular set of properties. Mainly, the performance of a fibrous composite is the result of complex interactions among the nature and characteristics of fibrous material, fibres treatments, non-fibrous materials, method of fabrication, as well as interaction of composite material with the parameters of the application environment (Bobu 2004).

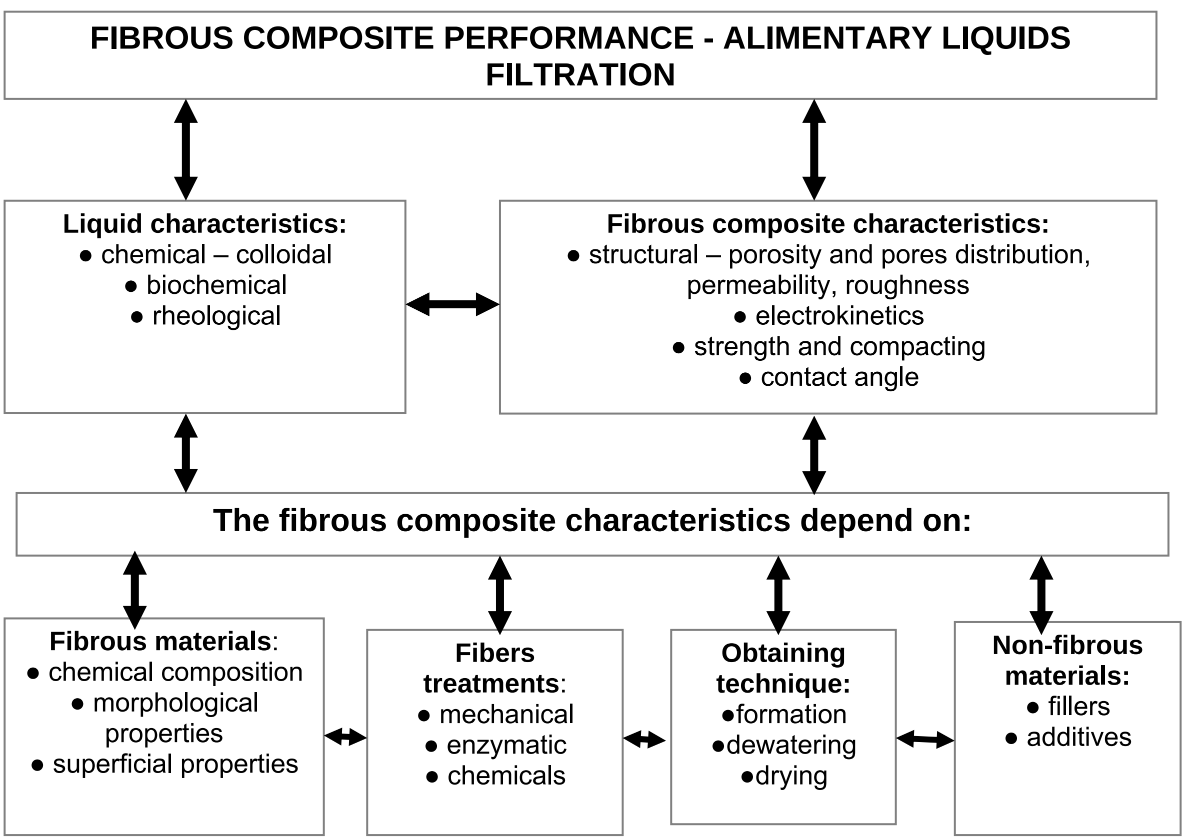

Fig. 1. Main factors determining the performance of filtering fibrous composite

Cellulose fibres are important in forming the filtering composite structure. Choosing a suitable pulp grade is essential in obtaining a composite with suitable filtering performance. The cellulose fibres, which account for 45 - 70% of composite network mass, should act as a powerful absorbent material able to retain especially colloidal substances from solution, and it has to maintain its absorbent potential along the whole period of the filtration process. It was found that the share of different cellulose fibres grades and their mechanical treatment (refining) have strong influences on fibrous composite properties and its behaviour in the filtration process.

