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PRELIMINARY ASSESSMENTS ABOUT THE SORBTIVE PROPERTIES OF NEW TYPES OF TEMPO-OXIDIZED CELLULOSE AND PULLULAN - PVA HYBRID HYDROGELS: ORGANIC DYES AND METALLIC IONS RETENTIONS

BY

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Abstract. Polyvinyl alcohol (PVA) is a biodegradable polymer, largely used in the last years for the production of biodegradable hybrid materials, as a substitute of traditional polyethylene or polypropylene polymers. These materials have proved beneficial applications in water filtration, paper industry, mats and films production, and packaging. However, the PVA itself suffer of poor mechanical strength, requiring other components able to improve this property. Thereby, we propose the use of various amounts of natural polymers, *i.e.* cellulose and pullulan, in the form of C_6 oxidized derivatives, as multifunctional key components, acting both as cross-linking agents, but also increasing the strengthening and stiffness properties of the as prepared hybrid PVA hydrogels. Therefore, several hybrid PVA hydrogels, with different amounts of incorporated polysaccharide (PVA-5P, PVA-10P, PVA-25P; PVA-5C, PVA-10C and PVA-25C) were synthesized and tested as sorbents for two models of dyes (Orange 16 and Methylene Blue) and Co^{2+} as metallic ions.

Keywords: hydrogels; cellulose; pullulan; dyes; metallic ions; sorbent.

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1. Introduction

Materials in different forms and structures, whether simple or composite, natural or synthetic, obtained by chemical synthesis or biotechnology, whether they are obtained by the processing of renewable raw materials or classical synthetic materials, underlie the development of various modern fabrication technologies high-quality products or at the basis of the development of performing separation methods applicable in the most diverse areas: from environmental protection to quality of life for people.

Nowadays we observe that the technic-informational development and demographic explosion generated many ecological imbalances, genetic mutations culminating with the dramatic reduction of the raw material resources. Due to this, it is urge to obtain new materials with better properties in sensitive areas as for performing cell separation, so called “biomaterials” which are compatible with cellular structures and membranes. Thus, a highly desired approach is the valorization of the renewable resources, organic wastes and also to study the living organisms capacity to synthesize materials, with specialized functions.

Biomaterials, as macromolecular materials gained a lot of interest in the last years, being used in several fields as adsorbents, medical devices, or pharmaceuticals, supports for enzyme immobilization or different active principles (Gorduza *et al*., 2002; Tathe *et al*., 2010; Ratner and Bryant, 2004).

Different biomaterials can be obtained through physical treatments, chemical synthesis or biotechnological procedures, in controlled environment, offering the possibility to use them alongside other conventional materials or even replace them, for biotechnological, medical and ecological purposes (Tanpichai and Oksman, 2016; Han *et al*., 2016; Morariu *et al*., 2015). We can apply specific fine organic syntheses combined with biotechnologies, genetic recombination approaches (Gorduza *et al*., 2002; Tathe *et al*., 2010; Lin *et al*., 2012; Yang *et al*., 2014; Zulkifli *et al*., 2015).

Thus, our present research is focused to obtain several types of biomaterials, with hydrogel macromolecular structures, by using renewable resources as matrix and crosslinking agent.

Polyvinyl alcohol (PVA) is a biodegradable polymer, largely used in the last years for the production of biodegradable hybrid materials, as a substitute of traditional polyethylene or polypropylene polymers. These materials have proved beneficial applications in water filtration, paper industry, mats and films production, and packaging. However, the PVA itself suffer of poor mechanical strength, requiring other components able to improve this property. Thereby, we propose the use of various amounts of natural polymers, *i.e.* cellulose and pullulan, in the form of C_6 oxidized derivatives, as multifunctional key components, acting both as cross-linking agents, but also increasing the strengthening and stiffness properties of the as prepared hybrid PVA hydrogels.

Therefore, the aim of this paper is about several hybrid PVA hydrogels, with different amounts of incorporated polysaccharide (PAV -5P, PVA -10P, PVA -25P; PVA -5C, PVA -10C and PVA -25C) were synthesized and tested them as sorbents for two organic dyes (*i.e.* Orange 16 and Methylene Blue) and metallic ions (*i.e.* Co^{2+}). The primary goal of the study was to synthesized, characterized and identifies the behavior in the sorption process of these new biomaterials and to establish certain optimal working conditions, in particular the sorbent structure that best fits the type of pollutant that should be retained.

