**CelluPhot**: Hybrid Cellulose-Bismuth Oxybromide Membrane for Pollutant Removal

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**ABSTRACT**: The simultaneous removal of organic and inorganic pollutants from wastewater is a complex challenge and requires usually several sequential processes. Here, we demonstrate the fabrication of a hybrid material that can fulfill both tasks: i) the adsorption of metal ions due to the negative surface charge, and ii) photocatalytic decomposition of organic compounds. The bio-inorganic hybrid membrane consists of cellulose fibers to ensure mechanical stability and of BiO\textsubscript{3}Br\textsubscript{2}/BiOBr nanosheets. The composite is synthesized at low temperature of 115 °C directly on the cellulose membrane (CM) in order to maintain the carboxylic and hydroxyl groups on the surface that are responsible for the adsorption of metal ions. The composite can adsorb both Co(II) and Ni(II) ions and the kinetic study confirmed a good agreement of experimental data with the pseudo-second-order equation kinetic model. CM/BiO\textsubscript{3}Br\textsubscript{2}/BiOBr showed higher affinity to Co(II) ions than to Ni(II) ions from diluted aqueous solutions. The bio-inorganic composite demonstrates a synergistic effect in the photocatalytic degradation of rhodamine B by exceeding the removal efficiency of single components. The fabrication of the biologic-inorganic interface was confirmed by various analytical techniques including SEM, STEM EDX mapping, XRD, and XPS. The presented approach for controlled formation of the bio-inorganic interface between natural material (cellulose) and nanooscopic inorganic materials of tailored morphology (Bi-O-Br system) enables the significant enhancement of materials functionality.

**INTRODUCTION**

The removal of both organic and inorganic pollutants from wastewater is one of the critical aspects that have to be considered for the human health. Organic dyes and pigments are common water pollutants, which are produced in large scale by textile, dyeing, paper and pulp, cosmetic, food, and paint industries.\(^1\)–\(^3\) In addition, many dyes are reluctant to biodegradation and could be harmful to human health due to their toxic character. In some cases, they have even carcinogenic character.\(^4\)–\(^5\) An example is rhodamine B (RhB), which is a typical fluorescent (xanthene) dye and is highly soluble in water. The carcinogenicity, toxicity including neurotoxicity toward humans and animals have been proven experimentally.\(^6\)–\(^9\) Conventional methods of removal of dyes include precipitation/separation of pollutants, coagulation by a chemical agent, ozone oxidation, or hypochlorite oxidation. For the latter method, the formation of halogenated organic products is still a challenging issue. In comparison to known techniques, photocatalytic decomposition of dyes as pollutant on semiconducting materials is expected to be a prospective alternative.\(^10\)

The remediation of complex metal-ion composition in industrial wastes can be achieved by variety of methods including precipitation, chemisorption, membrane filtration, but this methodology requires aggressive chemicals and is inevitably connected to the production of solid waste, which cannot be valorized into raw materials for further application. Alternatively, metal ions can be recovered at near-neutral pH values on membranes that can adsorb the metal ions by coulombic attraction, but short life cycle of the membranes, poor functionality in aggressive manufacturing condition and problematic recyclability remain limiting criteria for their extensive technical applications. Among promising membrane materials, cellulose has been identified as a sustainable candidate, because it offers several advantages. Cellulose as a biomaterial is one of the most naturally abundant biodegradable polymers.\(^11\)–\(^12\) It consists of polysaccharides with high amount of glucose and hydroxyl groups.\(^11\)–\(^13\) Cellulose-based materials are characterized by renewability, biodegradability, biocompatibility,\(^12\) and insolubility,\(^14\) and can be tailored with respect to mechanical stability, morphology and controlled growth of nanostructures.\(^15\) Hydroxyl and carboxylic groups of cellulose can effectively bind metal cations by means of chemical, coordination or physicochemical methods and remove them from liquid media, such as wastewater.

