THE INFLUENCE OF THE STRUCTURAL PROPERTIES OF CELLULOSE FILTERING COMPOSITES ON THE CONTAMINANTS RETENTION IN ALIMENTARY LIQUIDS

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Abstract: Cellulose filtering composites are as three-dimensional network defined by mechanical and structural properties enabling their runnability in the filtration process of the alimentary liquids. The functional characteristics and filtration behaviour of cellulose composites are influenced by many factors that comprise both the nature of the raw materials (fibrous materials, fillers, chemical additives) and processing conditions. The porous structure of the filtering composites is thus designed so the retention of contaminant particles in the liquids is carried out both at the surface (mechanical retention) and depth (electro kinetic adsorption). In order to ensure a good separation of micro-organisms by filtration, it is required to adapt appropriately the structure of pores within filtering medium both at the size of particles that are separated, and the physical and chemical properties of these contaminants. The paper presents the findings of some studies concerning the influence of structural properties on the retention capacity of yeasts and microorganisms from alimentary liquids (wine) of some cellulose composites for sterilizing filtration.
Key words: Filtering composites, Filtration, Alimentary liquids, Contaminants, Fibrous structure

Introduction

Separation of fine impurities and contaminants from the liquids is achieved by filtering process that is a set of techniques for separating whose principle consists in the passage of fluids through a porous medium that retains impurities. To act as a filter, porous medium must to allow passage of fluid and retain particles of contaminants contained therein. In the process of filtering through the fibrous composites, retention of contaminants from fluid is achieved through the action of one or both mechanisms: *mechanical filtration* (retention of contaminant particles on the surface of composite) and retention of particles by *electrokinetic adsorption* (with the attraction forces). (Figure 1a and 1b). [1]

a) b)

Fig. 1 Filtering mechanisms: a) mechanical retention; b)electrokinetic adsorption

The porous filtering composites known in the filtration of alimentary liquids as appropriate to retention of fine particulate contaminants consist of *fibres* - *fibres* or *fibres - mineral particles* mixtures. These materials are obtained in dynamic conditions by dewatering in vacuum, dried and finished. The fibrous components are cellulose based and mineral particles are composed of mixtures of diatomite and perlite (filler material) and various synthetic polymers. [1]

Objectives

1. Assessment the influence of fibrous composition on the structural properties and filtering performances of fibrous filtering composites for sterilizing filtration of alimentary liquids.
2. The evaluation of technical performances of fibrous filtering composites during industrial process of wine filtration (the effect on quality of filtered liquids)

Experimental

Materials and methods

Fibrous materials: *Dissolved pulps (Becocel 2000, Georgia)* **–** which ensure the formation of porous structure with high specific surface and give the retention capacity of microorganisms by adsorption; *Sulphate bleached softwood pulp (ECF, Crofton Canada)* **-** which allows the formation of the composite resistance structure and is obviously part in forming porous structure. Characteristics of fibrous materials are presented in Table 1.

Table 1 The physico-chemical properties of cellulose materials used in the fibrous composites

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	Diatomit FN1	Diatomit Celite S	Perlit 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 [4]; *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 [3]. Table 3 presents 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 composites obtaining**:** based on above presented materials previous, two receipts of filtering composites for sterilizing filtration of alimentary liquids were established. The two receipts are characterized as following: ***V1 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; ***V2 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 – 1,2 m/min, and finely were cutted as sheets of 400x400 mm.

Characterization and testing of filtering composites*:* the filtering composites were characterized in terms of quality characteristics, using standardized methods, and their testing 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*. Industrial filtering plant consists of a stainless steel filter with frames of size 400 x 400 mm. [2];

Results and discussions

The two samples of filtering composites were characterized by structural and filtering properties (Table 4).

Table 4 The characteristics of filtering composites

Characteristics	**Average values**	
	V 1	**V2**
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
Filtering properties		
Air pass strength, mm H_2O	275	420
Filtering flow, l/h x m^2	14225	7579
Average pore radius, µm	5,18	2,917
Total porosity, %	81,28	70,8
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.*

Regarding the structural characteristics of filtering composites can be made the following remarks: the V1 composite is characterized by higher thickness and lower apparent density than V2 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) lead to a substantial reduction of the dewatering rate on forming wire, which determines a higher but no-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 V1 composites is characterized by average diameter greater than the filler used to obtain of V2 composites.

