Environmental Engineering and Management Journal

February 2015, Vol.14, No. 2, 361-371
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

CHARACTERIZATION OF DYES LOADED POLYVINYL ALCOHOL (PVA) BASED HYDROGELS THROUGH CIELAB METHOD

Adina Papancea, Silvia Patachia*

"Transilvania" University of Brasov, Product Design, Mechatronics and Environment Department, 29 Eroilor Str., 500036 Brasov, Romania

Abstract

Hydrogel membranes obtained by neat polyvinyl alcohol (PVA) or PVA with various bio insertions like: Scleroglucan (Scl), Zein (Zein) or Cellulose (Cel), were subjected to diffusion and sorption/desorption experiments using different type of dyes such as: Crystal Violet (CV), Methylene Blue (MB), Congo Red (CR). If the sorption, desorption or diffusion of a dye in/from/through a hydrogel is usually monitored by the dye solution analysis, in this case the transport phenomena are followed by the membrane analysis. Photographic images of colored hydrogels obtained by PVA hydrogel immersion in aqueous solutions of different dyes, with different concentrations have been obtained by using a digital camera CANON Power Shot SX110 with 3456×2592 pixels resolution, in artificial light. The resulted images were processed by using Adobe Photoshop software, CS5 version, and analyzed through CIEL*a*b* system (CIELAB). This method gives the possibility to make difference between two very close colors by taking into account parameters such as: hue, saturation and luminosity.
As a particular case, the present study evidenced, by CIELAB method that all the prepared hydrogels have a good capacity to uptake dyes from aqueous solutions, the highest efficiency being obtained for PVA/Scl hydrogels. Our results are in good agreement with those obtained from SEM and DSC analysis of the loaded gels.

Key words: CIELAB, cryogel, dyes, method, PVA, sorption

Received: November, 2014; Revised final: February, 2015; Accepted: February, 2015

1. Introduction

Polyvinyl alcohol (PVA) cryogels have the ability to change their color, forming colored complexes in the presence of dyes (Dobritoiu and Patachia, 2013), metallic ions (Papancea et al., 2010b; Patachia et al., 2004), iodine (KI) (Patachia and Rinja, 2005), or some drugs (Patachia et al., 2007). In this paper, we proposed a new application of one method already used in perfume analysis (Korifi et al., 2013), food packaging or medicine but not yet in the gels domain. This is a direct method, that use the color analysis of the colored gels, named CIELAB method, instead of commonly used methods (Luís et al., 2014) which are indirect (through solution analysis, solutions that are light sensitive), expensive (using various reagents) and generating waste waters.

Since due to its properties, PVA is a good candidate for sorption and transport of dyes (Dobritoiu and Patachia, 2013), three types of PVA biopolymers based materials were used as adsorbents: PVA with scleroglucan (PVA/Scl), PVA with microfibers of cellulose (PVA/Cel) and PVA with zein (PVA/Zein).

To study the dyes sorption through PVA cryogels three dyes were used: Crystal Violet [CV] (due to its medical use as antiseptic) and Methylene Blue [MB] (due to its various applications in biology, chemistry and medicine), both cationic dyes and Congo Red [CR], a diazo dye used in dyeing industry but also in biochemistry and histology to stain microscopic preparations. The change in biobased cryogels color and in aspect after dyes sorption was

* Author to whom all correspondence should be addressed: e-mail: st.patachia@unitbv.ro; Phone: +40 741 649792; Fax: +40 268 410525

analyzed through CIEL*a*b* system (CIELAB). This color model, derived from the CIE system, is based on the way the describe color and not by quantifying it.

CIELAB gives the possibility to make difference between two very close colors by taking into account parameters such as: hue, saturation and luminosity. The CIELAB color space parameters are: L*, color luminosity, varies from 100 (white) to 0 (black); a* varies from red (+a*) to green (-a*) and b* varies from yellow (+b*) to blue (-b*).

In Fig. 1 there is a 3D representation of the CIELAB system, where it can be seen that the brightness scale (L) is centrally placed while C*ab axis is an open scale with the origin in zero including all neutral color, and the angle hab called "angle hue" can have values between 0 and 360 degrees (Vâlceanu et al., 2006).

Thus, CIELAB method could find various applications in fields like: environment, for monitoring the sorption of dyes (Confortin et al., 2010; Crini and Badot, 2008; Ikkai et al., 1996) or heavy metal ions from polluted waters (Croitoru et al., 2009; Papancea et al., 2010b; Patachia et al., 2011); sorption of iodine (Patachia et al., 1997) used like disinfectant, from waste-waters; medicine, where the PVA gels can be loaded with active substances, such as: dyes with antiseptic properties (ex. Crystal Violet, ionic liquids) (Patachia and Damian, 2014), porphirines, used in the cancer phototherapy (Patachia et al., 2007; Varga et al., 2008); pharmacy, for the monitoring and controlled release of the drugs or for study the substrate regeneration and substance recovery of some sorbed species.

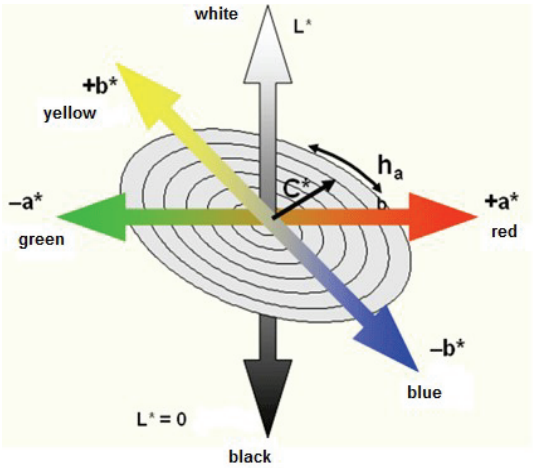


Fig. 1. Three-dimensional representation CIELAB color scale (Globalspec, 2014)

The aim of this paper is to demonstrate that the concentration dependent characteristics such as: adsorption equilibrium, sorption kinetics, sorption mechanism as well as dye-dye or dye-polymer interaction, could be determined through the color analysis of the colored gels, by using CIELAB method.