Fillers are introduced into the composition of filter media in order to obtain a structure with controlled porosity and improve the performance of filtering process. The filtering process is influenced by the particle size distribution of filler and structural and superficial-colloidal properties of the particles. Although depth filtering composites have a random distribution of pores on the surface and within their interior, their structure is always characterized by three types of pores: micro-pores, meso-pores, and macro-pores. Considering the mechanical retention mechanism of contaminants from alimentary liquids subjected to filtration, one can remark that the micro-pores determine the sterilizing capacity of filter, meso-pores the fine filtration, and macro-pores coarse filtration (Cotea 1985).

Generally, for the purpose of obtaining of filtering composites for depth filtration, the filler must to contain mostly very small particles with porous structure that gives a high specific surface area (pores area per unit volume of filtering composite) and high retention capacity of colloidal particles (yeast and bacteria) by adsorption. On the other hand, the choice of rate and composition of filler must take into account that the hydraulic resistance of filtering composite increases with fine filler content, but filtering capacity decreases. Therefore, the establishment of the dose and composition of filler will be based on a compromise between the optimal porosity and pores distribution, as well as the filtering capacity (Nechita *et. al.* 2007).

Chemical additives are used in obtaining fibrous filtering composites for many proposes. For instance, chemical additives may improve of formation and dewatering processes, increase dry and wet strength characteristics, or control the ionic balance. The following groups of additives have been evaluated in laboratory tests: *coagulation additives* - cationic polymers with high charge density and moderate molecular weight, which are applied for dewatering and cationic charge increase; *flocculation additives* - cationic polyelectrolytes with low charge density and high molecular weight, which are applied to control the aggregation degree of mineral particles and thus, the porosity of composite structure; and *micro- and nano-inorganic* particles with anionic or cationic charge, applied to balance ionic balance of the composite and also to increase specific surface area of the structure.

The selection of an additives system for filtering composite consisting of the following criteria must be considered: the *compatibility with the alimentary liquids*, which refers to the free of toxicity of chemical interactions with the filtering liquid and the possibility of microbiological contamination; *nature and ionic charge density,* the achievement of ionic balance of fibrous composite; *molecular weight* and aggregation mechanisms that they are developing since the aggregation state influences porous structure; and *compatibility with other additives* (Bobu 1998).

EXPERIMENTAL

Study Objectives

- Pilot trials to obtain the filtering fibrous sheets for alimentary liquids filtration, based on previous laboratory research.
- Technical performance evaluation of fibrous sheets in industrial process filtration of alimentary liquids, in terms of hydrodynamic conditions behavior and the influence on the quality of filtered liquids.

Materials and Methods

Fibrous materials: Dissolving pulp (Becocel 2000, Georgia) that ensures the formation of porous structures with high specific surface and gives the retention capacity of microorganisms by adsorption; *Sulfate bleached softwood pulp* **(**ECF and Crofton, Canada**)** that contributes to the formation of resistance structure in composite material and is obviously part in forming porous structure. The characteristics of fibrous materials are presented in Table 1.

Table 1. Physico-chemical Properties of Cellulose Materials

Characteristics	BECOCEL 2000	GEORGIA		CROFTON	
	30°SR	30°SR	50°SR	30°SR	50°SR
Density, g/cm^3	0.64	0.64	0.66	0.74	0.79
Breaking tensile load, N	45.5	61.4	73.9	128	137
Breaking length, m	4229	5472	6499	11469	12243
Bursting strength, kPa	158	196	234	582	575
Double folds	21	48	72	1058	1103
Average fibres length, mm	1.05	2.6		2.3	
α cellulose content, %	86.5	91		-	
Specific area, m^2/g	1.66	2.15	3.65	1.75	2.77
Water retention, WRV, g/g	1.41	1.55	1.72	-	-
Cation demand, CCD, μeq/ g	- 68	-38	-48	-47	-58

Mineral fillers: *Diatomite*- FN1, Celite S and *Perlite* - Harbolite H 350, which are characterized in Table 2.

