

VALORIZATION OF TEMPO-OXIDIZED CELLULOSIC FRACTIONS FOR EFFICIENT DYE REMOVAL FROM WASTEWATERS

GABRIELA BILIUTA,* DANIELA SUTEU,** TEODOR MALUTAN,**
ANDREEA-IRINA CHIRCULESCU,** IULIA NICA** and SERGIU COSERI*

*“Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Iasi,
41 A, Gr. Ghica Voda Alley, 700487, Iasi, Romania

**“Gheorghe Asachi” Technical University of Iasi, Faculty of Chemical Engineering and Environmental
Protection, 73, Prof. Dr. Docent Dimitrie Mangeron Blvd, 700050, Iasi, Romania

✉ Corresponding authors: Gabriela Biliuta, biliuta.gabriela@icmpp.ro

Daniela Suteu, danasuteu67@yahoo.com

Sergiu Coseri, coseris@icmpp.ro

*Dedicated to Acad. Bogdan C. Simionescu
on the occasion of his 70th anniversary*

Never-dried softwood bleached sulfite pulp (SBS) was oxidized employing a TEMPO-mediated protocol to introduce carboxylic groups. The content of the negatively charged groups was determined by potentiometric titration and thoroughly characterized. Never-dried oxidized cellulose (SBSox) was tested as potential sorbent for the reactive dye Brilliant Red HE-3B. Several parameters, including initial pH of the solution, sorbent dose, dye concentration, temperature and contact time, were evaluated. The values of these parameters were found to depend significantly on the behavior of the cellulose material studied under the specified experimental conditions and less on the dye behavior. The maximum values of dye percentage removal were obtained at pH = 1.3, cellulose dose of 2 g/L, dye initial concentration of 36-240 mg/L, temperatures around 20-25 °C, and equilibrium time around 400 min. Based on the experimental results, the oxidized cellulose material can be successfully used as sorbent for dye removal from colored wastewaters.

Keywords: cellulose sorbent, aqueous medium, operating variables, reactive dye, sorption

INTRODUCTION

Sorption is a valuable method for removing or recovering both organic and inorganic pollutants from aqueous environments, due to its undeniable advantages, such as increased process sensibility and selectivity, reduced matrix effects, simultaneous achievement of pre-concentration and proper estimation.¹⁻³ The main advantage of this method lies in the possibility to use various materials that have potential absorption properties as sorbents. Therefore, a key issue regards the selection of the sorbent, which should take into account several requirements regarding selectivity, capacity of sorption, favorable kinetic features, physical-chemical stability, good mechanical strength, regeneration and low cost.¹

The most frequently used sorbent in various depolluting applications, *i.e.* activated carbon, is

highly expensive, therefore its replacement with inexpensive alternatives derived from natural resources, such as polysaccharides, clay and fly ash, becomes highly demanded.⁴⁻⁸ Polysaccharides particularly, represent promising resources, especially due to their abundance and renewability. Cellulose, with its ubiquitous presence in nature, has been utilized for centuries in diverse traditional applications: pulp, paper, filters, films and textiles.⁹ Its C6 oxidized derivative, oxidized cellulose, a completely bioresorbable and readily degradable under physiological conditions material, is intensively investigated for several biomedical applications, as an efficient absorbable hemostatic scaffolding material^{10,11} and also as a postsurgical adhesion prevention layer.¹² Oxidized cellulose is alike a

carrier material in agricultural, cosmetic and pharmaceutical applications.^{13,14} For the preparation of oxidized cellulose, much effort has been made to improve the selectivity of the process, according to the desired site to be converted.^{15,16} A lot of progress in this field has been made by the implementation of stable nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), as potent mediators for the selective oxidation of the primary OH groups in polysaccharides.¹⁷⁻¹⁹ The protocol is quite simple, involving the presence of sodium hypochlorite and sodium bromide, at room temperature and a pH around 10. The most important feature of the TEMPO-mediated oxidation of cellulose (and other polysaccharides) refers to its high selectivity, only primary OH groups being oxidized, whereas the other two secondary ones from the anhydroglucose unit, remain unaffected.^{17,18} Another important step ahead in the area of cellulose selective oxidation has been recently reported, in which *N*-hydroxyphthalimide (NHPI) plays a decisive role,²⁰⁻²⁴ *via* its corresponding nitroxyl radical, phthalimide *N*-oxyl (PINO), generated *in situ*, acting as a mediator of C6 oxidation in cellulose, in the presence of sodium hypochlorite and sodium bromide, at alkaline pH and room temperature.²⁵⁻²⁹ The use of NHPI, instead of free radical TEMPO, brings some advantages as we have reported previously,²⁵ such as a lower cost and, very importantly, the preservation of the degree of polymerization of the oxidized product. Regarding this issue, it is worth mentioning that in the case of cellulose fiber oxidation, when the TEMPO protocol is employed, the degree of polymerization dropped from 380 to 49 (Tencel fibers) and from 680 to 38 (Bemliese fibers), but when NHPI was used instead, the degree of polymerization of the viscose or modal fibers suffered only a modest decrease after oxidation, from 308 to 283 and from 488 to 461, respectively.¹⁵ Nevertheless, the implementation of NHPI-mediated oxidation of cellulose is still a challenging issue, especially due to its poor solubility in water, and/or due to the necessity of including a supplemental reagent able to promote the generation of the PINO radical. Of particular importance for the desired application is the type of the cellulosic material chosen. Never-dried cellulose differs essentially from other cellulose types, including fibers, when high absorption capacities are required. Never-dried fibers have much narrower secondary walls, as well as larger

lumens, which grants higher water accumulation.^{30,31} Other studies performed on never-dried cellulose fibers have shown that they are able to adsorb more chemicals than the dried ones.³² Organic dyes are known as chemical compounds with high polluting potential on the surface waters; they are likely to reach surface waters as a result of the discharge of industrial effluents.

