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Photocatalytic properties of PVDF membranes modified with g-C₃N₄ in the process of Rhodamines decomposition



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ABSTRACT

The PVDF membrane modification was performed utilizing the graphitic carbon nitride $(g-C_3N_4)$ in order to generate photocatalytic properties under visible light irradiation. Graphitic carbon nitride was synthesized via heating of melamine. Commercial PVDF ultrafiltration membranes with cut-off of 150 kDa were activated with a carbonate buffer and g-C₃N₄ was subsequently attached by terminal amino groups. The structural and morphological properties of g-C₃N₄ and membrane materials have been characterized using TEM, SEM-EDX, FTIR and EDX analysis. The adsorption of Rhodamine B and Rhodamine 6G on modified membranes and their subsequent degradation of dyes were studied. Membranes with immobilized g-C₃N₄ possessed 10 times higher adsorption rate of Rhodamine 6G compared to Rhodamine B. The highest photocatalytic activity of modified membranes has been observed in alkaline media. Using isopropanol, tert-butylhydroquinone, potassium iodine and Cr(VI) as O_{1}^{-} , h^{+} and \bar{e} scavengers, it has been shown that the generated holes have been responsible for dyes degradation in acidic media and superoxide radicals in alkaline media, and both of them at neutral conditions. The transport through PVDF-g-C₃N₄ membranes have been characterized by the volumetric flux of 320–350 L/(m²·h) during the ultrafiltration of dyes. Rejection of Rhodamine B and Rhodamine 6G was of 96 and 94%, respectively. The yield of dyes decomposition was about 80% and 85% for Rhodamine B and Rhodamine 6G, correspondingly, within the range of dye concentration from 5 to 50 mg/L. PVDF-g-C₃N₄ membranes were characterized with high stability and reusability in process of dyes ultrafiltration in the crossflow mode. The loss of membrane activity after 5 cycles of ultrafiltration (total duration equal to 50 h) was approximately 15%.

1. Introduction

Wastewaters contaminated with dyes are usually produced by the textile, food, plastic, and printing industries. Most of the dyes possess toxic and carcinogenic properties because of aromatic rings in their structure. Various approaches are used for dye wastewaters purification, e.g. adsorption, oxidation water treatment, coagulation/flocculation, photocatalytic oxidation, and membrane technologies [1]. Photocatalytic oxidation is known as a green technology for removal of dyes owing to decomposition of pollutants without generation of secondary toxic materials [2], but the process possesses one important drawback, i.e. the necessity of catalyst removal from the treated water. The main disadvantage of membrane technologies is fouling occurring during the filtration processes which causes the flux decline. The combination of photocatalytic oxidation with membrane technologies eliminates the limitations of both methods and is recognized as a

promising approach for dye water purification. Firstly, immobilization of photocatalysts onto the membrane surface prevents fouling owing the photocatalytic degradation of foulants in the boundary layer. Moreover, immobilization of a catalyst does not require its subsequent separation from the solution and solves the problem of catalyst recycling [3].

Nanoparticles with photocatalytic activity such as TiO₂, ZnO, WO₃, are widely used for bulk and surface membrane modification [4]. Damodar et al. [5] demonstrated that adding of TiO₂ nanoparticles into the casting polymeric solution during the process of PVDF membranes forming the enhanced hydrophilicity, transport, antifouling, and antibacterial properties of membranes. Martins et al. [6] compared photocatalytic activity of TiO₂ nanoparticles in the suspension and immobilized into polyvinylidene difluoride-co-trifluoroethylene membranes. It was demonstrated that degradation efficiency of membranes reached 49–86% efficiency of suspended nanoparticles. The