The integration of biobased materials, such as cellulose, lignin or chitosan, with binary oxides has led to the development of sorbents that are characterized by ameliorated kinetics.\(^16\)–\(^17\) For instance, bio-inorganic composites of
lignin are highly efficient as sorbents for removal of metal ions.\textsuperscript{18} In the case of cellulose as sorbent material, hybrids have been prepared including metal-organic frameworks (MOFs)\textsuperscript{19} and metal oxide particles.\textsuperscript{20,21}

Mixed-anion bismuth compounds BiOX (X = Cl, Br, I) and Bi$_2$O$_3$NCN belong to the category of two-dimensional layered semiconductor photocatalysts with [Bi$_2$O$_2$]$^+$ slabs interleaved by double slabs of the second counter-anion X.\textsuperscript{5,22-30} Besides their intriguing crystal chemistry, this class of compounds exhibits potential photocatalytic activity due to their semiconducting properties.\textsuperscript{22-24,31} A representative for a p-type semiconductor among this class of compounds is BiOBr.\textsuperscript{32} The latter displays a high chemical stability under light irradiation and makes it applicable for different photochemical reactions.\textsuperscript{26,30-34} Due to its lamellar structure, BiOBr belongs to group of low-dimensional nanostructures, which are of high interest for photocatalytic applications because of more efficient charge carrier separation in comparison to bulk materials.\textsuperscript{35-40} Since BiOBr can harvest more light than bismuth oxychlorides and oxyiodates, originating from the narrower band gap of 2.7–2.9 eV, it exhibits relatively high photocatalytic activity.\textsuperscript{31,32,41} Despite the abovementioned advantage, pristine BiOBr has a limited practical application as photocatalyst due to the high recombination rate of photogenerated electron-hole pairs and the low light absorption efficiency.

A general strategy to improve charge carrier separation is the formation of semiconductor heterostructures. Several different ternary bismuth oxybromides are known from the literature, such as Bi$_2$O$_2$Br$_2$, Bi$_2$O$_3$Br, Bi$_2$O$_3$Br$_2$, Bi$_3$O$_3$Br$_6$, and Bi$_2$O$_2$Br$_3$.\textsuperscript{23,24,42} Su et al. synthesized Bi$_2$O$_3$Br$_2$/BiOBr heterojunctions with a plate structure by an one-pot hydrothermal method, whereas Panje et al. synthesized Bi$_2$O$_2$Br$_3$/BiOBr flower-like nanostructures. Increasing the bismuth content in the Bi-O-Br system is known to result in a negative shift of the conduction band. This results also in a reduction of the band gap and improves consequently the light absorption efficiency.\textsuperscript{42,44}

In the present work, we report on the fabrication of a bio-inorganic hybrid material that combines photocatalytic properties while being simultaneously a sorbent material. The developed material was characterized by means of STEM EDX, XPS, SEM, FT-IR, BET surface analysis and X-ray diffraction. The controlled growth of Bi$_2$O$_3$Br$_2$/BiOBr on a cellulose membrane (CM) enables a thin coating on the mechanically-stable membrane and shows faster degradation of RhB than on pure Bi$_2$O$_3$Br$_2$/BiOBr photocatalyst. The removal of inorganic pollutants, such as Co(II) and Ni(II), on the CM/Bi$_2$O$_3$Br$_2$/BiOBr composite was investigated with respect to its kinetic parameters.

**EXPERIMENTAL SECTION**

**Materials.** Bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), 98%, Alfa Aesar), potassium bromide (KBr, ACS), sodium hydroxide (NaOH, 98-100.5%, Honeywell, USA, long pine fibers from MetsåBoard and commercial grade microfibrillated cellulose (MFC) Exilva 01-V supplied as 10 wt% suspensions from Borregaard, Norway, were used for the production of the membranes. Pine fibers had a diameter of 25-30 mm and the MFC had diameters within the range of 10-100 nm.

**Synthesis of cellulose membrane (CM).** Cellulose membrane was produced in continuous mode using Experimental Paper Machine (XPM) pilot at MoRe Research, Örnsköldsvik, Sweden. Hybrid suspension of microfibrillated cellulose with long pine fibers (softwood pulp) was prepared in the middle chest and then pumped into machine headbox to produce composite membranes. Machine speed was same (1.4 m/min) and density of fabricated composite membranes was targeted to 60 g/m$^2$. The composite membranes of 5 x 1 meters in dimensions were prepared using the XPM machine.