Traditionally, the textile industry is a primary source of dyes utilization. Yet, in the last decades, several other industries, including rubber, plastic, food, cosmetic, leather, paper, and more recently printing, have utilized increased amounts of dyes. The effects of dye discharges in water depend on the structure of the dye molecules and might consequently hinder light penetration through the water, or, even worse, cause the release of side products with carcinogenic or mutagenic properties as a result of the decay and decomposition processes of dyes.¹ Considering this, the removal of dyes from industrial effluents, before their discharge into surface waters, becomes compulsory for industrial processes. Also, the removal of dyes from wastewaters represents a continuous concern in developed countries and has become a stringent issue due to the social and ecological impact that residual textile effluents have on large population areas. The retention of dyes from the aqueous environment using the absorption method has wide practical applications.¹⁻³ For this purpose, different materials with adsorptive properties can be used: ion-exchange materials, activated charcoal, cellulose adsorbents and lignocellulose waste.³³⁻⁴⁴

The main objective of this paper was to synthesize and characterize TEMPO-oxidized never-dried softwood bleached sulfite pulp (SBSox) and to further investigate its sorptive properties. The potential of this cellulose-based material to be used as an economical and efficient agent to remove Brilliant Red HE-3B reactive dye (BRed) from wastewaters was analyzed under batch conditions. The influence of several parameters, such as solution pH, sorbent dose, dye concentration, temperature and contact time, were carefully studied. The experimental results revealed only a moderate sorption capacity of the analyzed cellulose material, suggesting the necessity to complete the data with equilibrium, thermodynamic and kinetic studies in order to elucidate the absorption mechanism and the rate-limiting step.

EXPERIMENTAL

Materials

Sorbent. Never-dried softwood (spruce) bleached sulfite pulp (SBS) with moisture content of 88% was kindly provided by Lenzing AG. Before use, the pulp (50 g) was soaked in dilute HCl (4500 mL) at room temperature and pH~2 for 0.5 h, and then washed repeatedly with water by filtration. TEMPO, sodium bromide, 9% (wt) sodium hypochlorite and the other chemicals and solvents were of pure grade (Sigma Aldrich) and were used without further purification.

Dye. Brilliant Red HE-3B (Procion Red HE-3B; Reactive Red 120), with C.I. 25810, was selected as experimental dye. The selected dye is an anionic, bifunctional reactive dye, with molecular weight: $M_w = 1463$ g/mol and maximum absorption wavelength $\lambda_{max} = 530$ nm. It was used as an aqueous solution with a concentration of the stock solution of 500 mg/L and a concentration of the working solution of 25-400 mg/L.

Methods

TEMPO-mediated oxidation of cellulose

Briefly, the typical procedure of TEMPO-mediated oxidation of SBS consisted of the following steps: never-dried pulp (16.67 g) was introduced in a water solution (2500 mL) containing TEMPO (0.032 g, 0.2 mmol) and sodium bromide (0.2 g, 2 mmol). After adjusting the pH to 10, 9% NaClO solution (16.5 g, corresponding to 10.0 mmol/g cellulose) was added to the cellulose slurry, at room temperature under vigorous stirring. The pH of the slurry was carefully maintained at pH 10 by adding 0.5 M NaOH (to compensate the decrease of the pH due to formation of carboxylic groups), with a pH stat, for about 2 h, until no variation of the pH was observed.

Potentiometric titration

The experimental details regarding the potential titration of the oxidized samples are detailed in our previous papers.^{25,29} All the experiments were performed in triplicate, the value used for the negatively charged groups being the mean value of these experiments, with a standard deviation of the measurements within 4%.

Dye sorption

The sorption tests were achieved by the batch method, which consists in contacting diverse amounts of cellulose sorbent with 25 mL of solution, with different dye concentrations. Aqueous solutions of NaOH and HCl (1N and 0.1N) were used to adjust the desired value of the pH of the solutions. The HANNA pH/Ion analyzer was used for measuring the concentrations. Constant temperature was maintained with a thermostatic bath. The sorption systems were maintained under discontinuous stirring for 24 hours. After 24 hours, the concentrations of the dye in the supernatant were determined spectrophotometrically. For the measurements, a UV-VIS Digital

Spectrophotometer, model S 104D/WPA, was used. The sorption capacities of the cellulosic sorbent were evaluated by calculating the amount of dye adsorbed (Eq. 1):

$$q = \frac{C_0 - C}{G} \cdot V \quad (1)$$

and the percent of dye removal (Eq. 2):

$$R, \% = \frac{(C_0 - C) \cdot 100}{C_0} \quad (2)$$

where C_0 and C are the initial and equilibrium concentrations of the dye in solution in mg/L, G is the amount of cellulose (g) and V is the volume of solution (L).