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addition of photocatalysts into the casting solution caused their blockage in polymeric materials. Authors solved that problem by adding zeolites which triggered the membrane hydrophilization and formation of the interconnected porous structure, improving mass transfer. Martins et al. [7] tested also the photocatalytic activity of TiO₂/polyvinylidene difluoride-co-trifluoroethylene microporous membranes on the real pharmaceutical pollutants such as ciprofloxacin and ibuprofen. Obtained membranes were characterized with high efficiency, excellent stability and reusability in the process of drugs decomposition. Almeida et al. [8] showed that combination of TiO₂ with graphene oxide as a filler of poly(vinylidene difluoride-co-trifluoroethylene) fibrous membranes ensured the photocatalytic activity of membranes in the process of methylene blue decomposition not only under UV irradiation but also under the visible light exposure. Hong and co-workers [9] studied the self-cleaning properties of microfiltration PVDF membranes filled with ZnO nanoparticles. Increasing ZnO nanoparticles caused the diminution of the membrane resistance and the fouling resistance in the process of BSA and the reclaimed water filtration. Salazar et al. studied photocatalytic properties of solvent cast and electrospun membranes of poly(vinylidene fluoride-hexafluoropropylene) with TiO_2 and Ag- TiO_2 [10]. They demonstrated that membranes based on Ag-TiO₂ nanocomposite revealed higher degradation efficiency of norfloxacin under UV and visible radiation. Shafaei et al. [11] modified polysulfone membranes with WO₃ nanoparticles. Such membranes were characterized by antifouling and selfcleaning properties in the process of landfill leachate filtration under UV irradiation. You et al. [12] proved that the photocatalytic properties of PVDF-TiO₂ membranes were attributed to properties of TiO₂ selfassembled onto the plasma-grafted poly(acrylic acid) membrane surface. Gao et al. [13] reported the preparation of polysulfone membranes by modification of the membrane surface with TiO_2 and graphene oxide. These membranes were active both under UV and sunlight irradiation. The increasing rejection of Methylene Blue by modified membranes under sunlight was observed. Dzhodzhyk et al. [14] demonstrated the antifouling properties of polyethersulfone membranes modified with SnO₂ nanoparticles in the process of milk nanofiltration. Despite the antifouling and photocatalytic activity, membranes modified with TiO₂, ZnO, SnO₂ nanoparticles are active only under UV irradiation, causing technological inconvenience and damaging the membrane materials.

Recently graphitic carbon nitrite (g- C_3N_4) has become a promising photocatalyst owing to its low cost, simple synthesis, high chemical stability, and visible-light response [15], which is especially important in terms of the membrane modification. Arumugham et al. [16] reported on the fabrication of nanocomposite polysulfone membranes filled with CuO/g- C_3N_4 sheets. The obtained membranes possessed antifouling and filtration resistance properties during protein filtration. Li and co-workers [17] modified polyacrylonitrile membranes via filtration of g- C_3N_4 nanosheets. Rejection of Methylene Blue at the initial concentration of 200 mg/L was 99.83% at the permeability of 11.7 L/ (m²·h·bar). Zhang et al. [18] achieved 77% of Methyl Orange decomposition onto PES-Ag/g-C₃N₄ nanocomposite membranes with the flux of 268 L/(m²·h) under visible light illumination. Huang et al. [19] immobilized MCU-C₃N₄ onto the surface of PVDF membranes by a suspension filtration via vacuum pump with further filtration of PEG or glutaraldehyde as crosslinkers. The investigation of the degradation kinetics of Rhodamine B (5 mg/L) showed that the maximum degradation of dye was 84% during 4 h by such membranes under visible light irradiation. Li and co-workers [20] modified cellulose acetate membranes with a suspension of graphene oxide and graphitic carbon nitride in dopamine (DA) with further polymerization of DA. The obtained membranes exhibited above 99% rejection of Methylene Blue (5 mg/L) at the permeability of 20–30 L/(m²·h·bar) under visible light.

The main goal of this research aimed with the surface modification of polyvinylidene fluoride membranes (PVDF) with graphitic carbon nitride. The performance of the modified membranes used for the decomposition of Rhodamine B and Rhodamine 6G dyes at different pH values in the presence of scavengers was evaluated. The mechanism of dyes photodecomposition by membranes was additionally assessed. The examination of the initial dye concentration on the rejection and decomposition of Rhodamines by PVDF-g-C₃N₄ membranes was conducted in the dead-end filtration mode.

2. Materials and methods

Rhodamine B (RhB) and Rhodamine 6G (Rh6G) (Sigma-Aldrich, USA) were used for the evaluation of photocatalytic, adsorption, and transport properties of modified membranes (Fig. 1).

Melamine was purchased from Sigma-Aldrich. All other reagents and solvents were of analytical grade and were used without further purification.

2.1. Synthesis and characterization of graphitic carbon nitrite $(g-C_3N_4)$

Pyrolysis of melamine was used for a catalyst preparation [21]. For this purpose, a sample of melamine (5.0 g) was placed in a semi-closed alumina crucible and heated in a muffle furnace to 500 °C for 2 h with an initial heating rate of 20 °C/min. After that, the deammonization was performed at 550 °C for another 2 h. The obtained product was dispersed in isopropanol and sonicated for 1 h.