**Synthesis of CM/Bi$_2$O$_3$Br$_2$/BiOBr.** 20.6 mmol of Bi(NO$_3$)$_3$ and 16.8 mmol of KBr were dissolved in 10 ml of DI water, and then 1 M of NaOH was added dropwise to the solution until pH 13. The resulting solution was transferred into a 20 ml Teflon-lined stainless-steel autoclave filled up to 80% of the total volume followed by a hydrothermal treatment at 115 $^\circ$C for 20 h. After the reaction, the reactor was cooled to room temperature to collect the precipitate and washed with DI water until pH 7 was reached.

**Synthesis of CM/Bi$_2$O$_3$Br$_2$/BiOBr.** 20.6 mM of Bi(NO$_3$)$_3$, H$_2$O and 16.8 mM of KBr were dissolved in 10 ml of DI water, and then 1 M of NaOH was added dropwise to the solution to pH 13. Fragment (5 x 3 cm) of cellulose membrane was added to the solution. The latter was transferred into a 20 ml Teflon-lined stainless-steel autoclave filled up to 80% of the total volume followed by a hydrothermal treatment at 115 $^\circ$C for 20h. After the reaction, the reactor was cooled to room temperature to collect the precipitate and washed with DI water until pH 7 was observed.

**Fourier transform infrared (FT-IR) spectroscopy and powder X-ray diffraction (PXRD).** FT-IR spectra were carried out using a Varian 610-IR FT-IR spectrometer. The X-ray diffraction (XRD) pattern was determined on a Panalytical XPert Alpha1 using Cu K$_\alpha$ ($\lambda=1.5406$ Å) radiation in the 20 range from 10 to 80$^\circ$.

**Electron microscopy.** The morphology was evaluated using electron diffraction and high-resolution transmission electron microscopy on a JEOL 2100F operated at 200 kV, while elemental information was acquired using energy-dispersive X-ray spectroscopy (EDX) on an aberration-corrected Themis Z (Thermo Fischer) operated at 300 kV. The topography was evaluated using scanning electron microscopy (SEM) JEOL JSM-7000F. Thermal stability was evaluated using thermogravimetric analysis (TGA) in a Perkin Elmer TGA 7 thermobalance.

**X-ray photoelectron spectroscopy (XPS).** Measurements were performed on a Theta Probe™ (Thermo Fisher Scientific) System. The X-ray source was a monochromated Al K$_\alpha$ source at 1386.6 eV. The spectrometer was calibrated to 368.21 eV binding energy (BE) of the Ag 3d$_{5/2}$ line for metallic silver and the linearity was corrected to BE of 932.62 eV for the Cu 2p$_{3/2}$ line and 83.96 eV for the Au 4f$_{7/2}$ line. Charge compensation was done using a flood gun for low-energy electrons and argon ions at 1 eV. The binding energy scale was calibrated using the C 1s component at 285.0 eV (typical of C–C).

**Specific surface area and pore size distributions.** Specific surface area and pore volume were determined from nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2020 sorption analyzer). The samples were degassed at 80°C before the measurements. The pore size distributions (PSD) were calculated using Barret-Joyner-Halenda (BJH) method.

**Point of zero charge determination.** In order to measure pH$_{pzc}$ values in sequential order of co-precipitation process
after each surface modification, for this process pH drift method was applied. pH drift was chosen over other conventional methods, such as titrations, because it is less time consuming, results can be gotten in few steps using regular laboratory apparatuses which indeed lower the overall expenditure of the experiment and the result obtained from this method is in line with the ones obtained from other applied methods. According to this method, solutions of 0.01 mol L\(^{-1}\) NaCl in 10 ml flask were adjusted to pH values of 2 to 10 (pH\(_{\text{initial}}\)) using 0.05 mol L\(^{-1}\) NaOH and 0.05 mol L\(^{-1}\) HCl. After which, 5 mg of CM/Bl\(_2\)O\(_3\)Br/BlOBr was added to the flask and shaken at 180 rpm for 24 h. Then, the final pH (pH\(_f\)) of the samples were measured using a pH meter and plotted against initial pH. The point of intersection (point zero) of the resulting plot with the line passing origin (pH\(_e\)-pH\(_{\text{initial}}\)) gives pH\(_{\text{Pzc}}\).  