2. Experimental

2.1. Materials

The following categories of materials were used in our study:

- PVA 98–99% hydrolyzed (M = 146,000–186,000) from Sigma–Aldrich.
- Biopolymers: Scleroglucan (Actigum CS 11, Mw = 1,000,000 Da) from Cargill, St-Germain-en-Laye, France. Zein from Sigma–Aldrich. The polymers were used without further purification. Microfibers of cellulose were prepared by the method described by Kim et al. (2009).
- PVA cryogels with biopolymers synthesized according to the method presented by Dobritoiu and Patachia (2013)
- Crystal Violet purchased from Fluka, Methylene Blue, from USP, Powder, American Cyanamid Company, New Jersey and Congo Red was purchased from Merk. All dyes were used as received without further purification. In Fig. 2, the structures of dyes are presented. Solutions of dyes at desired concentrations (1×10^{-6} - 8×10^{-5} mol/L) were prepared by using distilled water. The concentration range considered was selected taking into account the solubility of dyes in water (S_{MB}= 40 g/L, S_{CV}= 16 g/L, S_{CR}= 25 g/L).

2.2. CIELAB method

To analyze the colour of the PVA cryogels after dyes sorption a digital camera (CANON Power Shot SX110 with 3456×2592 pixels resolution) was chosen and was used in artificial light. Unlike other devices that actually measure the colour of small areas (points) on the surface of an object, digital cameras have the advantage on measuring the colour characteristics of the entire object from the global point of view (Hang and Brindley, 1970).

The obtained images were processed by using Adobe Photoshop software, CS5 version, and the colour model: CIELAB. The parameters of the color space (L *, a *, b *) were determined in several points of the samples image (a minimum of ten points for each image), the reported results representing the average of the determinations for each image. Using difference in a*, b* and L* parameters (Eq. 1) the difference in color (ΔE^*_{ab}) (Eq. 2), in chromaticity (ΔC^*_{ab}) (Eq. 3) and in hue (ΔH^*_{ab}) (Eq. 4) were calculated (Schanda, 2007), where: X is one of the color coefficients L^*, a^* or b^*, whereas 1 and 0 indices, are the value for the cryogel dye loaded sample and the value for the reference cryogel (usual that immersed in the lowest concentrated dye solution).

$$\Delta X = X_1 - X_o \quad (1)$$

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (2)$$

$$\Delta C^*_{ab} = \sqrt{\Delta a^{*2} + \Delta b^{*2}} \quad (3)$$

$$\Delta H^*_{ab} = \sqrt{\Delta L^{*2} + \Delta E^{*2} + \Delta C^{*2}} \quad (4)$$

The obtained results for the CIELAB parameters are used to describe the dyes sorption/desorption and diffusion processes and they were compared with the results obtained by VIS spectroscopy.

2.3. Sorption studies

Samples with different masses were immersed in CV, MB and CR solutions (concentrations between: 1×10^{-6} - 8×10^{-5} mol/L). The sorption of dye into the PVA cryogels was monitored using two methods: the analysis of the colored cryogels using CIELAB method and the analysis of the dye immersion solutions at different periods of time after the sample immersion.

The change in solution absorbance was monitored using an UV/VIS Perkin Elmer spectrophotometer, Lambda 25-model (λ_{CV} = 590 nm, λ_{MB} = 640 nm, λ_{CR} = 498 nm). The sorption equilibrium was reached after 20 days. The experiments were made at room temperature.

2.4. Rate of sorption/desorption

To follow the sorption rate of the dye, PVA cryogel circular samples with masses between 0.6 - 0.8 g and 1 cm in diameter were immersed in 5 mL CV solution of $5*10^{-6}$ mol/L concentration.

The samples were removed from the dye solution every 15 minutes until one hour and then after 30, 60 minutes and 24 hours, respectively.

After 24 hours of CV sorption, the PVA cryogels were immersed in 5 mL of distilled water. At certain times (15, 30, 45, 60, 120, 150 and 1440 minutes) they were removed from water, whipped with filter paper and then pictures were taken. The sorption/desorption of dye was monitored through the analysis of the immersion solutions.

The change in solution absorbance was monitored using an UV/VIS Perkin Elmer spectrophotometer, Lambda 25-model (λ_{CV} = 590 nm).

3. Results and discussion

3.1. Analysis of CIELAB parameters used to determine the influence of gel composition on gel color

The change in cryogels color after the dye sorption, from white to: blue for MB, violet for CV or red for CR, is illustrated in Fig. 3 from where it is easy to observe that, at the same dye concentration the cryogels show different shades. This phenomenon could be explained through the dyes-substrate interactions and the substrate morphology, the dyes sorption proving to be dependent not only on the dye type but also on the type of substrate.

Using photographic images from Fig. 3 the color parameters L*, a*, b* were determined for each sample; with the obtained values, ΔL*, ΔE* and ΔH* were calculated. Values for a*, b* parameters and their ratio at the highest concentration (c_5), for each dye, are presented in Table 1.

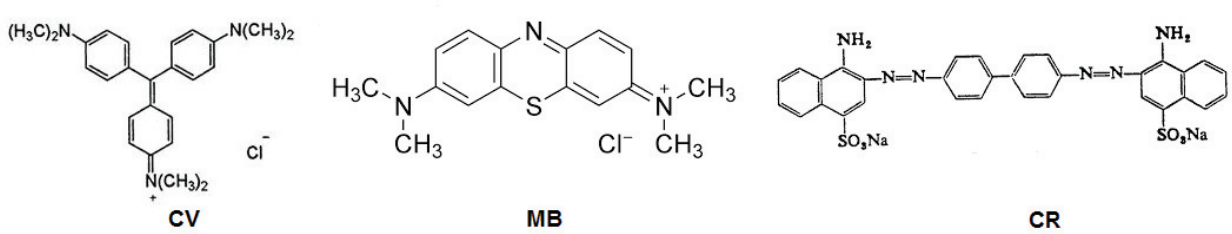


Fig. 2. Structure of Crystal Violet [CV], Methylene Blue [MB] and Congo Red [CR]

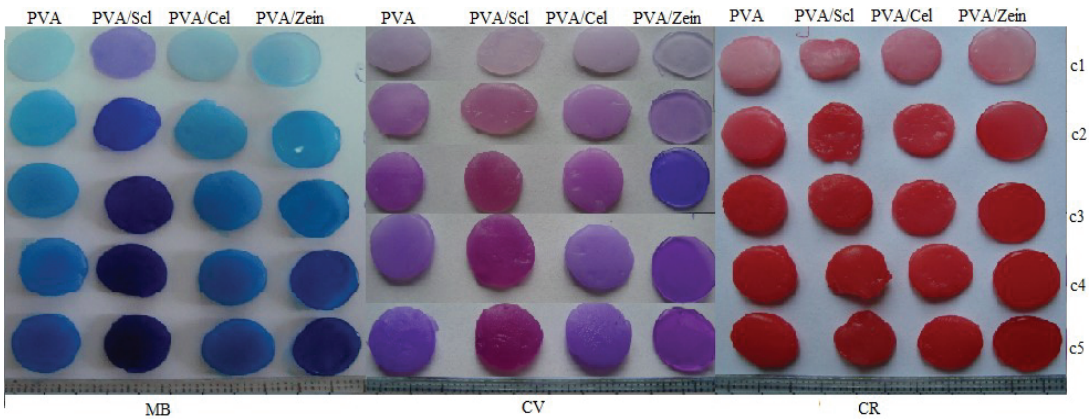


Fig. 3. PVA membranes after MB, CV and CR sorption in five different concentration solutions