Graphitic carbon nitride has been characterized by various techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and FTIR spectroscopy. The XRD patterns of g-C₃N₄ powder were recorded on Philips X'Pert PW 3040/60 diffractometer using Cu lamp (K α = 1.5418 Å) in 20 range 10-40°. TEM analysis was performed using a transmission electron microscope Tecnai G2 F20 X-Twin (FEI Europe) at an accelerating voltage of 200 kV. FTIR spectra were recorded on IRAffinity-1 IR-spectroscope (Shimadzu, Japan) in ATR mode.



Fig. 2. Schematic illustration of the crossflow ultrafiltration system.

2.2. PVDF membrane modification and characterization

Commercial PVDF membranes with a cut-off of 150 kDa (Microdyn Nadyr, Germany) were modified with graphitic carbon nitride through the carbonate buffer activation step. For this purpose, after soaking in the deionized water, samples of PVDF membranes were immersed in a suspension of $g-C_3N_4$ in 1 M carbonate buffer (0.5 mg/mL) and kept at 55 °C overnight. Further, membranes were washed with deionized water to neutral pH. The characteristics of membranes is provided in Table S1.

The morphological properties of the membranes were analyzed by scanning electron microscopy SEM (FEI Nova NanoSEM 650). Elemental analysis of membrane surface was conducted using an energy dispersive X-ray (EDX) system connected to SEM. FTIR-ATR spectra of membrane surface were recorded on IRAffinity-1 IR-spectroscope (Shimadzu, Japan). Dependence of zeta-potential of PVDF membrane surface on pH value was determined as described elsewhere [22]. The membrane surface free energy was evaluated by a goniometric technique (Goniometer Attention Theta from Biolin Scientific, Sweden) measuring contact angles of water, glycerol, and diiodomethane [23].

2.3. Adsorption and photocatalytic activity tests

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To investigate adsorption and decomposition, solutions of dyes at the concentration of 10 mg/L were used. Membrane samples of 4 cm² were immersed in 5 mL of aqueous dye solutions. pH values were adjusted by adding 0.1 M HCl or NaOH solutions. Adsorption experiments were conducted for 24 h in the dark to prevent photocatalytic degradation of Rhodamines. Kinetics of decomposition was performed for 2 h. under visible light irradiation by LED lamp (1200 Lm, Eurolamp, Ukraine) at 20 °C. The distance between lamp and membrane samples was 30 cm. Before the irradiation experiments, membrane samples were held in solutions of dyes in the darkness to reach the dye adsorption equilibrium. The effect of pH was examined preparing solutions of dyes at pH equal to 3.0, 5.0, 7.0, and 9.0.

The kinetics of the decomposition of dyes was fitted to the pseudofirst order kinetics according to Eq. (1) [24]:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt\tag{1}$$

where C_0 is the initial concentration of dye, mg/L; C_t is the concentration of dye at time t, mg/L; k is the rate constant, min⁻¹.

Concentrations of Rhodamine B and Rhodamine 6G were measured utilizing UV-vis spectrophotometer Helios Gamma (Thermo Electron Corporation, USA) at 554 and 530 nm, respectively. The UV-vis absorption spectra were recorded in the range 200–700 nm to analyze kinetics of dye decomposition.

The degradation pathway of RhB and Rh6G was confirmed by liquid chromatography - tandem mass-spectroscopy with electrospray ionization (Shimadzu LCMS-8030, Japan) using Kinetex 2.6 um XB-C18 100A column (100×3 mm). A mixture of methanol–water-formic acid was used as a mobile phase for 18 min.

All experiments were repeated three times to evaluate the repeatability of the data.

2.4. Determination of transport and photocatalytic properties of membranes

The transport properties of the pristine and modified PVDF membranes were investigated in the dead-end mode using Amicon 8050 cell (Millipore, USA) with an effective membrane area of 13.4 cm² and an initial volume of 50 mL. The effect of an initial dye concentration on the membrane flux and rejection was investigated by preparing solutions with 5, 10, 20, 30, 40, 50, 60, 70, and 100 mg/L of dye at the applied pressure of 200 kPa.

Membrane permeability, L_p and membrane resistance, R_m were calculated as described elsewhere [25].

The rejection (%) of Rhodamines was determined using Eq. (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\tag{2}$$

where C_p and C_f are the concentrations of dyes (mg/L) in permeate and feed, respectively.