**Photocatalytic dye degradation.** A RhB solution of 8 mg·L\(^{-1}\) in DI water and 0.013 M of hydrogen peroxide was prepared. For the photocatalytic tests, the CM/Bl\(_2\)O\(_3\)Br/BlOBr hybrid membrane was added to the solution and this mixture was irradiated with blue light 405 nm (20 W) light source. Subsequently, another photocatalytic test was performed with the mass of the inorganic semiconductor BlOBr:BiOBr, which was determined to be 17 mg from the thermal analysis (vide infra). The photocatalytic tests were carried out in darkness in order to avoid any other irradiation on the sample, therefore, only the light from the lamp could reach the sample. At 20 minutes intervals, 5 ml aliquots were taken from the solution for analysis. The absorption of these aliquots was taken at different intervals using a spectrometer. The absorbance value obtained were then converted to mg·L\(^{-1}\), and the observed concentrations were plotted against time to give the degradation rate.

**Batch adsorption of Co(II) and Ni(II) ions.** Cellulose membrane (CM) and CM/Bl\(_2\)O\(_3\)Br/BlOBr materials were tested and compared as feasible sorbents for heavy metal ions removal from aqueous solutions. For this study, we have decided to investigate the adsorption ability of our material towards Co(II) and Ni(II) ions, due to their hazardous nature for humans and environment. The adsorption kinetics for solutions of Co(II) and Ni(II) were measured using a static method. The batch adsorption experiments were performed by shaking 0.03 g of the cellulose membrane or modified cellulose membrane in flasks containing 25 ml solutions of Co(II) or Ni(II) with the concentration of 20 mg·L\(^{-1}\) and 50 mg·L\(^{-1}\). The flasks were shaken in a Heidolph Unimax 1010 incubating shaker (Germany) for 5, 24, 48, 72 and 94 h at 180 rpm and 22 °C. After that, the solutions were separated from the sorbents by filtration and the final concentration of metal ions was determined photometrically. The absorbance was measured using a UV-3100PC spectrophotometer (VWR, USA), by complexing Co(II) ions with 4-(2′-pyridylazo)resorcinol (at the wavelength of 500 nm) and Ni(II) ions with dimethylglyoxime (at 470 nm). To obtain high accuracy of the measurements, each sample was determined three times and the obtained results were taken as mean value. The adsorption capacity (q\(_e\)) for each sorbent was calculated according to the following equation:

\[
q_e = \frac{(c_0 - c_f)V}{m}
\]

where \(c_0\) and \(c_f\) are the initial and equilibrium concentration of metal ions respectively (mg·L\(^{-1}\)), \(V\) is the volume of the sample (L) and \(m\) is the sorbent mass (g).

The removal efficiency \((R)\) was calculated using the formula:

\[
R = \left(\frac{c_0 - c_e}{c_0}\right) \cdot 100\%
\]

where \(c_0\) and \(c_e\) are the initial and equilibrium concentration of metal ions respectively (mg·L\(^{-1}\)). The pseudo-first and pseudo-second order equations were applied to kinetics analysis of Co(II) and Ni(II) ions adsorption on the membranes. The pseudo-first-order equation:

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303t}
\]

The pseudo-second-order equation:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where, \(q_t\) and \(q_e\) are the amounts of metal adsorbed (mg·g\(^{-1}\)) at equilibrium time and at any instant of time \(t\). \(k_1\) (1·min\(^{-1}\)) is the rate constant of the pseudo-first order adsorption and \(K_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) is the pseudo-second order rate constant.