Table 1. Values of a*, b* and a*/b* CIELAB parameters for PVA and PVA with bio insertions cryogels after CV, MB and CR sorption

Dye type (concentration)	*CELAB parameters*	*PVA*	*PVA/Scl*	*PVA/Cel*	*PVA/Zein*
CV ($1*10^{-5}$ mol/L)	a*	36.67	39.33	32.22	45.33
	b*	-50.89	-12.44	-43.00	-47.44
	a*/b*	-0.72	-3.16	-0.75	-0.96
MB ($8*10^{-5}$ mol/L)	a*	11.44	6.67	6.11	14.56
	b*	-42.00	-18.67	-41.11	-37.00
	a*/b*	-0.27	-0.36	-0.15	-0.39
CR ($2*10^{-5}$ mol/L)	a*	46.55	45.22	47.67	46.55
	b*	32.22	31.11	29.33	35.22
	a*/b*	1.44	1.45	1.63	1.32

Based on data from Table 1, the following considerations can be made:

- the positive value of parameter a*, (+a*) for CV means absorption of green radiation, so red color of the gel, while the negative value of b* parameter, (-b*), means absorption of yellow radiation, so blue color of the gel. The combination between the two colors is the final color of the cryogel, and is mathematically represented by their ratio. For the membrane with Scl, the ratio value is -3.16, showing 3 times more red then blue color, so a pinkish-violet color of the gel will result, while for the PVA, PVA/Cel and PVA/Zein cryogels the subunit but close to 1 ratio gives a blue-violet color.
- like in CV case, +a* for MB means absorption of green light, so red color of the gels, while -b* means absorption of yellow light, so blue color of the gels. In contrast to the previous case, the value of the ratio a*/b* between the two colors is close to zero, for all four PVA cryogels, showing a much higher proportion of blue than red, the final color of the gels being blue not violet.
- high, positive value of parameter a* (+a*) for CR shows absorption of green light, so red color of the gel, is combining with the positive value of b* parameter (+b*), which shows absorption of blue light, so yellow color of the gel. The value of the ratio a*/b* between the two colors, for all cryogels, is higher than 1 with values between 1.32-1.63, so the final color is an intense red.

Using the method described above, even a person with color-blind deficiency can know the color of the gels after dyes sorption.

3.2. Analysis of CIELAB parameters used to determine the influence of the concentration of the immersion solution on gel colour

Taking the initial concentrations for the each dye solution and the highest values between a* and b* CIELAB parameters for the PVA cryogels, information about cryogel color - solution concentration dependence could be obtained.

From Table 2 it can observe that the parameters a* for CV, and b* for MB, representing red and respectively, blue color, are increasing with the initial concentration of dye solutions, showing a more intense color while the initial solution concentration is increasing. In CR case, the percent of red color, a* parameter, has a sudden increase but after c_2, the increase is very small, showing the same color intensity.

Table 2. CIELAB a* or b* parameter vs. dye solution initial concentration for PVA cryogels

Ci_{CV} *[mol/L]*	*a**	Ci_{MB} *[mol/L]*	*-b**	Ci_{CR} *[mol/ L]*	*a**
$1*10^{-6}$	7.11	$8*10^{-6}$	10.33	$2*10^{-6}$	21.11
$3*10^{-6}$	20.89	$2.4*10^{-5}$	29.89	$6*10^{-6}$	46.00
$5*10^{-6}$	33.78	$4*10^{-5}$	36.56	$1*10^{-5}$	46.00
$7*10^{-6}$	27.44	$5.6*10^{-5}$	40.44	$1.4*10^{-5}$	46.44
$1*10^{-5}$	36.67	$8*10^{-5}$	42.00	$2*10^{-5}$	46.55

Taking into account all above data, the change in the samples luminosity as well as the amount of the dye sorbed in the PVA cryogels at equilibrium (determined through the solution analysis) is shown in Fig. 4. Like a* or b* parameters, the luminosity of the samples is increasing with the initial solution concentration for CV and MB, while for CR, after the increase it remains constant.

Moreover, comparing the samples luminosity with the amount of the sorbed dye at equilibrium/ g PVA, for the three dyes, in the same concentration range (Fig. 4), it can be observed that the amount of CV sorbed is about 15% higher than for CR and double compared to MB.

3.3. Analysis of CIELAB parameters used to determine the type of interaction and the state of the dye into the gel

From the graphical representation of the CIELAB parameters vs. dye solution concentration, type of cryogel and type of dye, information about cryogel-dyes interaction and the aggregation type of dye in the cryogel can be obtained.

Fig. 5a shows the variation of the parameter +a* for all CV concentrations and all types of gels. Absorption of the green color in the visible range is a shift to lower wavelengths or a shift to blue (blue shift) and is correlated with the presence of dimers and molecular aggregates when the concentration of the dye increases (Ibrahim et al., 2010).

In accordance with the literature data (Gyu et al., 1989), for concentrations smaller than 5.10^{-6} M

(c_1-c_3), the dye cation is in the monomeric form CV^+, while the c_4-c_5 solutions contain the dye in the dimeric form (Stork et al., 1972). The difference in color (ΔE*) for CV loaded gels (Fig. 5c) shows the lowest values for PVA/Scl gels and the highest, for the PVA/Zein gels. The lighter color for PVA/Scl gels can be related to a highest contact surface and to a higher porosity (Papancea et al., 2015) that determine a better dye dispersion in the whole mass of the gel, while PVA/Zein gels darker color could be due to a more compact surface with low porosity (Papancea et al., 2015). This would determine a maximum agglomeration of the dye at the gel's surface, equivalent with a higher dye concentration. The lowest luminosity values are, as expected, for the PVA/Scl gel, which has the highest amount of the sorbed dye and for the PVA/Zein gels, which has the most compact structure.