Analytical methods for quantitative determinations

The spectrophotometrical method was used to identify the residual concentrations of the dye in aqueous samples. The absorbance was measured at the maximum dye wavelength of 530 nm (BRed). For the measurements, a UV-VIS Digital Spectrophotometer, model S 104D/WPA, was used and, for the interpolation a calibration curve (with working concentration range in the Lambert-Beer region) was used.

Characterization methods

Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR/ATR spectra of the initial cellulose and of the oxidized samples were recorded on silicon single-crystal parallelepiped internal reflexion elements (IRE) (55 mm x 5 mm x 2 mm, 45° incident angle), using a Bruker Vertex 70 instrument. All the spectra were the results of 256 co-added scans at a resolution of 4 cm^{-1} .

Environmental Scanning Electron Microscopy (ESEM)

A Quanta 200 instrument was used for ESEM analyses. All the samples were fixed on copper supports by means of colloidal silver and subjected to ESEM after previous gold coating by sputtering. The coated surface of each sample was examined by using an Environmental Scanning 200 apparatus, in the high-vacuum mode, operating at 5 KV, with secondary electrons.

X-Ray Photoelectron Spectroscopy (XPS)

The compositional analysis of the studied samples was carried out by X-ray Photoelectron Spectroscopy (XPS), using a PHI-5000 Versa Probe photoelectron spectrometer (Φ ULVAC-PHI, Inc.), provided with a hemispherical energy analyzer (with a resolution of 0.85 eV binding energy adequate for organic materials). All the samples represented "tablets" of dried fibers. Monochromatic Al $K\alpha$ X-ray radiation was used as excitation source, $h\nu = 1486.7$ eV was used. The standard take-off angle used for analysis was 45°, which can produce a maximum analysis depth between 3-5 nm. Three different locations, with an area

of 1 mm × 1 mm, on each sample were used for recording the spectra. For the low-resolution survey spectra, the operating parameters were the following: 0.5 eV steps with 117.4 eV analyzer pass energy, since for the high-resolution carbon (1 s) spectra, the used parameters were changed as follows: 0.1 eV steps with 58.7 eV analyzer pass energy. The XPS data were acquired using the PHI SUMMIT XPS for Versa Probe software.

RESULTS AND DISCUSSION

Sorbent fabrication

The oxidation of cellulose fibers employing the stable nitroxyl radical TEMPO takes place at the surface level of the fiber. Therefore, the most accessible sites are those originating from the amorphous regions and/or crystalline surface fibers, as schematically represented in Figure 1.

The TEMPO-oxidized cellulose had a carboxylate content of 0.7 mmol g⁻¹, as determined by the potentiometric titration method. This value means that about 12% of C6-OH groups in the original SBS were converted to sodium C6-carboxylate groups by the TEMPO-mediated oxidation.

Characterization of the cellulose material

Fourier Transform Infrared Spectroscopy (FTIR)

The oxidation reaction of cellulose using TEMPO can be satisfactorily and readily analyzed employing FTIR. Oxidized products should exhibit changes of the absorptions in the 1600-1800 cm⁻¹ range, corresponding to the C=O stretching frequency of carboxyl groups in their acidic form. In the oxidized samples, the peak at 1640 cm⁻¹ can be attributed to carboxylate ions (COO⁻), but could also be the result of adsorbed bound water. Nevertheless, this region does not change appreciably during the oxidation process. The absorption band at 1735 cm⁻¹ increased in the

oxidized sample SBSox. The analysis of the SBSox spectrum, in the range of hydroxyl absorption (3000-3600 cm⁻¹) reveals a slightly shifted absorption of the hydroxyl maximum to short wavelengths after the oxidation process. This shift can be attributed to the changes in the ratio of different types of hydrogen bonds (Fig. 2).

The oxidized sample exhibited a slight decrease of the absorption intensity of the OH groups, in the 3250-3400 cm⁻¹ wavenumber region, which could be interpreted as a reduction of the total number of -OH groups in the resulted product. This reduction is more visible if we look at sp³ hybridized C-H stretching absorption band at 2900 cm⁻¹ in the oxidized sample, which can be explained by the great extent of -CH₂-OH conversion into COOH groups.

Environmental Scanning Electron Microscopy (ESEM)

The SBS was mildly oxidized at room temperature for 2 h, introducing a sufficiently high amount of carboxylic groups. The mildness of the protocol was assessed by analyzing the possibility of fiber destruction or degradation during the oxidation. To this end, both original and oxidized samples were subjected to ESEM analyses (Fig. 3). As a result, it was found that only minor regions in the oxidized sample presented small strips and insignificant deteriorated areas at the surface level.

XPS analyses

The XPS technique allows detecting carbon and oxygen elements on the surface of cellulose fibers. In the first set of experiments, a low-resolution XPS scan was used to determine the percentages of the C and O atoms on the cellulose fiber surface before and after TEMPO-oxidation.