**RESULTS AND DISCUSSION**

**Structural characterization.** The identification and purity of inorganic component, i.e. the synthesis with no inserted CM substrate in the autoclave, was performed by means of XRD (Figure 1). The XRD patterns show presence of two ternary phases Bl\(_2\)O\(_3\)Br\(_2\) and BlOBr in the synthesized material at described reaction conditions. Obtained nanosheets differ from previously reported where photocatalytic activity has been evaluated for Bl\(_2\)O\(_3\)Br\(_2\) nanostructures. We did not attempt to obtain one of these phases as single-phase materials by increasing the reaction temperature due to possible changes in functionalization character of cellulose carrier.

![Figure 1. Comparison of experimental and simulated PXRD patterns of synthesized photocatalyst without nanocellulose. The simulated patterns were indexed for Bl\(_2\)O\(_3\)Br\(_2\) by using the crystallographic data from JCPDS-01-085-0862 and JCPDS-37-0699.](image-url)
The original CM consists of intergrown fibers that build up the macroscopic object (Figure 2a and b). Upon hydrothermal growth of the Bi$_4$O$_5$Br$_2$/BiOBr photocatalyst on the CM, changes on surface of the CM are observed (Figure 2c). The collected SEM micrograph at higher magnification shows the bio-inorganic interface, i.e. successful functionalization of the CM with the photocatalyst in the form of two-dimensional nanostructure which are stacked to each other (Figure 2d). After hydrothermal growth, the CM/Bi$_4$O$_5$Br$_2$/BiOBr sample demonstrates mechanical stability and was used for photocatalytic characterization and for adsorption processes.

The resulting maps were additionally blurred along their spatial dimensions. Although this results in a strong degradation of the energy and spatial resolution, the Bi and Br signals are clearly localized to the agglomerate, with a strong Bi contribution along the cellulose wires. In the final panel, the average EDX spectrum from each pixel within the agglomerate region is presented along with elemental labels. The peaks corresponding to O, Bi, and Br are clearly distinguishable. The C peaks originate from the support film, the Cu peaks arise from the use of a copper TEM grid, and Si is an impurity introduced during the preparation of the TEM sample for analysis. The exceedingly low count rate is highlighted by these very low averages values.

The surface composition of the CM/Bi$_4$O$_5$Br$_2$/BiOBr sample was determined by the XPS technique (Figure 4). In the XPS C 1s spectrum four components can be distinguished at 285.0 eV (C-C), 286.8 eV (C-OH), 288.2 eV (O-C=O and C=O) and 289.5 eV (O-C=O). Most intensive signal corresponds to C-O and O-C-O from the glucose units of cellulose, and the other states probably forming as a side product or contaminant. This proves that the synthetic conditions at relatively low temperature enables to maintain the carboxylic groups of cellulose and consequently its surface functionality (vide infra). Analysis of Bi 4f shows presence of three different states of Bi: two of them are related to bismuth oxybromides (Bi$_4$O$_5$Br$_2$/BiOBr) and additional Bi$^{3+}$ states on the CM/Bi$_4$O$_5$Br$_2$/BiOBr surface. Obtained results are in a good
agreement with the XRD analysis, where the presence of Bi$_4$O$_5$Br$_2$ and BiOBr phases has been confirmed. Bi$_4$O$_5$Br$_2$ is manifested by the doublet at 158.7 eV (4f$_{5/2}$) and 164.1 eV (4f$_{7/2}$), whereas BiOBr by the photoemission at 159.5 eV (4f$_{7/2}$) and 164.9 eV (4f$_{5/2}$). The difference in binding energies of Bi 4f$_{7/2}$ peaks for both phases calculated to be 0.8 eV clearly confirms various chemical environments of Bi$^{4+}$. Furthermore, in the measured sample additional Bi 4f components (at 161.0 eV – 4f$_{7/2}$ and 166.2 eV – 4f$_{5/2}$) are observed. So high values of binding energy suggest the existence of Bi in pentavalent form within the surface region, which shows lower kinetic energy of emitted photoelectrons compared to Bi$^{3+}$ due to larger Coulomb attraction.$^{59,60}$