The results led to conclusions that allow extension of the study on the sorption process of metal ions on PVA -25C material, having the largest amount of incorporated TEMPO-oxidized cellulose.

2. Experimental

Materials

As sorbents were tested several hybrid pva hydrogels, with different amounts of incorporated polysaccharides (cellulose–c and pullulan–p): PVA -5P, PVA -10P, PVA -25P, PVA -5C, PVA -10C and PVA -25C. Their characteristics were presented in Table 1.

Table 1

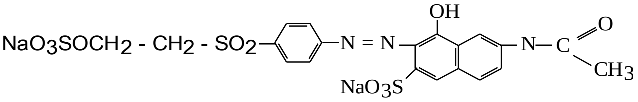
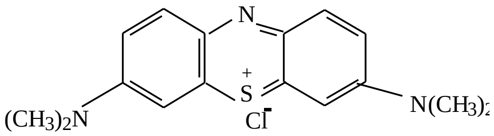
Characterization of the Hybrid PVA Hydrogels

Name of hydrogel	Amount of polysaccharide [%]	Pores size, [μm]
PVA	0	27-46
PVA -5P	5	25-35
PVA -10P	10	30-40
PVA -25P	25	45-65
PVA -5C	5	20-30
PVA -10C	10	30-35
PVA -25C	25	45-65

The selected chemical pollutant compounds are characterized in Table 2.

Table 2

Characterization of the Selected Chemical Pollutant Compounds

Structure	Characteristics
 Abbreviations: O16 - Orange 16	**Orange 16** (Reactive anionic dye) C.I. 18097; anionic, MW = 617.54 g/mol; λ_{max} = 495 nm; concentration of the stock solution = 710 mg dye /L
 Abbreviations: MB – Methylene Blue	**Methylene Blue** (Basic Blue 9); C.I. 52015; cationic, phenothiazine dye; MW=319.85 g/mol; λ_{max} = 660 nm; Concentration of the stock solution = 452 mg/L
Co^{2+}	**Metallic salts: $CoSO_4$** Concentration of the stock solution=599.0635 mg Co^{2+}/L

Hydrogel Synthesis

The hydrogels were obtained in two steps:

I) synthesis of the oxidized cellulose/pullulan in the presence of TEMPO/NaBr/NaOCl system and

II) preparation of the hydrogels. In the first step, 10 g of polysaccharides was imersed in 1200 mL distilled water.

A mixture of TEMPO (0.1 mmol/g polysaccharides) and NaBr (1 mmol/g polysaccharides) was then added drop wise under vigorous stirring. The 8% NaClO solution (20 mmol/g polysaccharides) was subsequently added to the polysaccharidic slurry under continuous stirring, moment denoting the start of the oxidation reaction. The suspension was then kept under stirring for 5 h. The reaction is carried out with a careful check of the pH, which is strictly maintained at about 10 by using 2 M NaOH solution. After 5h, the reaction was quenched. In case of cellulose the resulted oxidized fraction is filtered and washed several times with deionized water and 0.5 M HCl solution. The water-soluble collected fraction was precipitated with excess of ethanol (1:10 vol.) and the formed precipitate was separated by centrifugation. After centrifugation, the solid content was re-dissolved in water, the resulted solution being desalted, and oligomers are removed by diafiltration using a Millipore ultrafiltration membrane from polyethersulfone (cut-off: 12,000 g·cm^{-1}). The diafiltration was stopped when the filtrate conductivity was lower than 10 $\mu S \cdot m^{-1}$, the oxidized product was recovered by freeze-drying.

In the second step was prepared hydrogels. Homogeneous PVA solution was mixed with oxidized polysaccharides solution in the following ratios: 95/5, 90/10 and 75/25 (w/w), samples being labeled as PVA -5C, PVA -10C, PVA -25C, PVA -5P, PVA -10P and PVA -25P respectively. PVA -C/P mixture composites and pure PVA aqueous solution were subjected to 3 freezing thawing cycles in order to obtain physical networks. After each freezing cycle, the samples were kept at 4°C for a slow thawing which ensure the formation of a porous structure.