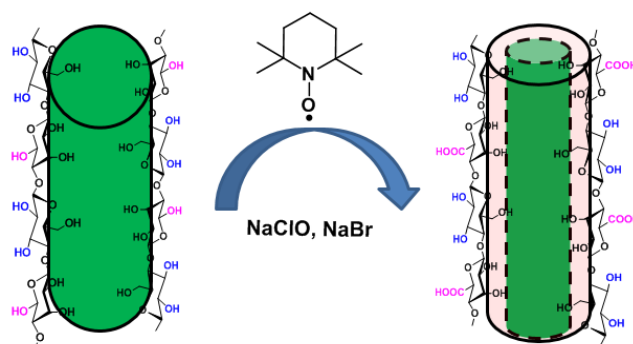


Figure 1: Schematization of cellulose surface oxidation using the TEMPO-mediated protocol

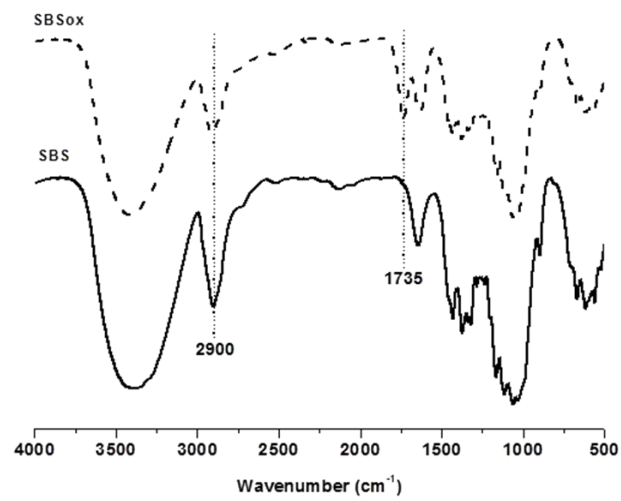


Figure 2: FTIR spectra of initial (SBS) and oxidized (SBSox) cellulosic samples

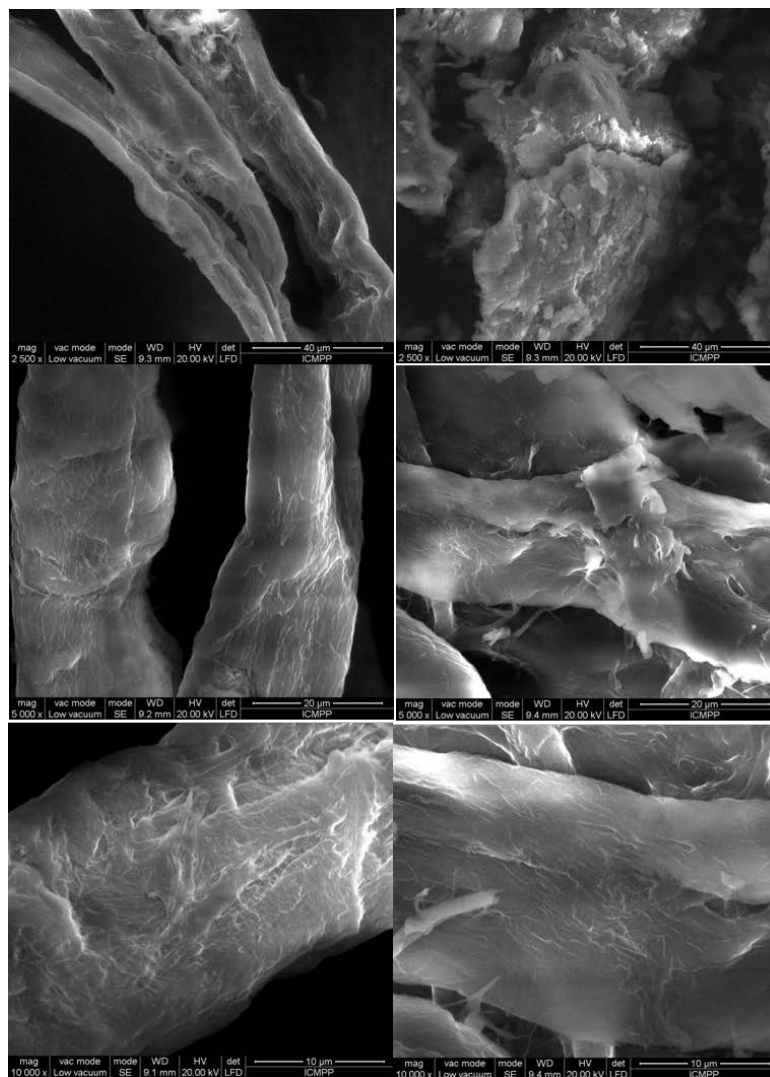


Figure 3: SEM images of SBS (left column) and SBSox (right column) samples at different magnifications

Any increase in the atomic ratio of oxygen to carbon is consistent with an initial indication of surface oxidation of the cellulose fibers. In the original sample, SBS, the O/C atomic ratio was 0.600, which increased after the oxidation to 6.24 in sample SBSox (Table 1).