Decomposition yield (%) of dyes by membranes was calculated by using Eq. (3) [26]:

$$D = \left(\frac{C_f \cdot V_f - C_r \cdot V_r - C_p \cdot V_p}{C_f \cdot V_f}\right) \cdot 100$$
(3)

where C_{f} , C_{r} , C_{p} are the concentration of dye in feed, retentate, and permeate, respectively; V_{f} , V_{r} , V_{p} are the volume of feed, retentate, and permeate, respectively.

The crossflow ultrafiltration experiments at constant pressure were conducted using a filtration system presented in Fig. 2. The transparent filtration cell (CF016A, Sterlitech, USA) had a membrane area of 20.6 cm² and a crossflow channel of 45.2 mm long, 39 mm wide and 2.3 mm deep. Crossflow velocity was 1 m/s. The cell was irradiated by LED lamp at room temperature. The initial feed volume was 2 L of 10 mg/L dye solution. In the process of ultrafiltration, a volume of the new solution equivalent to permeate volume was periodically added. Permeate samples were taken every 30 min and the contents of the dyes were examined using a UV–vis spectrophotometer. After each cycle, the crossflow ultrafiltration system was washed with deionized water for half an hour.

3. Results and discussion

3.1. Synthesis and characterization of $g-C_3N_4$

Graphitic carbon nitride was synthesized by direct heating of melamine (Fig. 3). Process was conducted at the temperature of 500–550 °C in a semi-closed system to prevent sublimation of melamine which occurs at the same temperature range as the thermal condensation [27]. Obtained yellow agglomerate was grounded into powder, dissolved in isopropanol, and sonicated for the exfoliation. As a result, after solvent evaporation a yellow powder was obtained.

The morphology of $g-C_3N_4$ was studied by the transmission electron microscopy. As can be seen in TEM images (Fig. 4A1-A2) the catalyst consists of irregular aggregated layered structures. An average size of two-dimensional nanosheets calculated by ImageJ software was of 200 \pm 10 nm.



Fig. 3. Scheme of graphitic carbon nitride synthesis.



Fig. 4. Characterization of synthesized graphitic carbon nitride: A1, A2 – TEM images of g-C₃N₄; B – Diffractogram g-C₃N₄; C – IR spectra of melamine and g-C₃N₄.

In diffractogram, presented in Fig. 4B, the observed weak diffraction peak at 13° is accorded to (1 0 0) plane of in-plane structural packing of graphitic carbon nitride. The strong diffraction peak at 28° corresponds to (0 0 2) plane of the interlayer stacking of conjugated aromatic systems of graphene related materials [28].

The formation of g-C₃N₄ was confirmed by IR spectroscopy (Fig. 4C). The IR spectrum of the melamine presented three main groups of bands: $3600-3000 \text{ cm}^{-1}$, $1700-1100 \text{ cm}^{-1}$, and 810 cm^{-1} (Fig. 4C). The $3600-3100 \text{ cm}^{-1}$ were assigned to N–H stretching vibrations, the $1650-1100 \text{ cm}^{-1}$ corresponded to the stretching vibrations related to C–N and C=N bonds of aromatic rings. Band at 810 cm^{-1} corresponded to out-of-plane deformation vibrations of C–N bonds. After the pyrolysis, the previously observed peaks in the range $3600-3100 \text{ cm}^{-1}$ have disappeared, and only one broad band remains. Hence, the most of N–H bonds were destroyed during the synthesis process of g-C₃N₄. Strong bands appeared in the $1650-1200 \text{ cm}^{-1}$ region which corresponded to the stretching mode of nitrogen-containing heterocycles (Fig. 4C).

3.2. PVDF membranes modification and characterization

Commercial PVDF ultrafiltration membranes with a cut-off of 150 kDa (Tab. S1) were activated with a carbonate buffer for HF elimination and double bonds formation [29]. Subsequently, graphitic carbon nitride flakes were attached by terminal amino groups according to the scheme presented in Fig. 5. A reaction proceeds through several stages (Fig. S1) [30]. At the beginning, the deprotonation of CH₂ group in the PVDF chain occurs under influence of high alkalinity and temperature. Subsequently, the resulted anion is stabilized by four electrons withdrawing atoms (fluorine). F⁻ ions which are stable in an aqueous medium act as a driving force of the double bond formation. Finally, nucleophilic substitution of fluorine at sp²-hybridized carbon [31].

The dependence of zeta potential of the pristine and modified membranes on pH is presented in Fig. 6A. The pristine PVDF membrane was characterized by an isoelectric point at pH 4.0 which results from the PVP layer on the surface. It is negatively charged with weak acidic, neutral, and alkaline media, and positively charged in an acidic medium. The dependence for the modified membrane had a similar shape with an isoelectric point at pH 3.5. Moreover, the values of zeta potential were lower in all of the pH range owing to the negative charge

of graphitic carbon nitride.