**Figure 4.** XP spectra of CM/Bi$_4$O$_5$Br$_2$/BiOBr membrane.

FT-IR analysis was performed to identify the functional groups of the CM/Bi$_4$O$_5$Br$_2$/BiOBr composites (Figure 5). A broad band in the range of 3666–3000 cm$^{-1}$ corresponds to the stretching vibrations of hydroxyl groups (O–H), whereas the band at 2896 cm$^{-1}$ is associated to C–H stretching.$^{14}$ The absorption band at 1643 cm$^{-1}$ corresponds to the O–H bending of adsorbed water in cellulose.$^{61}$ The bands at 1428 and 1317 cm$^{-1}$ were attributed to CH$_2$ wagging and CH$_2$ symmetric bending respectively, in the cellulose membrane molecular structure.$^{62}$ The band at 1159 cm$^{-1}$ is related to C–O anti-symmetric stretching and the sharp band at 1027 cm$^{-1}$ corresponds to C–O and C–C stretching. The absorption band at 892 cm$^{-1}$ is known for C–O–C stretching at β-linked glucose of cellulose.$^{63}$ The amount of the photocatalyst on the CM surface was determined by thermal analysis (Figure 6). The TG curve of CM/Bi$_4$O$_5$Br$_2$/BiOBr was collected in the temperature range from 100–700 °C. The weight loss above 100°C is connected to evaporation of adsorbed water and the subsequent weight loss starting 370 °C corresponds to the decomposition of cellulose.$^{64}$

**Figure 5.** FTIR spectrum of CM and CM/Bi$_4$O$_5$Br$_2$/BiOBr.

**Figure 6.** TGA curve of CM/Bi$_4$O$_5$Br$_2$/BiOBr

BET surface area was found to be 0.9 m$^2$·g$^{-1}$ for unmodified membrane with slightly increasing for cellulose membrane with immobilized catalyst to 1.8 m$^2$·g$^{-1}$. Since the surface charge for given pH range is a decisive parameter for potential sorbent capacity, the pH drift method was applied for the CM/Bi$_4$O$_5$Br$_2$/BiOBr composite. In this method, samples were dispersed in low ionic strength aqueous media and after equilibration, the drift in pH values were recorded in order to calculate the pH$_{PZC}$. Figure 7 illustrates the obtained curve for CM/Bi$_4$O$_5$Br$_2$/BiOBr with a pH$_{PZC}$ value of 3.9. This indicates that above this pH value, the material is suitable for adsorption of metal ions; even upon modification with the photocatalyst for dye degradation.
Dual functionality for removal of inorganic and organic pollutants.  

Photocatalytic degradation of RhB. Figure 8 depicts the results of photocatalytic degradation of RhB as a function of time under illumination with a 405 nm (20 W) lamp. The amount of the photocatalyst, being equal 17 mg (red curve), was determined by thermogravimetric analysis to ensure equal parameters for comparison. Consequently, the decay of the dye concentration could be improved if higher catalyst loading, i.e. higher surface area of the stand-alone CM/Bi$_2$O$_3$Br$_2$/BiOBr composite, would be used. The blue curve represents the baseline for the photocatalytic degradation and was recorded without the presence of the membranes. The pure cellulose membrane slightly decreases the concentration of the dye in solution, which is not an unexpected observation due to the known sorption capacity of cellulose toward organic substances. This decrease in RhB concentration is almost equal to the dye degradation on the bare Bi$_2$O$_3$Br$_2$/BiOBr photocatalyst. When comparing these performances to the CM/Bi$_2$O$_3$Br$_2$/BiOBr, a synergistic effect between the CM and inorganic semiconductor constituents can be observed. The bio-inorganic composite shows superior performance in comparison to its individual constituents, while maintaining its second functionality as potential sorbent material for removal of positively charged entities. The augmented photocatalytic behavior can be attributed to minimized agglomeration of the nanosheets, i.e. minimized loss of photochemically-exposed surface area.