More detailed information is acquired using a high-resolution scan on the C1s region. The C1s XPS spectra and deconvolution peaks of SBS and SBSox samples are presented in Figure 4. The deconvolution of the C1s peak can be made into the four sub-peaks: C1, C2, C3 and C4. The C1 peak corresponds to the unoxidized carbon, C-C, having the lowest binding energy: 284.4 eV. The C2 peak is assigned to the carbon atom linked to a single oxygen, -C-O, at 286.4 eV, the C3 peak can originate from the O-C-O bond or -C=O, at a binding energy of 287.8 eV, and the C4 sub-peak stands for the carbon atoms that are linked to a carbonyl and a non-carbonyl oxygen, O-C=O,

having the highest binding energy: 288.9 eV.⁴⁵ Cellulose, in its pure form, is a homopolysaccharide of β -D-glucopyranose units, with five carbon atoms linked to one of oxygen and one carbon linked to two oxygen atoms in each monosaccharide unit. Theoretically, only two peaks (C2 and C3) are expected in the XPS C1s spectrum of the SBS sample. However, besides these two peaks, other two peaks, corresponding to C1 and C4, are present, which could be due to a contamination of fibers and/or to a chemical change in the fiber structure.⁴⁶

The introduction of carboxyl groups in the cellulose backbone after the TEMPO-mediated reaction will increase the contribution of the C4 in the C1s spectrum. Table 1 shows that, indeed, the atomic percentage value of the C4 sub-peak in the C1s spectrum increased from 2.60 in the SBS sample to 8.22% in the oxidized (SBSox) sample.

Table 1
XPS analysis of the SBS and SBSox samples

Sample	Surface composition			Binding energy (eV)			
	O	C	O/C	284.8	286.4	287.8	288.9
				C1 (at.%)	C2 (at.%)	C3 (at.%)	C4 (at.%)
SBS	37.9	63.1	0.600	25.61	51.34	20.45	2.60
SBSox	39.2	60.6	0.647	25.22	50.10	16.46	8.22