To determine the hydrophilicity/hydrophobicity of the membrane surface, the contact angles of three liquids (water, glycerol, and diiodomethane) were measured. Water contact angle for the pristine membrane was equal to $71.2 \pm 1.6^{\circ}$. After activation with a carbonate buffer, membrane surface tended to hydrophilization (water contact angle was $65.0 \pm 1.4^{\circ}$). Deposition of g-C₃N₄ layer did not affect the wetting of the surface with water (water contact angle slightly changed and was equal to $66.1 \pm 1.2^{\circ}$). The surface free energy of modified membranes increased compared to the pristine one due to increasing both polar and dispersive parts (Fig. 6B).

ATR-FTIR spectra shown in Fig. 7 were recorded in order to understand the mechanism of membrane modification. IR spectra confirmed the presence of $g-C_3N_4$ on the membrane surface. New bands in the range $1600-1400 \text{ cm}^{-1}$ were observed that corresponded to the stretching vibrations of C=N and C-N bonds.

Fig. 8A-B shows the surface morphology of the pristine PVDF membrane and the membrane modified with $g-C_3N_4$. As can be seen for the pristine membrane, the surface is uniform with many pores. After modification, a layer of $g-C_3N_4$ together with agglomerated nanoparticles was observed on the surface of the membrane. It can be concluded that the nanoparticles were immobilized both by the covalent attachment and by the adsorption. EDX analysis (Fig. 8C-D) also confirmed the presence of $g-C_3N_4$. Carbon and fluorine atoms prevailed on the surface of the unmodified membrane, whereas after modification, the agglomerates of carbon and nitrogen atoms were observed.

3.3. Photocatalytic properties of membranes modified with $g-C_3N_4$

Rhodamines are widely used at the industrial level, however their use can cause the damages after getting into the environment, because of the toxic and carcinogenic effects [32]. Therefore, Rhodamine B and Rhodamine 6G were chosen as representatives of organic pollutants to evaluate the photocatalytic activity and transport properties of membranes modified with graphitic carbon nitrite.

At the first stage, adsorption of Rhodamines by membranes from the solutions of an initial concentration of 10 mg/L in darkness was conducted (Fig. 9). As it can be seen, the adsorption of Rhodamine B was nearly 60 μ g/cm² for all membranes because of electrostatic repulsion between the negatively charged membrane surface and negatively charged dye. The adsorption yield of Rhodamine 6G on the modified membranes is much higher than that of the pristine membrane (Fig. 9).



Fig. 5. Scheme of PVDF membranes modification with g-C₃N₄.



Fig. 6. Dependence of zeta potential of membranes on pH (A) and surface free energy of membranes (B): 1 – the pristine PVDF membrane; 2 – PVDF membrane activated with a carbonate buffer; 3 – PVDF membrane modified with g- C_3N_4 .



Fig. 7. IR spectra of pristine PVDF membrane and membrane after modification with $g\text{-}C_3N_{4.}$

which may be associated with more negative charge of the surface, as well as with an increase in the surface area due to the grafting and adsorption of the nanosheets of graphitic carbon nitride. In the case of Rhodamine B, the dye molecules cannot approach the surface of the membrane closely, and thus, the increase in surface area does not affect the adsorption yield.

It was found that the adsorption equilibrium was established within 20–23 h depending on the type of membranes (Fig. S2). Therefore, prior to studying the kinetics of decomposition of Rhodamines, membrane samples were immersed in dyes solutions for 24 h to prevent the effect of adsorption on the decomposition kinetics of dyes.

The kinetics of the decomposition of dyes was measured at different pH values under visible light irradiation. The control experiments were conducted without adding membranes with immobilized photocatalyst. As was reported previously, the photolysis of Rhodamine B and 6G was very low, in the range of 5–10% [33,34]. It can be seen from Fig. 10 that the photocatalytic activity of the membrane toward RhB is higher in an alkaline medium compared to that in acidic and neutral media and that can be explained by the electrostatic attractions between the negatively charged membrane surface and the positively charged

molecules of dye. Regarding Rh6G, the lowest photoactivity was observed in the acidic medium because of the electrostatic repulsions between the positively charged membrane surface and the positively charged dye molecules. Moreover, such behavior could be explained by changes of the hydrophilic-hydrophobic equilibrium of the molecules of dyes, which become more hydrophobic under basic conditions and enable easier contact with hydrophobic surface of graphitic carbon nitrite [35]. Therefore, the adsorption stage is crucial in the process of photocatalysis on PVDF-g-C₃N₄ membranes.