Table 2. Dimensional and Superficial Colloidal Characteristics of Filler

Characteristics	Diatomite FN1	Diatomite Celite S	Perlite H350
Particles average diameter, μm	13.0	10.0	10% > 25
Anionic charge, μeq/g	64.5	72	61.5

Chemical additives: cationic resin (Kymene 611) used to increase the wet strength and partly the dry strength, that influences also the ionic balance and coagulation / flocculation phenomena (Bobu 2004); *Cationic colloidal silica Levasil 200 S* consists of particles at nanometer level, which creates within the system a large number of interfaces with positive charge, giving a high retention capacity to porous structure through adsorption; *Anionic colloidal silica Levasil 200* produces a dispersing effect, which is contributing to a better distribution of solid components in the composite material structure, and influence also the ionic balance. Table 3 presents the ionic character and charge density of the additives.

Table 3. The Charge Density of Additives used to Obtain Filtering Composites

Additive	Kymene 611	Colloidal silica Levasil 200S	Colloidal silica Levasil 200
Charge character	Cationic	Cationic	Anionic
Charge density, μeq/g	1100	625	550

Filtering fibrous sheet preparation**:** Based on previous laboratory experiments, two receipts of filtering composites for sterilizing filtration of alimentary liquids were established. The two recipes were characterized as follows:

C1 composite: prescription of fibrous material that includes only chemically modified celluloses, cellulose Georgia and Becocel 2000; composition of filler, calculated to give an average particle diameter of about 15.5 μm; the total added additives of 5%, with doses that lead to an *anionic charges/cationic charges* ratio within pulp slurry of about 2.5;

C2 composite: prescription of fibrous material that includes a mixture of Georgia pulp and softwood pulp; composition of filler calculated to give an average particle diameter of about 13 μm, the total added additives of 8%, with doses leading to an *anionic charges/cationic charges* ratio within pulp slurry of about 1.43.

The filtering composites were obtained on an industrial paper machine with the width of 1600 mm and speed of 1 to 1.2 m/min, and finely were cut as sheets of 400x400 mm.

Characterization of Filtering Composites

The filtering composites were characterized in terms of quality characteristics, using standardized methods according to the general scheme shown in Fig. 2.

Fibrous Composites Testing in Industrial Process of Alimentary Liquids Filtering

Testing of filtering composites was performed in the industrial filtration process for sterile filtration of two wine grades: *white wine - Feteasca Regala 2007* and *red wine - mixture of Merlot + Cabernet Sauvignon, 2007*. The industrial filtering plant consisted of a stainless steel filter with frames of size 400 x 400 mm (Fig. 3).