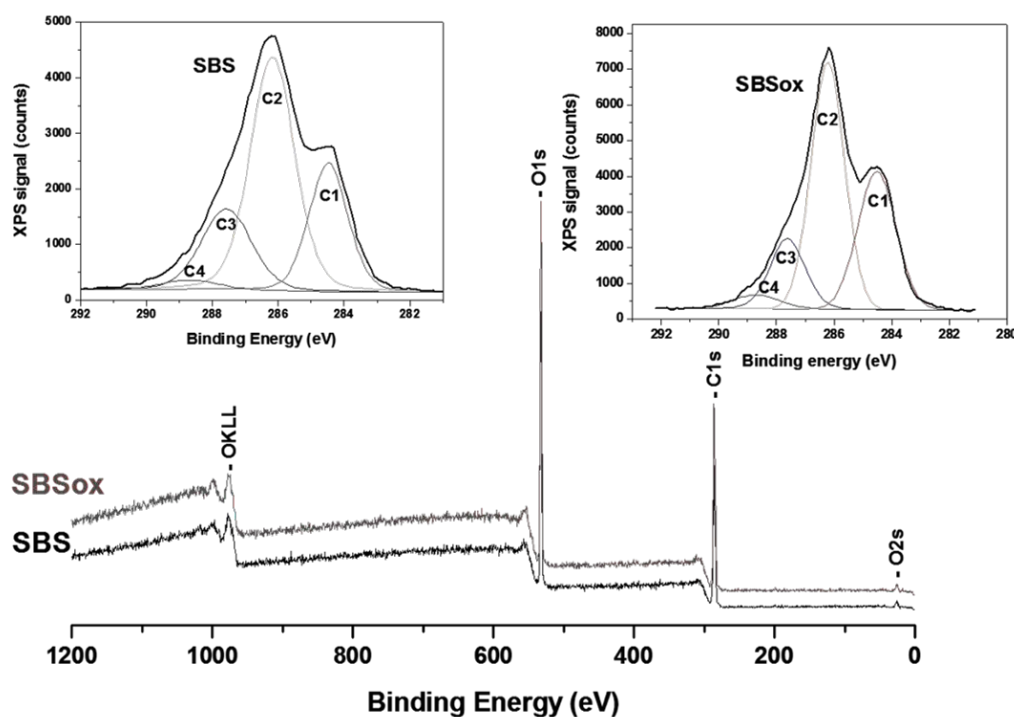


Figure 4: XPS survey spectra and scan of C1s region of SBS and SBSox

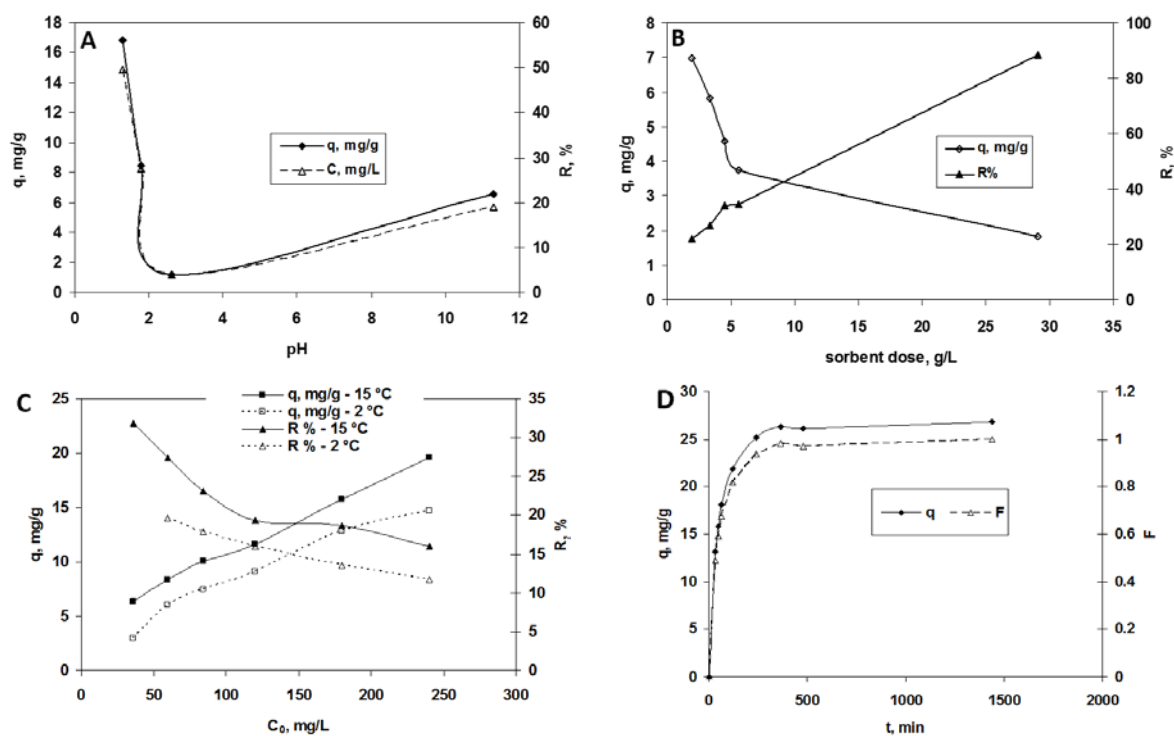


Figure 5: Effects of (A) pH at $C_0 = 60$ mg/L, sorbent dose = 2 g/L, 24 h, $T = 15$ °C; (B) sorbent dose at $C_0 = 60$ mg/L, contact time of 24 h, pH = 1.3; (C) initial dye concentration and temperature at contact time of 24 h, pH = 1.3, sorbent dose of 2 g/L; and (D) contact time phases at pH = 1.3, $T = 15$ °C, sorbent dose of 2 g/L, $C = 55.5$ mg/L, on the sorption of BRed dye onto SBSOx sorbent

Adsorption of Brilliant Red HE-3B reactive dye on SBSOx sorbent

Effect of solution pH

The two phases of the sorption system were influenced by the pH: the behavior of the functional groups from the dye structure and their total charge, as a consequence of the presence of different functional groups.

The fluctuation of the dye uptake (q , mg/g) and residual dye concentration (C , mg/L) as a function of the initial solution pH (Fig. 5A) indicates that there could be better sorption of the anionic dye from an acidic medium/environment at a pH around 1.3. This could be the result of the availability of dye exchange positions ($-\text{SO}_3\text{H}$) and also of the fluctuation of the sorbent surface charge as a function of the pH of the solution. Working with sorbents in an acidic cellulosic environment requires the consideration of certain features.^{47,48}

Thus, if it is expected to obtain a specific working pH, it should be pointed out that many inorganic acids present in relatively low concentrations can lead to interfibrillar swelling of the cellulose matrix. Moreover, in some cases,

it can even cause the dissolution of the cellulose and also its esterification. In this situation, hydrochloric acid is used to obtain the necessary acidity of the environment. It is known that at low concentrations, hydrochloric acid does not produce the swelling of cellulose more than in the case of using water. When using a NaOH solution, which changes the environmental pH to around 12, some effects on the cellulose matrix are observed: swelling with breaking intermolecular hydrogen bonds. This can also go up to the point where it changes the crystal network. In this case, a competition for the active centers occurs. This competition takes place between the dye molecules and the hydrated sodium ions. It is clear that this will not meet the parameters required for obtaining a high sorption capacity.

Effect of sorbent dose

Since the aim was to determine the proper dose of the wet cellulose, different amounts of material entered into contact with 25 mL of solutions which were containing certain concentrations of tested dyes. This contact lasted for 24 hours, at the established initial pH (1.3).

Figure 5B clearly indicates an accrument of the dose of the wet cellulose from 1.9 to 29.1 g/L. This leads to an increase of the percentage of dye removal from 22.01% to 88.27%. At the same time, it decreases the amount of reactive dye retained per unit weight of the sorbent from 6.98 to 1.82 mg/g. This behavior can be explained by the reduction of dispersion inside the solid sorbent mass due to the dye steric effect and better retention of the chemical compound only at the external surface of the sorbent towards the inside of the solid structure.