The absorption spectra of aqueous Rhodamines solutions of the initial concentration of 10 mg/L are shown in Fig. 11. The decrease in the absorption intensity with time indicates the decomposition of the dyes by the membrane sample with the immobilized g-C₃N₄. The disappearance of the peak with maximum at 554 nm for Rhodamine B and 530 nm for Rhodamine 6G and the appearance of new peaks in UV region presumes that the chromophores were destroyed with the formation of new compounds.

LC-Q-ESI/MS was used to identify intermediates formed during the photodegradation of Rhodamines. The chromatograms of the initial solutions of dyes and solutions after 1 and 24 h of irradiation, and the mass spectra of dyes and intermediates are presented in Fig. S3 and S4. For Rhodamine B only one intermediate with m/z 318 was identified which corresponds to cleavage of a carboxylic group and formation of 6-(ethylamino)-9-phenyl-9a,10a-dihydro-3H-xanthen-3-iminium

(Fig. 12). After that, cleavage of chromophore occurred with further mineralization of the dye molecules.

The decomposition pathway of Rhodamine 6G was more complex (Fig. 13). Firstly, deesterification was observed with 9-(2-carbox-yphenyl)-3,6-bis(ethylamino)-2,7-dimethylxanthylium formation with m/z = 415. Subsequently, N-de-ethylation of amino groups occurred with a formation of an intermediate 6-amino-9-(2-carboxyphenyl)-2,7-dimethyl-9a,10a-dihydro-3H-xanthen-3-iminium with m/z = 362. Finally, 2-(3,8a-dihydro-2H-chromen-4-yl)benzoic acid (m/z = 255) was formed after ring opening and a cleavage of chromophore.

Quenching experiments were conducted to determine the role of active species such as h^+ , OH, O_2^- , and \bar{e} in the process of the degradation of dyes. Various scavengers were added to the Rhodamines solutions to achieve their concentration of 1 mmol, and the kinetics of the dyes decomposition was studied in media with different pH values. As can be seen from Figs. 13 and 14, isopropanol did not influence the degree of Rhodamine B and 6G decomposition neither in acidic, neutral, nor alkaline media, indicating that OH radicals were not generated in the system. On the other hand t-BQ, potassium iodine, and Cr



Fig. 8. SEM and SEM-EDX images of the pristine (A, C) and the modified PVDF membrane (B, D).



Fig. 9. Adsorption yield of Rhodamines by membranes: 1 – the pristine PVDF membrane; 2 – PVDF membrane activated with a carbonate buffer; 3 – PVDF membrane modified with $g-C_3N_4$.

(VI) as 'O₂⁻, h⁺ and \bar{e} scavengers presented the pH dependence behavior. A significant decrease of dye decomposition was observed in the presence of KI in acidic media. The opposite effect was shown for Cr (VI), denoting the dominant role of generated h⁺ in the photocatalytic system at pH 3.0 and 5.4. The influence of Cr(VI) can be explained by the fact of \bar{e} capturing and preventing a recombination of photoinduced electrons and holes. The degradation of dyes decreased after addition of t-BQ in neutral and alkaline media, revealing the great contribution of 'O₂⁻ to Rhodamines degradation.

The kinetics of the decomposition of dyes with and without additives is described by a pseudo-first-order kinetics (Table S2). The observed rate constant of Rhodamine B decomposition in neutral medium was 0.0072 min^{-1} , which was almost 2 times higher than the rate constant calculated for the non-immobilized graphitic carbon nitride [36]. It can be explained by agglomeration of the catalyst in the suspension, resulting in the decrease of an active surface area. On the other hand, the immobilized g-C₃N₄ is evenly distributed over the membrane surface and easily accessible for the interactions with photons and dye molecules. The value of k was 3.8 times higher than the rate constant reported by Cui et al. for g-C₃N₄-PVDF membranes obtained *via* phase inversion method [37]. Therefore, such results indicate the effectiveness of surface grafting of carbon nitride compared with its addition into suspensions or the polymer matrix.

In the presence of 1 mmol Cr(VI) the rate constant increased in 30–50% in acidic media for both dyes, while the presence of 1 mmol KI dramatically decreased the photocatalytic degradation. Therefore, the main factor responsible for the decomposition of dyes in acidic



Fig. 10. Influence of pH of dyes solutions on the decomposition kinetics of Rhodamine B (A) and Rhodamine 6G (B).