From the data presented in Table 4 is observed that the rate of air filtration differs slightly between the two types of composites because depends mainly by the total volume of pores, which appear no differ too much. Flow filtration of water is much higher in V1, which in this case indicate a higher percentage of large pores in the total volume of pores. In the acetic and lactic bacteria field, V2 composites exhibit a higher retention rate than V1 composites. (Figure 2a and 2b)

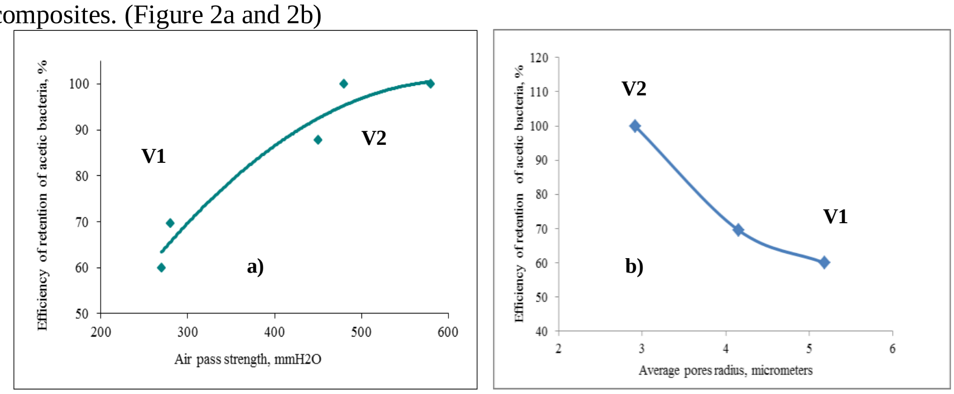

Fig. 2 Efficiency of retention of acetic bacteria versus the air pass strength (a) and pores dimensions (b)

This behaviour can be explained by the fact that the micro-pores structure of V2 composite is characterized by small pores compared with V1 composites, favourable to retention of acetic bacteria. In case of V2 composite, the filler structure has been established so as to obtain a greater share of material with fine particles (average particle size calculated was 13 μm versus 15,5 μm for V1). Better efficiency in filtering for V2 composites can be attributed to higher content of cationic charges that are in system, exactly an *anionic charge/cationic charge* ratio lower of these composites.

Having in view the characteristics of the experimental composites, presented above, only the composite V2 was tested at 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 has been 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 were 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) before and after filtration. The results on microbiological contamination are presented in Table 6. One can remark that the retention of microbial contaminants is 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. [5]

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

Conclusions

As result of studying the corellations between structural characteristics and filtering performances of fibrous composites for sterilizing filtration of alimentary liquids, the following conclusions can be emphasized:

- effectiveness of microorganisms and germs retention from filtered liquids is especially good as the porous structure of composites is characterized by pores size smaller;
- found that the efficiency of separation of microorganisms can be enhanced by greater content of cationic charges, exactly by the anionic charge/cationic charge ratio that were of a lower values (see table 7, also). [6]

Table 7 Ionic balance and filtering performances of some ficbrous composite samples

Composite sample	Additive charge, %	Ionic balance, µeq/g	Anionic/cationc charge ratio	Retention rate, $\log N_0/N_v$		
				Yeasts	Lactic bacteria	Acetic bacteria
P1	9	(-) 2963	1,7	3	2,16	1,61
P2	9	(-) 4115	2,0	3	2,34	1,62
P3	9	(-) 3475	1,82	3	2,34	0,62
P4	9	(-) 3350	1,79	3	2,99	2,21

[*)] *In this case the retention rate is log from initial and after filtration concentration ratio (value 3 for retention rate is equal with 100% retention or filtered liquid microorganisms free)*

This data base can be used to formulate the recipes and process parameters for obtaining filtering composites with defined characteristics by applying two principles: (i) 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 system; (ii) directing ionic balance of the composite toward a positive charge, which favour the electrokinetic retention of particles smaller then diameter of structural pores.

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