Effect of temperature

The observation of the impact of the temperature on the evolution of the dye sorption process selected for the tested wet cellulose is narrowed by the behavior of cellulose under the working conditions: strong pH acids (1.3), contact time of 24 hours and the specified temperature range. The effect of temperature on the sorption process is illustrated in Figure 5C. Between 2 and 15 °C, it can be noticed that the quantity of retained dye from the solutions with an initial pH of 1.3 and initial dye concentration of 60 mg/L rises with an increase in temperature (the removal percentage attains the value of 31.84%). This behavior suggests two things: on the one hand, it indicates that the sorption of dye onto wet cellulose can be an endothermic process and, on the other hand, it points out that the increasing temperature favors the diffusion of the dye molecules at the external surface of the sorbent. It is important to point out that temperatures exceeding 20 °C (in strongly acidic medium) can determine a change in the structure of the adsorbent-cellulose complex. This is a consequence of the thermodynamics of the dye-binding process.

Effect of dye concentration

The sorption capacity of wet cellulose for reactive dye was determined in solutions with an initial pH of 1.3 and with various dye concentrations. The results presented in Figure 5C point out that the amount of dye sorbed rose from 7.07 up to 19.6 mg/g at 15 °C temperature, and from 2.96 to 14.67 mg/L at 2 °C, respectively, with increasing the initial concentration of the reactive dye from 36 to 240 mg/L. Simultaneously, the percent of dye removal decreased from 31.84 to 16.04% at 15 °C and from 13.26 to 11.72% at 2 °C.

The maximum amount of dye retained during the sorption process is around 19.6 mg dye/g cellulose; this relatively low value may be attributed to the large molecular size of the dye, which inhibits sorption on the external surface of the cellulose sorbent. However, the sorption capacity of SBSox at a temperature of 15 °C is comparable with the values reported in the literature for some other synthetic or low-cost cellulosic sorbents and dyes.^{1,35-41,44}

Effect of contact time

The influence of contact time on the adsorption of Brilliant Red HE-3B reactive dye onto the SBSox sorbent was evaluated and the results are presented in Figure 5D. The experimental data point out that the removal rate of the reactive dye by the cellulose adsorbent is relatively high in the first 30 minutes of the contact period ($t_{50\%}$ values correspond to about 35 min at the initial dye concentration of 55.5 mg/L), then increases slowly up to 400 minutes and after that changes insignificantly. This shows that equilibrium is reached quickly, therefore, the optimal contact time between phases can be considered to be within 2-3 hours for the following studies.

Potential valorization of the dye loaded sorbent

An interesting direction to further utilize the loaded sorbents would be by introducing the colored pulp in the papermaking process. The samples of paper presented in Figure 6 were obtained in the laboratory, on a Rapid-Köthen trainer/STANDARD TAPPI T-205, using cellulose paste of 0.5% consistency, which included colored cellulose as well (Fig. 6).



Figure 6: Paper sample obtained from cellulose sorbent (SBSox) loaded with red dye

CONCLUSION

The sorption capacity of never-dried oxidized cellulose was evaluated as a function of some physical parameters, such as initial solution pH, dye concentration, sorbent dose, temperature and contact time. The highest sorption capacity of the dye present in concentrations of 36-240 mg/L was obtained under the following conditions: solution pH = 1.3, sorbent dose of 2 g/L, 15-20 °C temperature, and contact time of phases up to 400 min. The results could be considered a starting point for further studies regarding the equilibrium, kinetics and thermodynamics of Brilliant Red HE-3B dye sorption onto oxidized cellulose materials. These will be necessary to clarify the sorption mechanism and the applicability of this cellulose material as sorbent for removing other textile dyes from colored wastewaters.

ACKNOWLEDGEMENTS: This work was supported by a grant of the Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI, project number PN-III-P4-ID-PCE-2016-0349, acronym ERAW.