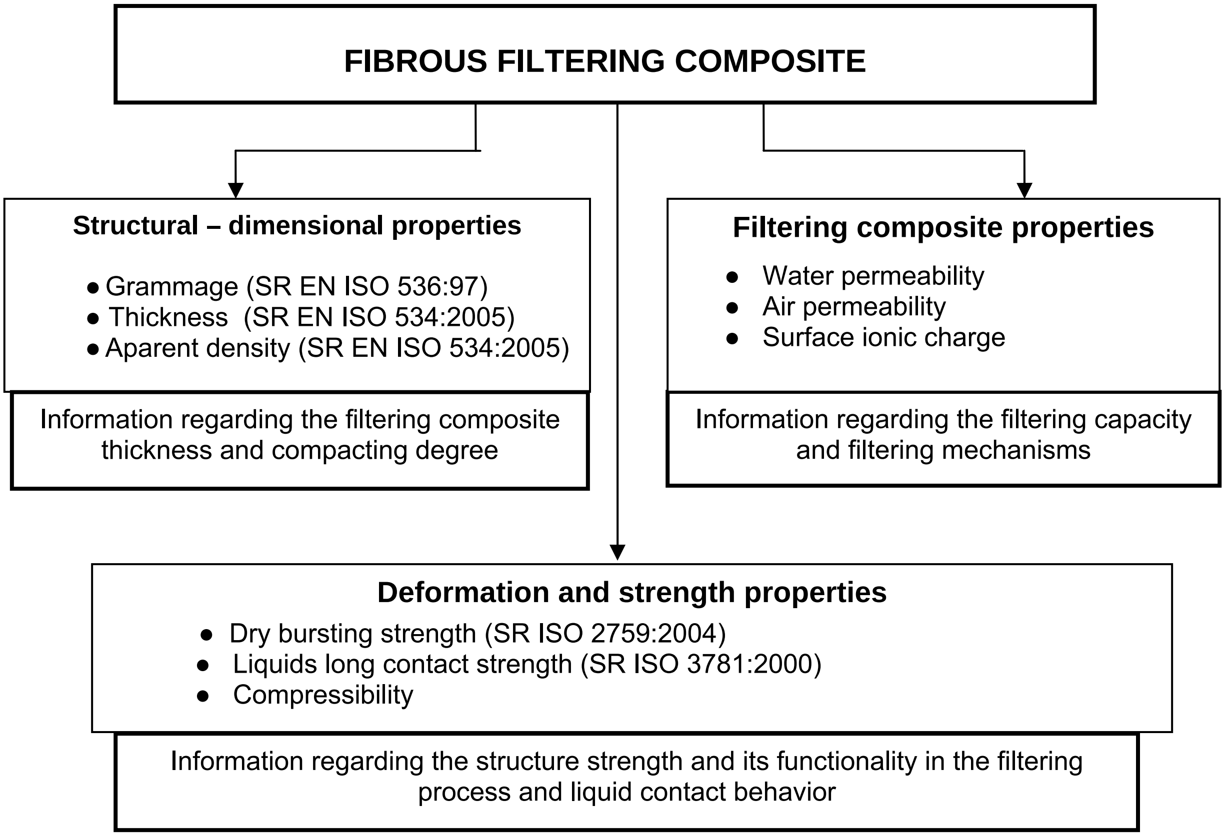

Fig. 2. General scheme for filtering composites characterization

Fig. 3. Equipment used in industrial filtration of wine

RESULTS AND DISCUSSIONS

Filtering Composites Characterization

The two samples of filtering composites, denoted C1 and C2, were characterized by structural, deformation, and mechanical strength properties and by filtering properties (Table 4).

Table 4. Characteristics of Filtering Composites

Characteristics	Average values	
	C 1	C 2
Structural properties		
Grammage, g/m^2	1542	1566
Thickness, mm	3.84	3.57
Density, g/cm^3	0.40	0.44
Ash content, %	51.86	46.38
Deformation and mechanical strength properties		
Dry breaking load, MD/CD, N	217/200	373/324
Wet breaking load, MD/CD, N	46.7/41.75	88.74/74.8
Wet bursting strength, kPa	69.35	164.47
Liquids long contact strength, %	21.4	31.9
Max. deformation, %	69.5	66.5
Filtering properties		
Air pass srength, mm H_2O	275	420
Filtering flow, l/h x m^2	14225	7579
Anionic/Cationic ratio	3.03	1.95
Efficiency of retention of yeast *), %	100	99.85
Efficiency of retention of lactic bacteria *), %	98.85	99.7
Efficiency of retention of acetic bacteria *), %	64.78	99.9

*) Retention rate is the ratio of the initial charge of microorganisms (UFC/ml) and the charge recorded after filtration (UFC/ml). Work procedure: the suspension of microorganisms was cast in the filter and filtration was achieved by introducing air at the constant pressure of about 1.0 bar. Filtrate was collected in a sterile vessel after the microbial charge was determined.

MD/CD =machine direction/cross direction

The C1 composite was characterized by higher thickness and lower apparent density than C2 composites. These differences are due to both the fiber composition (100% cellulose chemically modified leading to structures with higher porosity) and technical formation parameters on the paper machine. For example, a high fines content of the Becocel pulp and low dosage of wet strength additive (Kymene 611) led to a substantial reduction of the dewatering rate on forming wire, which determines a higher but non-uniform retention of filler in z direction, resulting in a loose structure formation. Lower density could be also due to filler composition, which in case of C1 composite was characterized by average diameter greater than the filler used to obtain the C2 composite.

The C2 composite presented better strength properties in comparison with the C1 composites. High dry bursting strength was correlated with structure density, which may be mainly due to relatively high content of sulfate softwood pulp. The high liquid long contact strength of C2 composites was obviously due to the addition of higher dosage of Kymene 611 resin. The higher compressibility of C1 composite structure was the result of combined structural properties (lower density, higher porosity) and mechanical resistance (lower bonding energy).