Fig. 11. UV/vis adsorption spectra of Rhodamine B (A) and Rhodamine 6G (B) before and after decomposition on PVDF- C_3N_4 membrane under visible light irradiation.



Fig. 12. Proposed transformation pathway of Rhodamine B in aqueous solution catalyzed by PVDF-g-C₃N₄ membrane under visible light irradiation.

conditions is the generation of holes. On the contrary, photocatalytic degradation was highly suppressed by the addition of *tert*-butylhydroquinone in the alkali medium. The rate constant decreased from 0.0106 min⁻¹ to 0.0040 min⁻¹ for Rhodamine B and from 0.0152 min⁻¹ to 0.0061 min⁻¹ for Rhodamine 6G. Since t-BQ is a good scavenger of O_2^- radicals, and superoxide radical formation is crucial in the alkaline environment. From the Figs. 14 and 15 and Table S2 the tendency of the mechanism changing from the formation of holes to the formation of O_2^- radicals with increasing pH value was observed. For transitional pH values, the influence of both holes and O_2^- radicals on the decomposition of Rhodamines was observed. Thus, directly photogenerated holes oxidation of Rhodamines occurred in acidic medium, whereas the oxidation with superoxide radicals occurred in the alkaline environment.



Fig. 13. Proposed transformation pathway of Rhodamine 6G in aqueous solution catalyzed by PVDF-g-C₃N₄ membrane under visible light irradiation.



Fig. 14. Kinetics of Rhodamine B decomposition in the presence of different scavengers at different pH values: A - 3.0; B - 5.5; C - 7.0; D - 9.0.



Fig. 15. Kinetics of Rhodamine 6G decomposition in the presence of different scavengers at different pH values: A - 3.0; B - 5.5; C - 7.0; D - 9.0.



Fig. 16. Dependence of the water flux through membranes on the applied pressure difference.

The results correlate to the results of Rhodamine B decomposition investigation by g- C_3N_4 as catalyst reported by Hu and coworkers [36]. They stated that O_2^- were the main active species in the studied photocatalytic system that can be explained by more negative value of the electrons reduction potential in g- C_3N_4 than the redox potential of O_2/O_2^- . Moreover, generation of superoxide radicals by g- C_3N_4 was proven by ESR technique [38].

3.4. Transport properties of membranes modified with $g-C_3N_4$

Initially, the pure water permeability of the membranes was measured by varying the applied pressure in a dead-end mode (Fig. 16). Compared to the unmodified membrane, activation of the membrane surface with the carbonate buffer significantly improved the membrane permeability (L_p = $9.87 \cdot 10^{-10}$ vs. $4.26 \cdot 10^{-10}$ m³/(m²·s·Pa)) and decreased the membrane resistance (R_m = $1.0 \cdot 10^{12}$ vs. $2.3 \cdot 10^{12}$ 1/m) owing to the changes of its hydrophilicity. A slight decrease of the membrane permeability (L_p = $7.10 \cdot 10^{-10}$ m³/(m²·s·Pa)) and an increase of the membrane resistance (R_m = $1.4 \cdot 10^{12}$ 1/m) was observed after modification of membrane with g-C₃N₄.

Ultrafiltration experiments of Rhodamines were conducted with various concentrations of dyes (5–100 mg/L) at the applied pressure of 200 kPa in the dead-end mode. It should be mentioned that the flux was stable during the experiment, amounting to 650 L/(m^2 ·h). The recovery rate was fixed at 70%. Two parameters were evaluated, i.e. rejection, which was investigated by measuring the concentration in the permeate



Fig. 17. Rejection (A) and decomposition degree (B) of Rhodamines by PVDF-g-C₃N₄ membranes.



Fig. 18. Photocatalytic activity of PVDF-g- C_3N_4 membranes over 5 cycles in the crossflow mode under visible light irradiation: A – Rhodamine B; B – Rhodamine 6G; $\Delta P = 200$ kPa; dye concentration – 10 mg/L.