Adsorption of Co(II) and Ni(II) ions. Both CM and CM/Bi$_2$O$_3$Br$_2$/BiOBr composite were tested for adsorption of Co(II) and Ni(II) ions. The CM/Bi$_2$O$_3$Br$_2$/BiOBr composite unifies the mechanical stability and relatively easy manufacturing of cellulose membranes for sorption of metal ions.\textsuperscript{65-68} The adsorption rate provides crucial information on efficiency of adsorbent material and the possibility to use it on a large scale. Therefore, we investigated the influence of phases contact time on the adsorption efficiency of membranes before and after catalyst immobilization with respect to Co(II) and Ni(II) ions.

Figure 7. The pH$_{adc}$ of the bio-inorganic composite CM/Bi$_2$O$_3$Br$_2$/BiOBr.

Figure 8. Photocatalytic degradation of RhB. Experiments were carried out under 405 nm illumination (20 W) with addition of hydrogen peroxide. The loading of the semiconducting photocatalyst (red curve) was 17 mg.

For that, bivalent metal ions solutions were adsorbed from aqueous solutions with initial concentration 20 mg·L$^{-1}$ and 50 mg·L$^{-1}$ by modified and unmodified membranes in the neutral media during 5 h, 24 h, 48 h, 72 h and 96 h in order to reach an removal efficiency close to 100%. The dependency of phase contact time for Co(II) and Ni(II) ions adsorption on CM and CM/Bi$_2$O$_3$Br$_2$/BiOBr on removal efficiency is presented in Figure 9. It can be seen that 70-80% of Co(II) ions could be adsorbed during the first 5 h of contact with metal solutions of initial concentration of 20 mg·L$^{-1}$ and 50 mg·L$^{-1}$. In the case of Ni(II) ions, the adsorption occurs more slowly, i.e. during the same time it is possible to remove 47.5-48.0% of the Ni(II) ions from solutions with initial concentration of 20 mg·L$^{-1}$ by both membranes. For higher initial concentration of Ni(II) (50 mg·L$^{-1}$), the removal efficiency was found to be 50.9% and 58.7% for CM and CM/Bi$_2$O$_3$Br$_2$/BiOBr, respectively. The removal efficiency towards both metals increased slowly up to 94-100% during 5-96 h. Based on experimental data the adsorption capacity towards Co(II) was 28.7 mg·g$^{-1}$ for CM and 37.3 mg·g$^{-1}$ for CM/Bi$_2$O$_3$Br$_2$/BiOBr; towards Ni(II): 29.7 mg·g$^{-1}$ for CM and 30.2 mg·g$^{-1}$ for CM/Bi$_2$O$_3$Br$_2$/BiOBr. Thus, CM/Bi$_2$O$_3$Br$_2$/BiOBr showed higher affinity to Co(II) ions than to the Ni(II) ions from diluted solutions (20 – 50 mg·L$^{-1}$).

The kinetics of adsorption of Co(II) and Ni(II) ions on the membranes was studied by application of pseudo-first and pseudo-second order equations in order to understand the mechanisms of adsorption and the rate-controlling step of the process (Figure 10). The parameters were calculated from the fitting of experimental data with applied kinetic models (Table 1). The linear relationship and high values of correlation coefficients ($R^2$=0.95–0.99) confirm that the pseudo-second equation kinetic model fits well experimental data and is suitable for description of the kinetics of Co(II) and Ni(II) ion removal on both modified and unmodified membranes. These results indicate that the adsorption capacity of the CM membrane is independent of the coating with the photocatalyst. The adsorption mechanism of the metal ions on the cellulose surface may be attributed to the presence of carboxyl groups on the surface; as evidenced based on the XPS analysis. Increasing the initial metals concentration from 20 to 50 mg·L$^{-1}$ caused a slight
decrease of adsorption rate for all systems. The rate of adsorption was found to be higher for the systems CM/Co(II): 0.014 g·mg⁻¹·min⁻¹, and CM/Bi₄O₅Br₂/BiOBr/Co(II): 0.010–0.008 g·mg⁻¹·min⁻¹, than for the same systems with Ni(II) ions: 0.005–0.003 g·mg⁻¹·min⁻¹. Since the first adsorption step was found to be relatively fast with high percentage of removal of selected metals from initial solutions (20 and 50 mg·L⁻¹) it could be concluded that the membranes with immobilized catalyst could be applied in a large scale where fast and effective adsorption of metals are required.