The rate of air filtration differed slightly between the two types of composites because it depends mainly on the total volume of pores, which did not differ substantially. However, the flow filtration rate of water was much higher in the case of the C1 composite, which in this case indicates a higher percentage of large pores, reported as the total pores volume. The distribution of pores size and percentage of small pore size was better reflected by air pass strength, which seems to be correlated with bacteria retention rate. Figure 4 shows clearly that acetic bacteria retention increased with air pass strength. This behaviour can be explained by the micro-porous structure of composite C2, which was characterized by small pores in comparison to the C1 composite, and was favorable for retention of acetic bacteria. In case of the C2 composite, the filler composition was chosen in order to obtain a greater share of material with fine particles (average particle size calculated was 13 µm versus 15.5 µm for C1). At the same time, higher filtering efficiency of the C2 composite can be attributed to higher content of cationic charges.

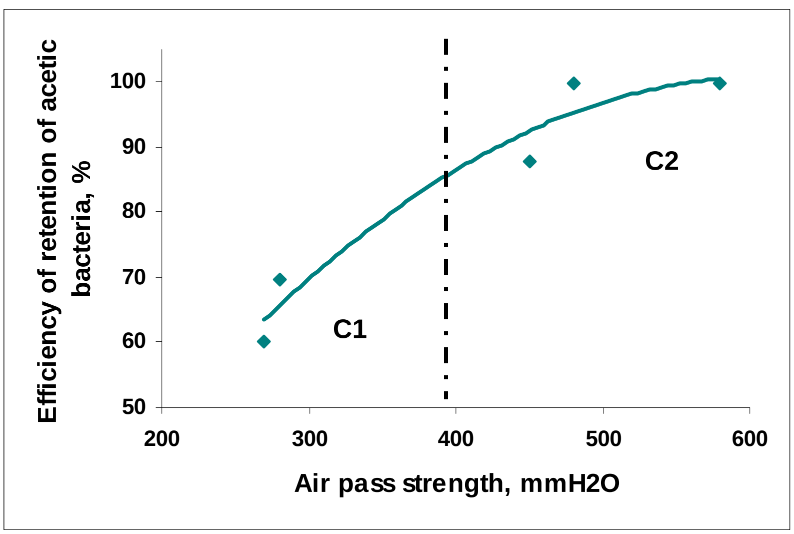

Fig. 4. Efficiency of retention of acetic bacteria versus the air pass strength

Concluding Remarks for Characterization

To summarize the results for characterization of materials, the C1 composite was characterized by lower apparent density and wet and dry mechanical strength. The low level of strength may affect the stability and structural integrity of composites during the operation. On the other hand, low density obtained through recipe of fibrous material and filler can be beneficial in terms of efficiency separation of microorganisms by adsorption because confers to composite structure high specific surface.

The C2 composite was characterized by very good strength, both in dry and wet states, but by very high apparent density. Obviously, these composites were superior in terms of stability and preservation of physical integrity during operation. Higher density and better dry strength were the result of use a high percentage of sulfate softwood pulp, and probably in part, of the filler composition. This structure was characterized by a lower inner surface per unit volume, which could affect the efficiency of separation of microorganisms.

However, the efficiency of separation of microorganisms can be enhanced by a higher content of cationic charges, exactly by the lower anionic charge/cationic charge ratio for this composite.

Behaviour of Filtering Composites in Industrial Filtration of Wine

Having in view the characteristics of the experimental composites, as presented above, only the composite C2 was tested for the industrial filtration of wine. The tests were performed for a period of 4.5 hours for white wine and about 6 hours for red wine. At the same filter area, a volume of 8640 liters white wine and 12168 liters red wine were filtered. Table 5 presents main parameters of industrial filtration process for the two wine grades.

Table 5. Filtering Parameters

Filtering parameters	White wine	Red wine
Number of composites that was fitted filter	30	30
Filtering area, m^2	4.8	4.8
Filtering duration, hours	4.5	6.17
The volume of wine filtered, liters	8640	12168
Flow filtration - l/h - $l/m^2 x\ h$	 1920 400	 1972 411

The quality of filtered liquid was evaluated by microbiological (acetic and lactic bacteria content) and chemical contamination (toxic metals content) before and after filtration.