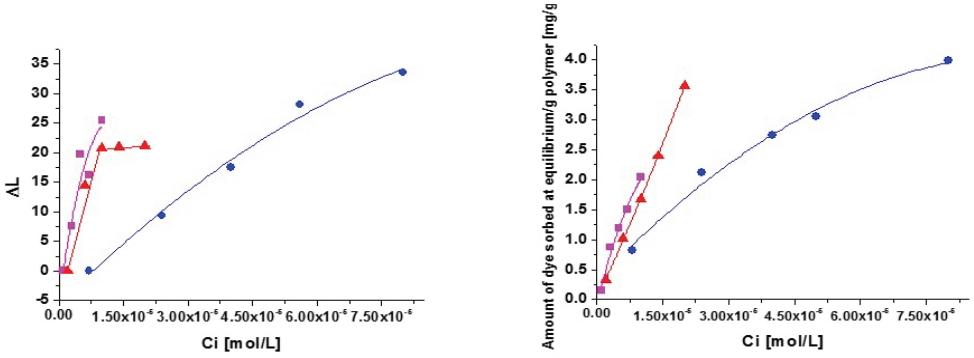
Fig. 6a shows that the increase of the −a* parameter (green component) followed by a decrease observed for PVA, PVA/Cel, and PVA/Zein cryogels in the small concentrations range, is caused by a shift of the absorption band of MB at higher wavelengths (red-shift) than 664 nm. According with the literature data (Ahmad and Kumar, 2010) the sorbed MB in cryogels is in a monomer form (MB^+). At higher concentration, +a* parameter increases meaning sorption at the cryogels surface of $(MB^+)_2$ and respectively $(MB^+)_3$ forms. For PVA/Scl cryogels, +a* parameter increases should mean green light color absorption and blue shift in VIS spectrum (Wang and Wang, 2008) and consequently, $(MB^+)_2$ and $(MB^+)_3$ sorption on the gel substrate.

In Fig. 6c, the total color difference ΔE* is the highest for PVA/Scl cryogels at small concentrations, meanwhile at higher concentrations a slight decrease of the ΔE* parameter could be due to the decrease of samples luminosity. For the other cryogels the parameter increases with the concentration increase. Samples luminosity, ΔL* evidences a continuous decrease with the increase of MB concentration, but the lowest luminosity is shown by the PVA/Scl cryogels (Fig. 6d). Thus, at small concentrations of dye, all parameters indicate a maximum dye adsorption for the PVA/Scl samples; at the higher concentrations, the color parameters are not representative, due to luminosity decrease (Fig. 6c).

Fig. 7a shows that the parameter +a* increases (red component) in all cryogels and for all concentrations. CR has a relatively high ion and is negatively charged for a large range of pH (>5) (Dobrogowska et al., 1991). Correlating the very low concentration gradient of the most diluted solution and the large size of the anion RC, it can be concluded that the adsorption occurs on the surface of the gel by adsorbing a small number of anions. Close values of the parameter a* for all samples in medium and high concentrations of CR solution could indicate adsorption of monomeric forms of CR, mainly on the surface of the gels.

In contrast to the parameter +a*, the +b* parameter (yellow component) is changing significantly with increasing concentrations (Fig. 7b). At c_1, this parameter has very low values, which emphasizes (together with the parameter +a*) that the concentration gradient is very small and adsorption takes place on a small number of active centers. At c_2-c_5 there is a significant increase in this parameter for PVA/Zein samples. Since these cryogels have the lowest swelling and crystallinity degree (Dobritoiu and Patachia, 2103) and a more compact structure (Papancea et al., 2015), the large dye anions, are adsorbed on the external surface of these gels, causing color intensification. Analysis of the color difference ΔE*, chromaticity ΔC* and hue ΔH*, shows higher values for the PVA/Zein cryogels at medium concentrations while at high concentrations a slight decrease in these parameters can be observed; this decrease could be due to the increased brightness of the samples.

There is a small increase of +a* parameter (red color) for PVA/Cel cryogel comparing to the other cryogels (Figs. 5a, 6a and 7a) that may be due to a favorable orientation of dye cation plan on the gel surface considering the presence of more ordered micro-cellulose formations contained in the cryogel.



a. b.

Fig. 4. The samples luminosity variation and the amount of CV (■), CR (▲) and of MB (●) sorbed in PVA cryogels at equilibrium

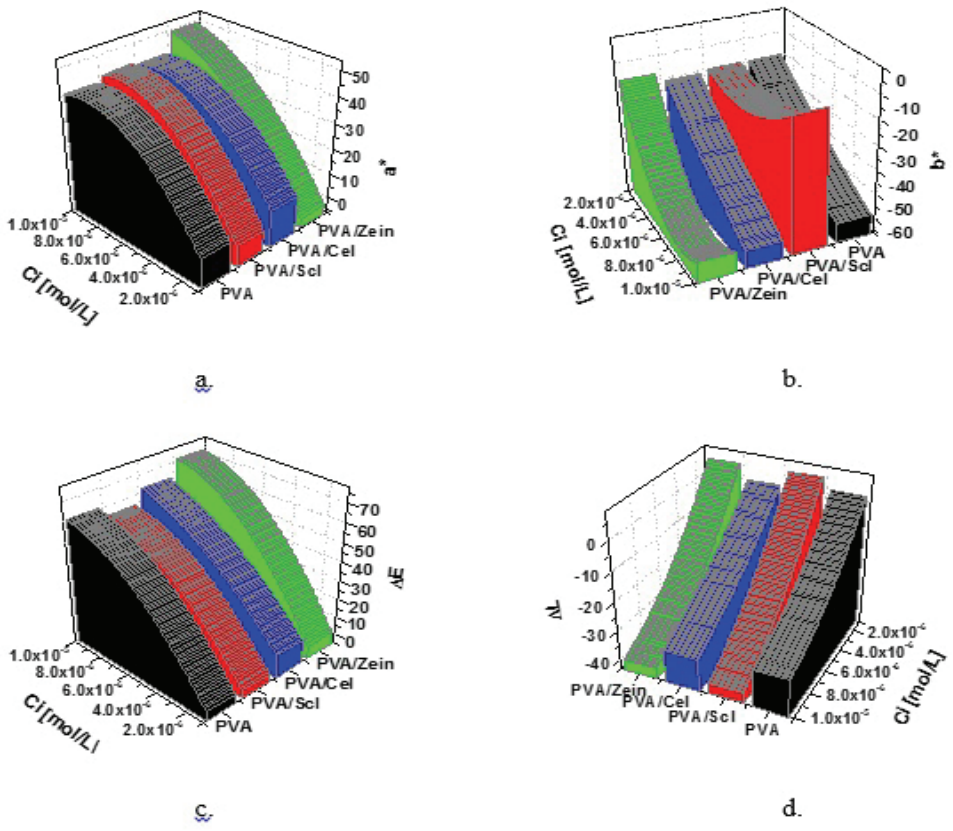


Fig. 5. a*, b*, ΔL*and ΔE* CIELAB parameters variation vs. CV initial concentration