REFERENCES

- V. Da Silva, J. B. Lopez-Sotelo, A. Correa-Guimaraes, S. Hernandez-Navarro, M. Sanchez-Bascones *et al.*, *Cellulose Chem. Technol.*, **51**, 127 (2017).
- M. N. Rashed, in "Organic Pollutants – Monitoring, Risk and Treatment", edited by M. Nageeb-Rashed, INTECH Publisher, 2013, pp. 167-194.
- A. Abbas, M. A. Hussain, M. Sher, N. S. Abbas and M. Ali, *Cellulose Chem. Technol.*, **51**, 167 (2017).
- G. Crini, *Prog. Polym. Sci.*, **30**, 38 (2005).
- P. Wu and Z. M. Liu, *Cellulose Chem. Technol.*, **51**, 521 (2017).
- J. Febrianto, A. Kosaisih, J. Sunarso, Y. H. Ju, N. Indraswati *et al.*, *J. Hazard. Mater.*, **162**, 616 (2009).
- L. Huang, C. Xiao and B. Chen, *J. Hazard. Mater.*, **192**, 832 (2011).
- W. S. Ngah, L. C. Teong and M. A. K. Hanafiah, *Carbohydr. Polym.*, **83**, 1446 (2011).
- D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem. Int. Ed.*, **44**, 3358 (2005).
- G. J. Dias, P. V. Peplow and F. Teixeira, *J. Mater. Sci. Mater. Med.*, **14**, 739 (2003).
- J. E. Rodriguez-Chanfrau, M. Luiz dos Santos, C. dos Santos Riccardi, G. Molina de Olyveira, M. Hernández-Escalona *et al.*, *Cellulose Chem. Technol.*, **51**, 673 (2017).
- D. M. Wiseman, L. Saferstein and S. Wolf, US Patent, 6500777 B1, 2002.
- J. Milanović, K. Mihajlovski, T. Nikolić and M. Kostić, *Cellulose Chem. Technol.*, **50**, 905 (2016).
- B. Jin and W. T. Wu, WO Patent, 2005020997 A1, 2005.
- S. Coseri, *Biotechnol. Adv.*, **35**, 251 (2017).
- S. Coseri, G. Biliuta, B. C. Simionescu, K. Stana-Kleinschek, V. Ribitsch *et al.*, *Carbohydr. Polym.*, **93**, 207 (2013).
- A. E. J. de Nooy, A. C. Besemer and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, **113**, 165 (1994).
- N. Masruchin, B. D. Park and V. Causin, *Cellulose Chem. Technol.*, **51**, 497 (2017).
- S. Wang, T. Huang, C. Lai, T. Xi, S. Liao *et al.*, *Cellulose Chem. Technol.*, **50**, 853 (2016).
- S. Coseri, *Eur. J. Org. Chem.*, **2007**, 1725 (2007).
- L. Melone, P. Tarsini, G. Candiani and C. Punta, *RSC Adv.*, **6**, 21749 (2016).
- M. Petroselli, L. Melone, M. Cametti and C. Punta, *Chem.-Eur. J.*, **23**, 10616 (2017).
- S. Coseri, *Cat. Rev. Sci. Eng.*, **51**, 218 (2009).
- F. Recupero and C. Punta, *Chem. Rev.*, **107**, 3800 (2007).
- K. Kasperczyk, B. Orlińska and J. Zawadiak, *Cent. Eur. J. Chem.*, **12**, 1176 (2014).
- S. Coseri, G. Biliuta, L. Fras Zemljič, J. Stevanic Srndovic, P. T. Larsson *et al.*, *RSC Adv.*, **5**, 85889 (2015).
- G. Biliuta, L. Fras, S. Strnad, V. Harabagiu and S. Coseri, *J. Polym. Sci. A. Polym. Chem.*, **48**, 4790 (2010).
- G. Biliuta, L. Fras, M. Drobot, Z. Persin, T. Kreze *et al.*, *Carbohydr. Polym.*, **91**, 502 (2013).
- S. Coseri and G. Biliuta, *Carbohydr. Polym.*, **90**, 1415 (2012).
- M. Spanu, N. dos Santos, N. Le Moigne and P. Navard, *Cellulose*, **18**, 247 (2011).
- W. Tsuji, T. Nakao, A. Hirai and F. Horii, *J. Appl. Polym. Sci.*, **45**, 299 (1992).
- R. N. Ibbett, S. Kaenthong, D. A. S. Phillips and M. A. Wilding, *J. Mater. Sci.*, **42**, 6809 (2007).
- R. M. Bozlur, S. Shibata, C. F. Diba and M. Uono, *IACSIT Int. J. Eng. Technol.*, **2**, 468 (2012).
- D. K. Mahmoud, M. A. M. Salleh and W. A. W. A. Karim, *J. Purity Util. React. Environ.*, **1**, 451 (2012).
- M. Hubbe, K. Beck, W. O'neal and Y. Sharma, *BioResources*, **7**, 2592 (2012).
- F. S. Abbas, *Adv. Environ. Biol.*, **7**, 1019 (2013).
- Y. Akama, S. Suzuki and Y. Manobe, *Cellulose Chem. Technol.*, **50**, 147 (2016).
- S. Dawood and T. K. Sen, *J. Chem. Proc. Eng.*, **1**, 1 (2014).
- D. Suteu, G. Biliuta, L. Rusu, S. Coseri and G. Nacu, *Environ. Eng. Manag. J.*, **14**, 525 (2015).
- V. V. Panic, S. I. Seslija, A. R. Nestic and S. J. Velickovic, *Hem. Inf.*, **67**, 881 (2013).
- M. N. Almaghrabi, S. Matar and M. A. Hashem, *Sci. Res. J.*, **4**, 55 (2015).
- M. Wawrzekiewicz and Z. Hubicki, *Cent. Eur. J. Chem.*, **9**, 867 (2011).
- M. Greluk and Z. Hubicki, *Chem. Eng. J.*, **162**, 919 (2010).

⁴⁴ B. Ramaraj, P. M. K. Reddy and C. Subrahmanyam, *Environ. Prog. Sustain. Energ.*, **33**, 38 (2013).

⁴⁵ X. Hua, S. Kaliaguine, B. V. Kokta and A. Adnot, *Wood Sci. Technol.*, **27**, 449 (1993).

⁴⁶ C. M. G. Carlsson and G. Strom, *Langmuir*, **7**, 2492 (1991).

⁴⁷ T. Malutan and V. I. Popa, in “Chimia celulozei” [Cellulose Chemistry], Politehniun, Iasi, 2008.

⁴⁸ D. W. O’Connell, C. Birkinshaw and T. F. O’Dwyer, *Bioresour. Technol.*, **99**, 6709 (2008).