Characterization of Hydrogels

FTIR

The FTIR spectra of hydrogel samples were obtained using an attenuated total reflection configuration (ATR) on a Golden Gate accessory (diamond crystal, Specac Ltd.) using a Vertex 70 spectrometer (Bruker, Germany). The spectra were recorded in the mid IR range 4000–600 cm^{-1}.

ESEM

The morphology of the composite hydrogels was checked using environmental scanning microscopy (ESEM). The ESEM microphotographs were acquired on samples fixed by means of colloidal silver on copper supports. The samples were previously coated by a thin layer of gold. Each coated surface was then examined using an Environmental Scanning 200 instrument, operating at 5 KV with secondary electrons in High Vacuum Mode.

Sorption Experiments

The sorption experiments were conducted in the batch system, where different amount of PVA hydrogel were contacted with 25 mL of aqueous dye/metallic ions solutions of established initial concentration in 150 mL Erlenmayer flasks placed in a thermostated bath at particular temperature. The initial solution pH was adjusted to the necessary value using HCl 1N or NaOH 1N solutions, and determined with a Radelkis OP-271 pH/Ion analyzer. After a contact time of 24 h, the spectrophotometric technique (the calibration curve method) was selected to determine the concentration of chemical species studied in supernatant: for dyes was used the direct reading of the absorbance, and for the cobalt ion was read the solution absorbance after treatment with rubeanic acid 0.05% in borate buffer (pH=9).

It was used an UV-VIS Digital Spectrophotometer, model S 104D /WPA.

The sorption capacity of the sorbent was evaluated by the Eq.(1).

$$q = \frac{C_0 - C}{G} \cdot V \text{ [mg of dye (g of sorbent)}^{-1}\text{]} \qquad (1)$$

where: C_0 and C are the initial and the equilibrium (residual) concentration of chemical species in solution, [mg·L^{-1}], G is the amount of sorbent, [g] and V is the volume of solution, [L].