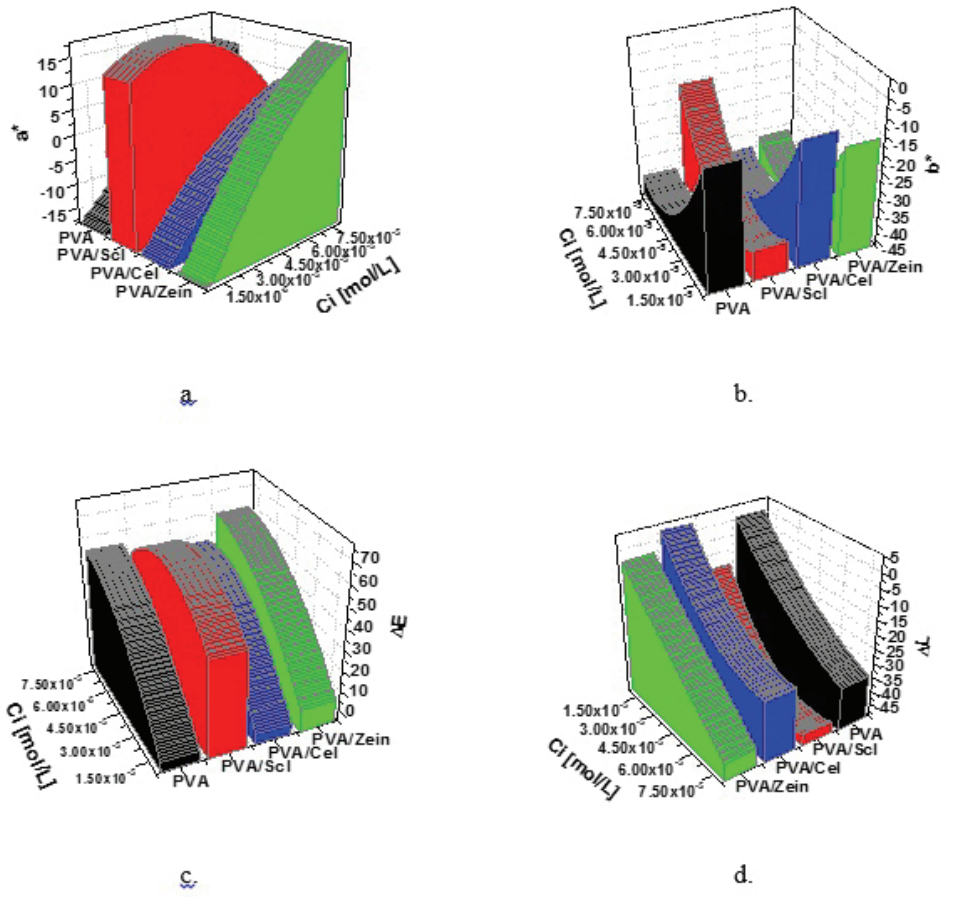


Fig. 6. a*, b*, ΔL*and ΔE* CIELAB parameters variation vs. MB initial concentration

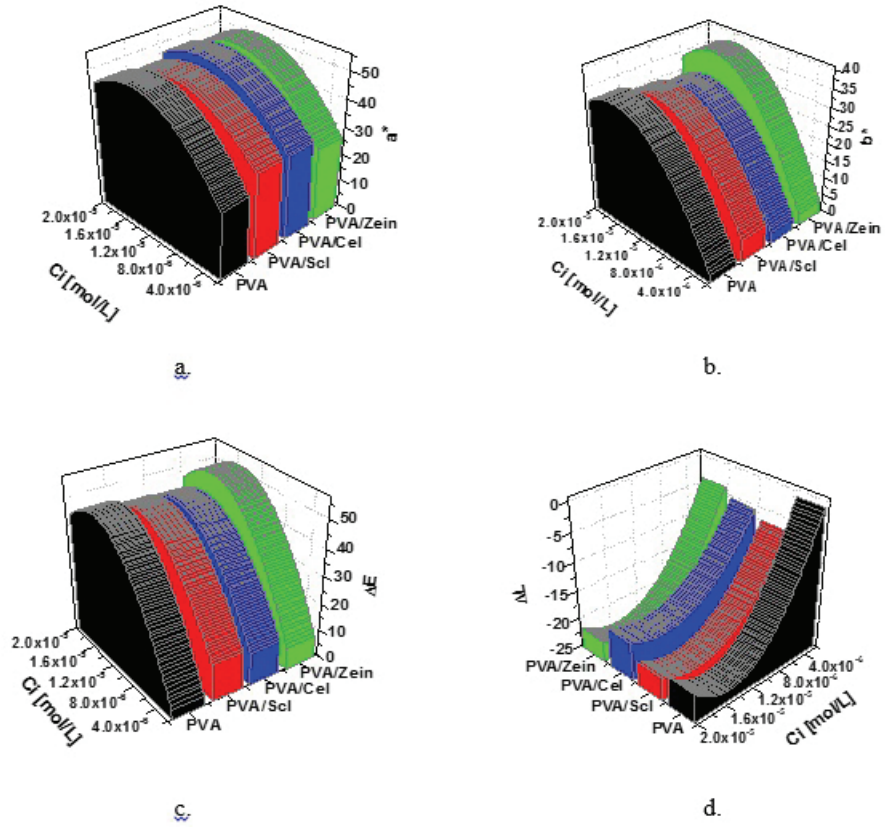


Fig. 7. a*, b*, ΔL*and ΔE* CIELAB parameters variation vs. CR initial concentration

Comparing the values for the difference in color (ΔE*) for all samples it can be observed that they are in good agreement with the extinction coefficient, ε (87.000 $M^{-1}cm^{-1}$ for CV, 95.000 $M^{-1}cm^{-1}$, for MB and 45.000 $M^{-1}cm^{-1}$, for CR) (Adams and Rosenstein, 1914; Cenens and Schoonheydt, 1988; Steensma, 2001), the samples with CR having the lowest values. In addition, from the graphical representation of a*/b* ratio the following information can be obtained.