The results on microbiological contamination are presented in Table 6. One can remark that the retention of microbial contaminants was higher for white wine, especially in the case of yeast and lactic bacteria. It is estimated that for sterilizing filtration of the white wine (which raises the biggest problems in the process of filtration and stabilization), the filter composite obtained under the experimental is satisfying technical parameters required on the filtering of these alimentary liquids (Nechita *et al.* 2008).

Table 6. Microbiological Contamination of White/Red Wine Before and After Sterile Filtration

Parameter	Unfiltered wine	Filtered wine	Retention rate, %
White wine			
Yeasts, UFC/ml	5.33	0.0025	99.95
Lactic bacteria, UFC/ml	3.17	0.25	92.12
Acetic bacteria, UFC/ml	4.72	0.71	84.95
Red wine			
Yeasts, UFC/ml	1.36	0.44	67.65
Lactic bacteria, UFC/ml	4.71	1.22	74.09
Acetic bacteria, UFC/ml	7.40	3.44	53.51

The results related to chemical contamination (Table 7) provide evidence that both wines contained metal ions in lower concentration than maximum admitted limits (according to Ord. 975/1998). Filtering composites that were tested in industrial filtration did not release metal ions; rather it produced a slight reduction of their concentration. The effect could be explained by the fact that part of the metal ions was associated with retained microbiological contaminants. The content of toxic metal ions in the filtered liquids was below the maximum admitted (according to Ord. 975/1998 of the Ministry of Health).

Table 7. Chemical Contamination of White/Red Wine Before and After Sterile Filtration

Parameter	Unfiltered wine	Filtered wine	Limits max. admitted according to Ord. 975/1998
White wine			
Fe (mg/l)	1.21	0.96	-
Pb (μg/l)	2.34	1.15	0.3 ppm
Hg (μg/l)	0.17	0.14	0.05 ppm
Red wine			
Fe (mg/l)	5.54	5.76	-
Hg (μg/l)	0.4	0.15	0.05 ppm

Concluding Remarks: Filtering Results

During industrial operation, the filtering composite exhibited normal filtering capacity and good mechanical strength, maintaining their structural and dimensional integrity along whole filtering period.

The effectiveness regarding the retention of the microorganisms and germs from wine was higher for white wine, in comparison to red wine. This was an unexpected result, since usually the difficulties are higher to achieve the expected quality of white wine, especially for lactic bacteria content. Obviously, more tests are necessary to verify these results.

The content of toxic metal ions in the filtered liquid was below that of samples before filtering, suggesting that the tested fibrous composites did not release any chemical ions during filtration process.

GENERAL CONCLUSIONS

The study is approaching a methodology to obtain fibrous composites for the filtration of alimentary liquids, which is based on data obtained by numerous laboratory experiments. This data base can be used to formulate the recipes and process parameters for obtaining filtering composites with defined characteristics by applying two principles:

- Controlling the porous structure of fibrous composite by - cellulose fibre types and their treatment, composition of mineral filler, ratio cellulose fibres/mineral filler, and aggregation mechanisms developed by additive systems;
- Directing ionic balance of the composite toward a positive charge, which favours the electrokinetic retention of particles smaller than the diameter of structural pores.

Two filtering composites (C1 and C2) were obtained at pilot scale, using the recipes and forming conditions established based on the above principles. The characterisation of the composites evidenced clear differences for all groups of properties, which could be explained mainly by the adopted recipes. It was found that the composite C2 with higher air pass resistance and higher cationic charge content gave better efficiency in sterile filtration - lactic and acetic bacteria removal. Good quality of the composite C2 based on laboratory characterisation was confirmed during industrial filtration tests.

ACKNOWLEDGEMENTS

The authors are grateful to Romanian Ministry of Education – National Scientific Research Agency, for financial support of project *„Advanced microfiltering composites – efficient solution for food safety - FILTRAL”* CEEX R&D Programme, 2006 – 2008, contract 63/2006.

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Article submitted: June 10, 2009; Peer review completed: July 20, 2009; Revised version received and accepted: August 10, 2009; Published: August 12, 2009.