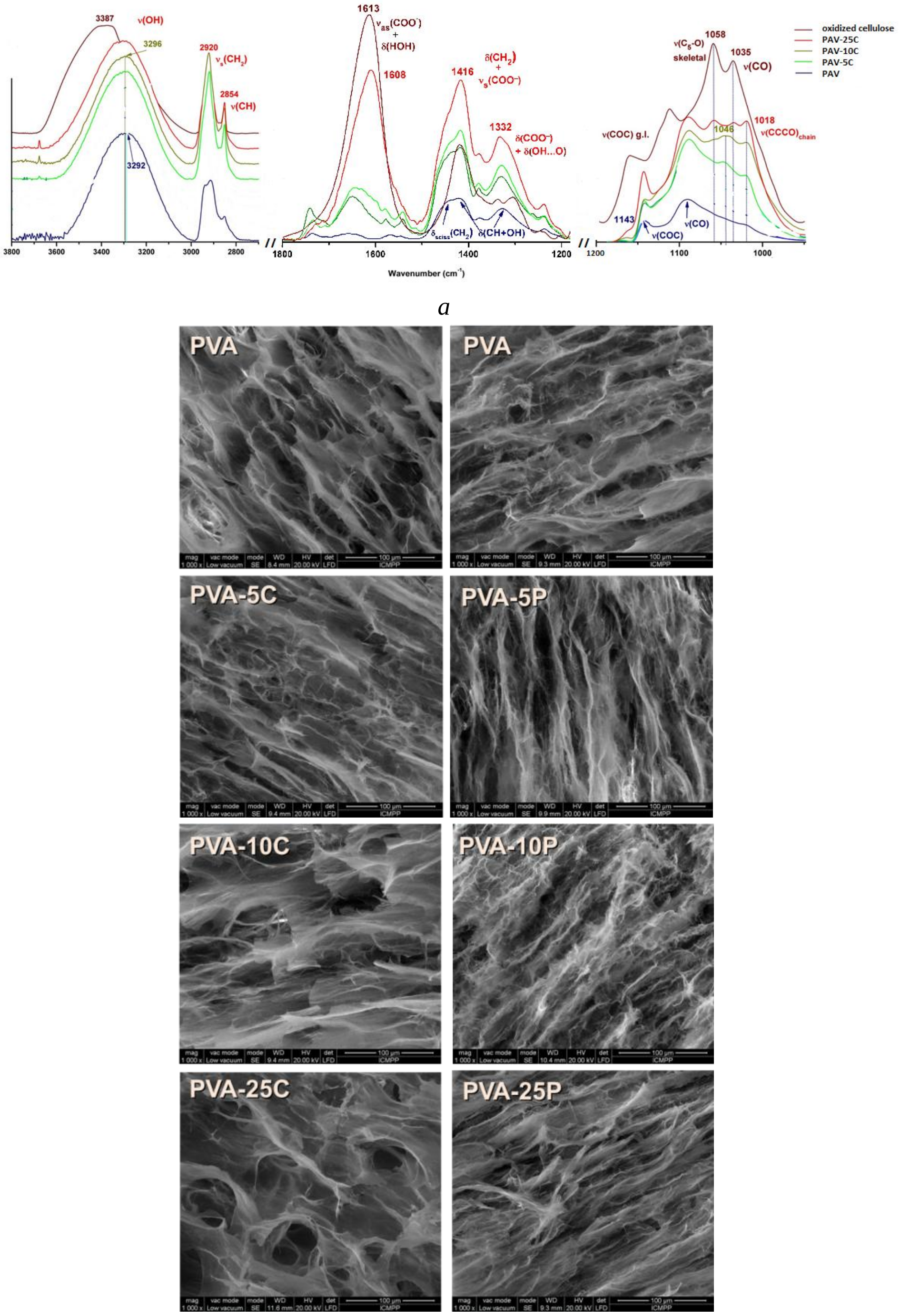
3. Results and Discussions

Characterization of Sorbents

The ATR-FTIR spectra of the oxidized cellulose, PVA -25C, PVA -10C, PVA -5C and PVA blends are presented in Fig. 1*a*. As we can see from spectra the PVA hydrogels in comparison to that of PVA and oxidized cellulose, show that the critical changes, specials in the alcoholic region. The emergence of the characteristic asymmetric stretching vibration of carboxylate units of oxidized cellulose is observed around 1610 cm^{-1}, while the distinctive ν(CO) vibration in PVA microcrystals at 1143 cm^{-1} presents a small reduction in intensity. The maximum of the band is centered on 3292 cm^{-1} in pure PVA and is characteristic to double hydrogen bonds built in the crystalline domains, when the hydroxyl group acts as both donor and acceptor of protons. This band enhances in intensity and shifts to the red when oxidized cellulose increases in the blends where it reaches 3296 cm^{-1} (PVA -5C and PVA -10C). On further increasing the oxidized cellulose amount, the ν(OH) band slightly decreased in intensity, became broader and with an evident asymmetry on the high wavenumbers side (PVA -25C). The opposite shift may be a result of the increased contribution of the ν(OH) band of oxidized cellulose and of a change in the intermolecular interactions, with the increased involvement of oxidized cellulose. With increase of amount of oxidized cellulose in PVA hydrogels the $\nu_{as}(COO^-)$ of carboxylate groups moves from 1613 cm^{-1} in oxidized cellulose to 1608 cm^{-1} in PVA -25C. The new appeared band at 1018 cm^{-1} is observed in all specimens, being an enhancement of the respective shoulder in the pure PVA.

SEM

Scanning electron microscopy imagines of PVA, PVA -5C, PVA -10C, PVA -15C, PVA -25C, PVA -5P, PVA -10P, PVA -25P hydrogels are shown in Fig. 1*b*. At the first sight, the images reveal a rather homogeneous composition of the hydrogels, with no evidences of crowded or irregular areas, suggesting thus a good compatibility of the two constituents. All composite samples exhibit large porous structures with interconnected pores, the pore size increasing with the increase of the amount of oxidized polysaccharides.



a

b

Fig. 1 – Characterisation of PVA hydrogels: (*a*) FTIR spectra and (*b*) SEM pictures.

Sorptive Behaviour of Synthetised Hydrogels Evaluation

For appreciation the sorptive behaviour of the synthetised material it will be used them as sorbent for retention two dyes and one metallic ion from aqueous solutions.

The dyes sorption onto synthetised hydrogels

In this connection, our attention was directed to two textile dyes, having different structures, but also different molecular weights. Some informations aquired after preliminary studies performed on Methylene Blue and Orange 16 dyes are presented in the Table 3.