The pink-violet color of PVA/Scl cryogels after CV sorption evidenced by the highest value for the ratio between a*/ b* parameters (Fig. 8) could be explained through the fact that CV is a metachromatic dye (Confortin et al., 2010) that can determine - after its sorption- a shift of the absorption bands (the O–H stretching vibration band in FTIR spectrum of PVA/Scl shows a shift from 3262 cm^{-1} to 3278 cm^{-1} and in PVA case, from 3266.06 cm^{-1} to 3282 cm^{-1}) in the presence of substances with appropriately arranged anionic groups. This is because of the dye molecules that are getting close enough to form dimeric and polymeric aggregates.

For MB, the a*/b* ratio represented in Fig. 9, the value is increasing with concentration decrease for PVA, PVA/Cel and PVA/Zein cryogels showing a dependence between color intensification and solution concentration. This dependence can be observed also in Fig. 3. For PVA/Scl the ratio value does not change with concentration (the values are ranging between 0.35-0.47).

The ratio a*/b* for CR sorption shows decreasing values with concentration increase for all cryogels except PVA/Scl where the values remain almost constant (Fig. 10). This could be due to fact that PVA/Scl gels are highly porous (Papancea et al., 2015) and determines a better dye dispersion in the whole mass of the gel. On the other hand, the luminosity parameter is increasing with concentration increase in all cases.

3.4. CIELAB parameters used to determine the permeability of a dye through the gel membrane

In Fig. 11, pictures of the PVA membrane subjected to CR diffusion for 515 hours (Papancea et al., 2010a) in a diffusion cell with two compartments (A- the donor compartment and B- the receptor compartment) are presented. As previously observed (Papancea et al., 2010a), strong interactions between CR and PVA determine the impermeability of the PVA membrane against CR. The both sides of the PVA membrane subjected to the diffusion process were analyzed using CIELAB method and all parameters were calculated and are graphically represented in Fig. 12. Comparing the values for all CIELAB parameters (Fig. 12) for the two sides (side A, membrane in contact with CR solution and side B, membrane in contact with water) of the PVA membrane, higher values are observed for the membrane in contact with the CR solution than for the membrane in contact with water. The high differences (double as values) in luminosity, in hue and in color are confirming the results obtained through solution analysis from B compartment, showing that no permeation occurs.

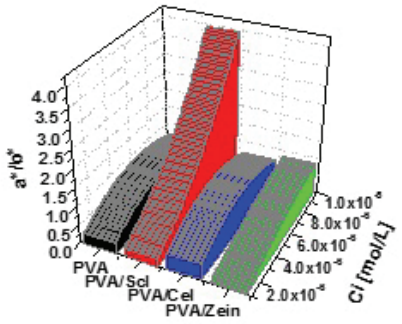


Fig. 8. Variation of a*/b* ratio in case of CV sorption vs. cryogel composition

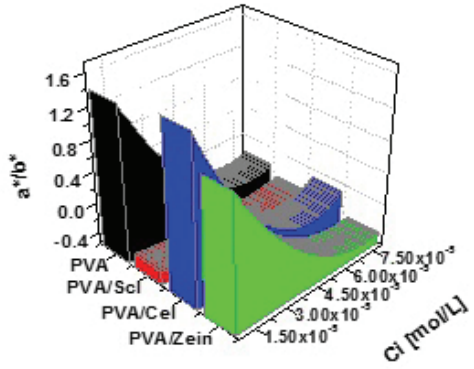


Fig. 9. Variation of a*/b* ratio in case of MB sorption vs. cryogel composition

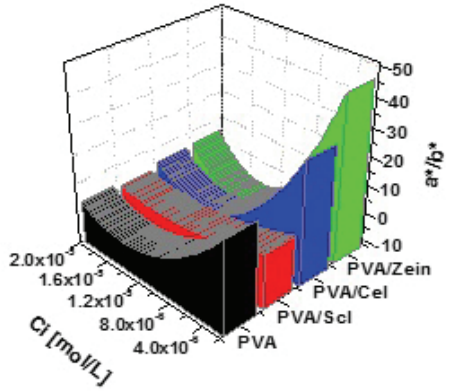


Fig. 10. Variation of a*/b* ratio in case of CR sorption vs. cryogel composition

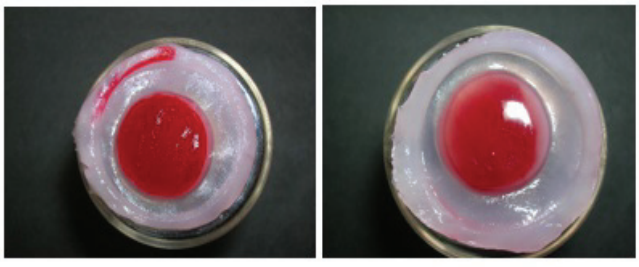


Fig. 11. PVA membranes after CR diffusion: side A – membrane in contact with CR solution; side B – membrane in contact with water

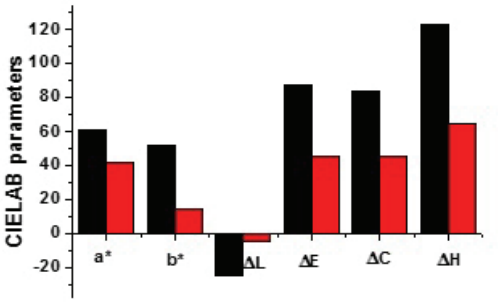


Fig. 12. PVA membranes after CR diffusion: black – side A, membrane in contact with CR solution; red – side B, membrane in contact with water

3.5. CIELAB parameters used to determine the kinetic of the dye sorption and desorption

Photographic images of the samples immersed in $5*10^{-6}$ mol CV/L solution for a certain period of time are presented in Fig. 13. For these images, CIELAB parameters were calculated and correlated with the values for the mass of CV sorbed /g of polymer obtained by solution analysis (after removing cryogel) through UV-VIS spectrometry. With these data, the sorption rate and the equilibrium time were calculated. The rate of sorption calculated as the slope of a* vs. time has a value of 0.068 with R= 0.94 and for the mass of CVss vs. time the rate of sorption is $6.35*10^{-3}$ mg CV/g PVA*min. Comparing the graphical representation of the a* parameter vs. time with that of the mass of sorbed dye/g of PVA determined by solution analysis through UV-VIS method, versus time (Fig. 14), the equilibrium time was found to be around 360 minutes in both cases. The photographic images after desorption are presented in Fig. 15.