These results indicate a high potential of the CM/Bi₄O₅Br₂/BiOBr composite for heavy metal recovery from wastewater; even with the decrease of sorption capacity for metal ions compared to pure CM was observed. By combining photocatalytic properties of Bi₄O₅Br₂ compounds with sorption ability of cellulose membrane, we end up with a promising material for simultaneous adsorption and photodegradation for wastewater purification from heavy metals and organic dyes.

Figure 9. Influence of phase contact time on Co(II) and Ni(II) ions adsorption using CM and CM/Bi₄O₅Br₂/BiOBr composites.

Figure 10. Pseudo-first order plots and pseudo-second order plots for Co(II) and Ni(II) ions adsorption kinetics by CM and CM/Bi₄O₅Br₂/BiOBr membranes.
CONCLUSION

We have demonstrated the fabrication of a bio-inorganic membrane based on cellulose and Bi$_2$O$_3$Br$_2$/BiOBr nanosheets, which can remove both inorganic and organic pollutants by two complementary mechanisms. The bio-material in form of cellulose ensures the mechanical stability of the membrane and can adsorb metal ions. The composite can adsorb both Co(II) and Ni(II) ions and our kinetic study confirmed that the pseudo-second equation kinetic model fits well experimental data and is suitable for description of the kinetics of Co(II) and Ni(II) ions on both modified and unmodified membranes. The controlled growth of the inorganic semiconducting nanosheets directly on the cellulose fibers enables photocatalytic decomposition of organic dyes, which has been shown on the example of RhB. The bio-inorganic composite CM/Bi$_2$O$_3$Br$_2$/BiOBr system, the hybrid material may be also an attractive candidate for a plethora of photocatalytic reactions.

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Table 1. Kinetic parameters for the adsorption of Co(II) and Ni(II) ions on the CM and CM/Bi$_2$O$_3$Br$_2$/BiOBr membranes.

| Kinetics model | Parameter symbol, unit | Co(II) | Ni(II) |
|----------------|------------------------|--------|--------|
|                | 20 mg·L$^{-1}$         | 50 mg·L$^{-1}$ | 20 mg·L$^{-1}$ | 50 mg·L$^{-1}$ |
| CM             |                        |        |        |        |
| Pseudo-first order | $q_e$, cal, mg·g$^{-1}$ | 4.49   | 4.78   | 10.47  | 17.60  |
|                | $K_d$, 1·min$^{-1}$     | 0.025  | 0.016  | 0.036  | 0.027  |
|                | $R^2$                   | 0.9756 | 0.9350 | 0.8917 | 0.9752 |
|                |                        |        |        |        |
| Pseudo-second order | $q_e$, cal, mg·g$^{-1}$ | 12.79  | 28.82  | 14.37  | 32.15  |
|                | $K_d$, g·mg$^{-1}$·min$^{-1}$ | 0.014  | 0.014  | 0.005  | 0.003  |
|                | $R^2$                   | 0.9942 | 0.9974 | 0.9694 | 0.9851 |
| CM/Bi$_2$O$_3$Br$_2$/BiOBr |                        |        |        |        |
| Pseudo-first order | $q_e$, cal, mg·g$^{-1}$ | 5.82   | 6.05   | 12.39  | 14.22  |
|                | $K_d$, 1·min$^{-1}$     | 0.020  | 0.010  | 0.033  | 0.023  |
|                | $R^2$                   | 0.9884 | 0.8833 | 0.9026 | 0.9743 |
| Pseudo-second order | $q_e$, cal, mg·g$^{-1}$ | 17.12  | 37.45  | 17.61  | 31.75  |
|                | $K_d$, g·mg$^{-1}$·min$^{-1}$ | 0.010  | 0.008  | 0.004  | 0.003  |
|                | $R^2$                   | 0.9694 | 0.9851 | 0.9490 | 0.9864 |
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