Table 3

Preliminary Results about Dye Sorption onto PAV Based Hydrogel

Observations	Dye	
	Methylene Blue	Orange 16
pH	pH =10	acidic medium, pH=1-2
Molecular size of dye	The molecular size (MW=320mg/g) favors a better adsorption in the case of micropors structres of sorbents, causing a better retain ability	
Type of sorbent	Hydrogels presents a diferent sorbtiv behavior due to the nature and quantity of the chemical compound incorporated in the PVA structure. Thus, the PVA -P hydrogels offers a smaller adsorption capacity than those obtained through cellulose usage. Also, PVA -C hydrogels offer diferent adsorption capacities to both dyes, due to the quantity of cellulose used, in which we distinguish PVA -25C.	
PVA -C hydrogels	Regardless of the celulose percentage used, there is critical concentration of MB dye in the solution, which determines the modification of system behavior. It was found that at 5.42mg/L MB occurs only the dye sorption (R% =74.07% MB pe PVA -25C), since at 54.2 mg/L MB, beside the sorption, after 24h a flocculation phenomenon is clearly visible. This suggest that process is more effective, the removal of the dye from the aqueous solution being over 70 %.	

The metallic species sorption onto synthetised hydrogels

In this study, the Co^{2+} originating from its sulphate salt has been employed. The pH solution is 2.5. The preliminary results are presented in the Table 4. It can be observed that the retention capacity of the Co^{2+} is much higher than in the case of dyes. Moreover, there is observed a different behavior of the studied hydrogels, depending on the constituent polysaccharides, i.e. cellulose, or pullulan, which dictates the pores size.

Table 4
Preliminary Results about Co^{2+} *Sorption onto PVA Based Hydrogel*

Conditions: Initial ion concentration, C_0, [mg/L] Sorbent dose, [g/L]; Solution pH	Hydrogel type (particle size, [µm])	q, [mg/g]
119.813 mg/L (0.44-0.64) g/L pH=2.5	PVA -5P (25-35)	42.73
	PVA -10P (40-65)	20.75
	PVA -5C (40-60)	51.18
	PVA -10C (30-45)	84.17
101.725 mg/L ; 0.4 g/L ; pH = 2.5	PVA -25C (160)	199.177

3. Conclusions

The experimental results lead to a few preliminary comments and underline some directions for further studies that should be performed:

❑ PVA hydrogels exhibit different sorption behaviour due to the nature and quantity of incorporated polysaccharides in the PVA structure, microcellular structure of hydrogel and the type of chemical polluting species which needs to be retained.

❑ PVA -polysaccharides hydrogels show a satisfactorily capacity of sorption for metallic ions, as compared to other types of synthetic adsorbents, which suggest the opportunity to extend the detailed study of sorption balance and its application to other types of metallic ions.

❑ PVA –25C hydrogels proved to be the most efficient in retaining through the sorption process of Methylene Blue dye. It is of great interest to continue the study of Methylene Blue dye retention from the aqueous medium present in small concentrations, from waste waters resulted by the pharmaceutical industry.

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STUDII PRELIMINARE ASUPRA PROPRIETĂȚILOR SORBTIVE ALE HIDROGELURILOR HIBRIDE TEMPO-CELULOZA OXIDATĂ – PVA: REȚINEREA DE IONI METALICI ȘI COLORANȚI ORGANICI

(Rezumat)

Alcoolul polivinilic (PVA) este un polimer biodegradabil care se utilizează în ultimii ani pentru producerea de materiale hibride biodegradabile, ca înlocuitor al polimerilor tradiționali din polietilenă sau polipropilenă. Aceste materiale s-au dovedit a avea aplicații benefice în filtrarea apei, industria hârtiei, producția de acoperiri, filme și ambalaje. Prezintă rezistență mecanică slabă, necesitând alte componente capabile să-i îmbunătățească această proprietate. De aceea am propus utilizarea diferitor cantități de polimeri naturali (celuloză și pullulan), sub formă de derivați oxidați C6, ca și componente cheie multifuncționale, acționând atât ca agenți de reticulare, cât și de creștere a proprietăților de întărire și rigiditate ale unor hidrogeluri hibride PVA. De aceea, s-au sintetizat și s-au testat mai multe hidrogeluri PAV hibride, cu diferite cantități de polizaharidă încorporată (PVA -5P, PVA -10P, PVA -25P; PVA -5C, PVA -10C și PVA -25C) pentru sorbția coloranților orange 16 și albastru de metilen și a ionului metalic de Co^{2+}.