It can observe that there is a very small difference in color for the first 6 samples but after 24 hours (1440 min) the PVA cryogel has a lighter but more violet color. The slow decrease of +a* parameter (red component, absorption of green color) together with the slow increase of -b* (blue component, absorption of yellow color) and the luminosity increase indicates that the color lighten up meaning dye desorption. Like in sorption case, the desorption rate was calculated both as slope of variation of a* vs. time and of mass of CV dss/g PVA vs. time respectively. The obtained values were 0.04 with R= 0.89 and respectively, $5.11*10^{-5}$ mg/g PVA*min with R= 0.96 (Fig. 16). Comparing the values after desorption with the values after sorption, it can observe that a*, b* and L values after 24 hours of desorption are comparable with those obtained after 150 minutes of sorption, indicating that a large amount of the dye remains inside of the polymeric matrix, as can be observed in the photographic images from Fig. 15. This hypothesis is confirmed by sorption rate value ($6.35*10^{-3}$ mg CV/g PVA*min), which is two orders of magnitude higher than the desorption rate ($5.11*10^{-5}$ mg/g PVA*min).

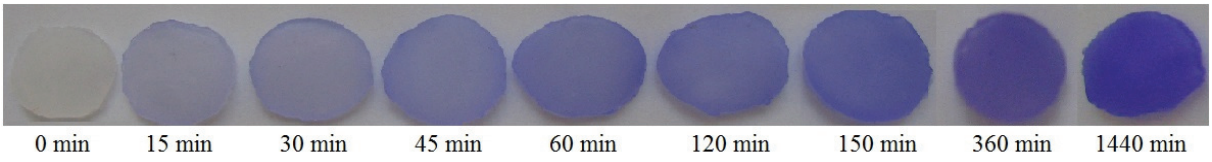


Fig. 13. Photographic images of PVA membranes after CV solution sorption (Ci=5*10^{-6} mol/L)

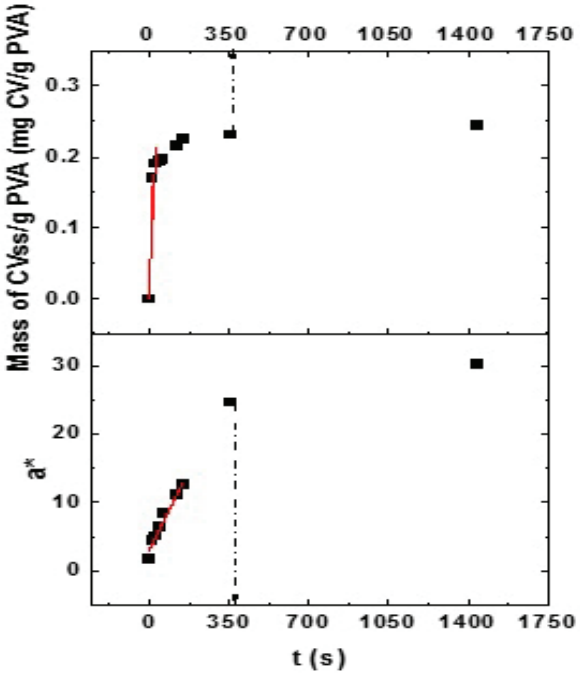


Fig. 14. Variation of a* parameter vs. time and the mass CV sorbed into PVA vs. time

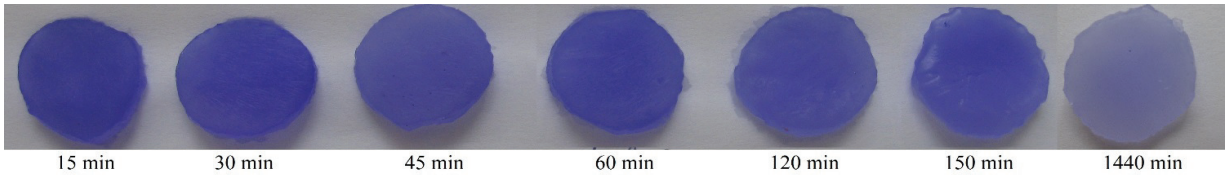


Fig. 15. Photographic images of PVA membranes after CV desorption

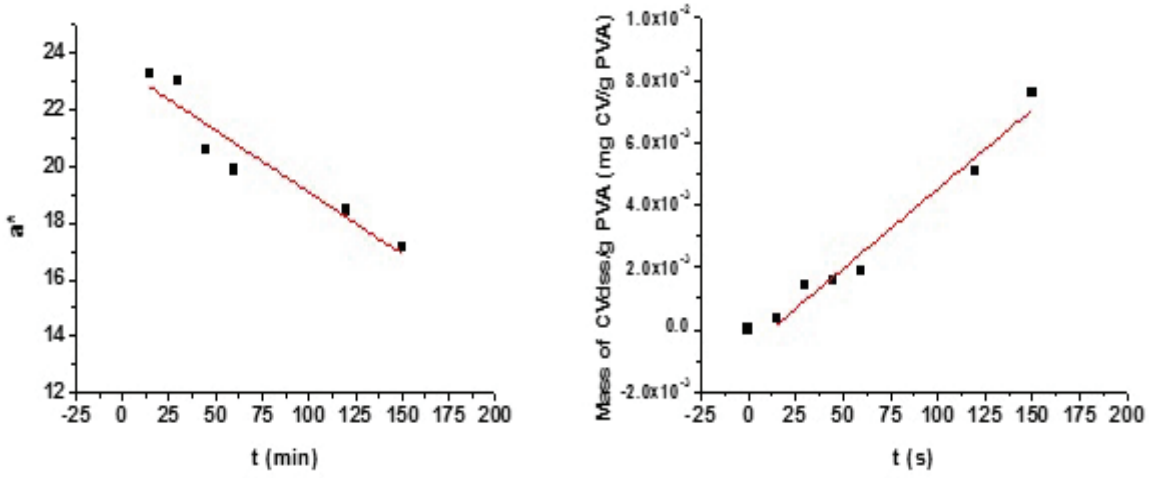


Fig. 16. Variation of a* parameter vs. time and the mass CV sorbed into PVA vs. time

4. Conclusions

The proposed CIELAB method, applied for colored hydrogels, gives important information concerning the structure and the state of the dye inside of the polymer. It was determined that the color effect is dependent on the dye–dye and dye–polymer interactions, on the chemical composition of the gel, on the crystalline structure of the polymer, and by the nature of the immersion media.

Nevertheless, CIELAB method could be correlated with other methods of analysis and could successfully replace them being easier, time saving, un-expensive and non-polluting. As a case study, it was proved to be very efficient for PVA based hydrogels characterization.

Acknowledgments
This paper is supported by the Sectorial Operational Program Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the project number POSDRU/159/1.5/S/134378.