(Eq. (2)), and decomposition yield, which included concentration of dyes in both the permeate and retentate (Eq. (3)). As could be seen from Fig. 17A, rejection of Rhodamine B and Rhodamine 6G were equal at the range of dyes concentration of 5-20 mg/L. While increasing of concentration caused the diminution of RhB rejection more intensely compared to the rejection of Rh6G. This phenomenon might be caused by formation of larger molecular associates of Rhodamine 6G due to the absence of negative charge in the side chains compared to Rhodamine B [39,40]. The rate of decomposition was about 80% and 85% for Rhodamine B and Rhodamine 6G, respectively, at the range of concentration of 5-50 mg/L (Fig. 17B). Further increase in concentration caused a decrease in decomposition yield because of a saturation of the adsorption centers of the catalyst on the membrane surface. Moreover, an increase in the concentration of the dyes causes a decrease in the contact of their molecules with the surface of catalyst, allowing more Rhodamine molecules to pass through the membrane.

In order to study the stability and the reusability of membranes with graphitic carbon nitride, 10 consecutive cycles of dyes decomposition were conducted in the crossflow mode under visible light irradiation (Fig. 18). Constant pressure of 200 kPa was maintained during the experiment corresponding to the flux of 620 \pm 20 L/(m²·h). As it can be seen (Fig. 18), the highest loss of photocatalytic activity in the process of dyes decomposition was observed at the first cycle. Rejection of Rhodamine B and Rhodamine 6G declined by 13 and 11%, correspondently, during 10 h. Membrane cleaning with deionized water allowed to restore 90-95% of the initial activities of membrane samples. Over the subsequent cycles, rejection did not change so dramatically. The loss of membrane activity after 5 cycles, i.e. during 50 h of ultrafiltration, was approximately 15%. The obtaining results are comparable with the photocatalytic activity decrease of poly(vinylidenedifluoride)-co-trifluoroethylene membranes with immobilized TiO2 and ZnO nanoparticles in the process of methylene blue decomposition, reported by Teixeira et al. [41]. Therefore, membranes with immobilized graphitic carbon nitride are promising for wastewater treatment of the textile industry owing to their high efficiency, stability, and reusability in the process of dyes ultrafiltration/decomposition.

4. Conclusions

Commercial PVDF ultrafiltration membranes with a cut-off of 150 kDa were activated with a carbonate buffer and subsequently graphitic carbon nitride was attached by the adsorption to the terminal amino groups. The g-C₃N₄ was synthesized via deammonization of melamine with further exfoliation by sonication. IR, SEM-EDX, and zeta potential analysis confirmed that the modification was successfully achieved. As a result of g-C₃N₄ immobilization, membranes acquired photocatalytic properties under the visible light irradiation. The adsorption and photocatalytic properties of modified membranes were studied in the process of decomposition of Rhodamine B and Rhodamine 6G. Membranes with immobilized g-C₃N₄ possessed 10 times higher adsorption yield of Rhodamine 6G compared to Rhodamine B. The highest photocatalytic activity of modified membranes was observed at pH 9.0. Kinetics experiments in the presence of additives showed that the generated holes were responsible for the degradation of dyes in acidic media, superoxide radicals in alkaline media, and both of them under the neutral pH conditions. Compared to the pristine membrane, activation of membrane surface with a carbonate buffer and modification with g-C₃N₄ significantly improved the membrane permeability ($L_p = 7.10 \cdot 10^{-10}$ vs. $4.26 \cdot 10^{-10}$ m³/ (m²·s·Pa)) and decreased the membrane resistance ($R_m = 1.4 \cdot 10^{12}$ vs. 2.3 · 10¹² 1/m) owing to changes of its hydrophilicity. PVDF-g-C₃N₄ membranes have been characterized by the volumetric flux of 320-350 L/(m²·h) during the ultrafiltration of dyes, with Rhodamine B and Rhodamine 6G rejection of 96 and 94%, respectively. The yield of the decomposition of dyes was about 80% and 85% for Rhodamine B and Rhodamine 6G, correspondingly, at the range of dye concentration of 5-50 mg/L. PVDF membranes with grafted graphitic carbon nitride were characterized with high stability and reusability in process of dyes ultrafiltration in the crossflow mode. The loss of membrane activity 50 h of ultrafiltration was approximately equal to 15%.

CRediT authorship contribution statement

Iryna Kolesnyk: Conceptualization, Funding acquisition, Methodology, Investigation, Data curation, Formal analysis, Visualization, Writing - original draft. Joanna Kujawa: Methodology, Data curation, Formal analysis. Halyna Bubela: Investigation, Data curation, Formal analysis. Viktoriia Konovalova: Data curation, Formal analysis, Writing - original draft. Anatolii Burban: Conceptualization, Supervision. Aleksandra Cyganiuk: Methodology, Data curation, Formal analysis. Wojciech Kujawski: Funding acquisition, Methodology, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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