References

Adams E.Q., Rosenstein L., (1914), The color and ionization of Crystal-Violet, *Journal of American Chemical Society*, **36**, 1452–1473.

Ahmad R., Kumar R., (2010), Adsorptive removal of Congo Red dye from aqueous solution using bael shell carbon, *Applied Surface Science*, **257**, 1628–1633.

Cenens J., Schoonheydt R.A., (1988), Visible spectroscopy of methylene blue on hectorite, Laponite B, and barasym in aqueous suspension, *Clay and Clay Minerals*, **36**, 214–224.

Confortin D., Neevel H., Brustolon M., Franco L., Albert J., Kettelarij, Williams Renè M., van Bommel M.R., (2010), Crystal violet: study of the photo-fading of an early synthetic dye in aqueous solution and on paper with HPLC-PDA, LCMS and FORS, *Journal of Physics: Conference Series*, **231**, 012011.

Crini G., Badot P.M., (2008), Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batchstudies: a review of recent literature, *Progress in Polymer Science*, **33**, 399–447.

Croitoru C., Patachia S., Moise G., Porzsolt A., Scarneciu C.,(2009), *Dichromate Anions Sorption from Wastewaters using PVA Cryogels*, Proceeding of 20th DAAAM Conf., Annals of DAAAM and Proceedings, **20**, 1771-1772.

Dobritoiu R., Patachia S., (2013), A study of dyes sorption on biobased cryogels, *Applied Surface Science*, **285P**, 56– 64.

Dobrogowska C., Hepler L.G., Ghosh D.K., Yariv Sh., (1991), Metachromasy in clay mineral systems. Spectrophotometrie and calorimetric study of the adsorption of crystal-violet and ethyl violet by Na-montmorillonit and by Na-kaolinite, *Journal of Thermal Analysis*, **37**, 1347-1356.

Globalspec, (2014), Three-dimensional representation CIELAB color scale, On line at: http://www.globalspec.com/learnmore/manufacturing_process_equipment/inspection_tools_instruments/color_appearance_instruments.

Gyu B., Jung R.S., Kim K.J., (1989), Aggregation of crystal violet with tetraphenylborate anions in aqueous solutions, *Bulletin of Korean Chemical Society*, **10**, 148-151.

Hang P.T., Brindley G.W., (1970), Methylene Blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (Clay-organic studies XVIII), *Clays and Clay Minerals*, **18**, 203-212.

Ibrahim M.M., El-Zawawya W.K., Nassarb M.A., (2010), Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films, *Carbohydrate Polymers*, **79**, 694–699.

Ikkai F., Shibayama M., Nomura S., Han C.C., (1996), Complexation of poly(viny1 alcohol)-Congo Red aqueous solutions. 3. Dynamic light scattering study, *Journal of Polymer Science: Part B: Polymer Physics*, **34**, 939-945.

Kim J. , Montero G., Habibi Y., Hinestroza J.P., Genzer J., Argyropoulos D.S., Rojas O.J.,(2009), Dispersion of cellulose crystallites by nonionic surfactants in a hydrophobic polymer matrix, *Polymer Engineering Science*, **49**, 2054–2061.

Korifi R., Le Dreau Y., Antinelli J.-F., Valls R., Dupuy N., (2013), CIEL*a*b* color space predictive models for colorimetry devices – Analysis of perfume quality, *Talanta*, **104**, 58-66.

Luís P.M.S.S., Cheng C.-Y., Boaventura R.A. R., (2014), Adsorption of a basic dye onto Esmegel clay, *Environmental Engineering and Management Journal,* 13 (2), 395-405.

Papancea A., Valente A.J. M., Patachia S., (2010a), Diffusion and sorption studies of dyes through PVA cryogel membranes, *Journal of Applied Polymer Science*, **115**, 1445–1453.

Papancea A., Valente A.J. M., Patachia S., (2010b), PVA cryogel membranes as a promising tool for the retention and separation of metal ions from aqueous solutions, *Journal of Applied Polymer Science*, **118**, 1567-1573.

Papancea A., Patachia S., Dobritoiu R., (2015), Crystal violet dye sorption and transport in/through biobased PVA cryogel membranes, *Journal of Applied Polymer Science*, DOI: 10.1002/app.41838.

Patachia S., Tica R., Savin G., (1997), A comparative study on iodine complexing with ethyl alcohol and ethyl acetate, *Revista de Chimie*, **48**, 947-951.

Patachia S., Isac L., Rinja M., (2004), New methods for copper and sulphide ions retaining from the waste water, *Environmental Engineering and Management Journal*, **3**, 661-667.

Patachia S., Rinja M., (2005), Ecological method for iodine separation from iodide aqueous solution, *Proceedings of International Symposium EnvEdu*, Brasov, Romania.

Patachia S., Ion R., Varga St., Rinja M., (2007), Porphyrin encapsulation in nanostructured hydrogels, *Journal of Optoelectronics and Advanced Materials*, **6**, 1816-1820.

Patachia S., Dobritoiu R., Coviello T., (2011), Determination of the sorption efficiency of Poly(vynil alcohol)/Scleroglucan cryogels, against Cu^{2+} ions, *Environmental Engineering and Management Journal*, **10**, 193-198.

Patachia S., Damian N., (2014), Cryogels based on Poly(Vinyl Alcohol) [PVA]/ ionic liquids [ILs]: from obtaining to antimicrobial activity, *Soft Materials*, **12**, 371-379.

Schanda J., (2007), *Colorimetry: Understanding the CIE System*, John Whiley Sons Ink. Hoboken, New Jersey, USA.

Steensma D.P., (2001), Congo Red: Out of Africa?, *Archives of Pathology and Laboratory Medicine*, **125**, 250–252.

Stork W.H.J., Lippits G.J.M., Mandel M., (1972), Association of crystal violet in aqueous solutions, *Journal of Physical Chemistry*, **7**, 1772–1775.

Vâlceanu A., Vârlan C., Schiller E., (2006), *Physiology and Pathology of Chromatic Dental* (in Romanian), Orizonturi Universitare Press, Timisoara, Romania.

Varga S., Patachia S., Ion R., (2008), *Analysis of Mass Transfer of Encapsulated Porphyrins from PVA Based Hydrogels: an Experimental Study on Cylindrical Gels and Membranes*, Proceeding of the 5th International Conference HMT'08, Book series: Mathematics and Computers in Science and Engineering, 231-236.

Wang L., Wang A., (2008), Adsorption properties of congo red from aqueous solution onto N,O-carboxymethyl-chitosan, *Bioresource Technology*, **99**, 1403–1408.