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Application of the Cu@PET Composite Track-Etched Membranes for Catalytic Removal of Cr(VI) Ions

The features of obtaining composite track-etched membranes based on copper microtubes using various compositions of a deposition solution and various types of reducing agents such as formaldehyde (Cu_CHOH@PET), dimethylamine borane (Cu_DMAB@PET), glyoxylic acid (Cu_Gly@PET) were studied in this research. The structure and composition of the membrane composites were studied by scanning electron microscopy and X-ray phase analysis. It was shown that in the case of using dimethylamine borane as a reducing agent, the obtained composites consisted of copper(I) oxide (37.4 %) and copper(0) (62.6 %), in other cases single-component copper microtubes were obtained. The reduction reaction of chromium(VI) ions was used in order to evaluate the catalytic ability of prepared composites. It was shown that the removal efficiency of chromium ions reached up to the 95–97 % in the case of single-component composites; the presence of a copper(I) oxide phase in the structure of the Cu_DMAB@PET composites significantly reduced the activity of catalysts and under similar conditions only 41% of the contaminant was removed from the reaction system. The degradation reaction of Cr(VI) was found to follow the Langmuir-Hinshelwood mechanism and a pseudo-first-order kinetic model. The calculated value of the reaction rate constant ka for composites of the Cu_DMAB@PET composition (0.017 min^{-1}) was more than 9 times less than that of composites obtained using glyoxylic acid (0.156 min^{-1}) and more than 15 times less than the ka value of Cu_CHOH@PET samples (0.249 min^{-1}). Effect of temperatures on the catalytic ability of composites was studied in the temperature range of 10–38 °C. Some thermodynamic characteristics such as activation energy, enthalpy and entropy of activation were calculated. It was found that the minimum value of the activation energy was obtained for the Cu_CHOH@PET samples.

Keywords: composite track-etched membranes, catalysts, copper microtubes, chromium removal, template synthesis, electroless plating.

Introduction

In recent decades, technological waste based on heavy metals has been considered one of the most significant environmental problems in the world, and emissions containing heavy metals are still a big problem for the aquatic ecosystem of our planet [1].

Chromium is the seventh most common element on Earth, which is distributed in underground and surface waters due to its extensive industrial applications such as chromite mining, leather, textile and electroplating industries, steel and rubber production, pigment synthesis, etc. Cr(VI) is considered its most harmful form and is usually represented as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions [2, 3]. Compounds based on Cr(VI) are among the 14 most significant chemicals that pose a threat to humans even at ppb concentrations. The Environmental Protection Agency (EPA) identified it as a group of pollutant and proposed a maximum permissible limit of Cr(VI) concentration in drinking water of 0.05 mg/L [4].

According to the World Health Organization (WHO), the maximum permissible limits of Cr(VI) content in drinking water and its discharge into inland waters are also 0.05 mg/L and 0.1 mg/L, respectively. All types of Cr(VI) are toxic to bacteria, animals, plants and humans because of their permeability and biotransformation properties. They are not only potentially carcinogenic and mutagenic [5], but they can also cause many harmful health consequences such as allergic reactions, weakened immune system, kidney and liver damage, stomach ulcers, skin rash, genetic changes, irritation of the epidermis and even death [6].

Due to the above-mentioned serious impact of Cr(VI) on human health and the environment, the issue of wastewater treatment containing Cr(VI) compounds before being released into the environment or converted into less toxic forms is relevant and very much in demand. In several previously published papers, various approaches were used to remove Cr(VI) from aqueous solutions, such as adsorption, photocatalysis, membrane technologies, ion exchange, coagulation, etc. [1, 7–9]. Photocatalysis is one of the most popular techniques due to the simplicity of the hardware design, high efficiency and low cost of the process [10, 11]. Various types of nanoscale materials have previously been studied as effective catalysts for the removal of chromium(VI) ions [8, 12–15].

Composite track-etched membranes (TeMs) are flexible nanoporous membranes with deposited nano- and microtubes of various metals or their oxides. A characteristic feature of this class of composites is the high precision of the density and distribution of pores and their diameters. The composite TeMs are due to the high chemical resistance of these polymers and their exceptional performance characteristics. Moreover, the directed modification of the polymer template is one of the effective ways to increase the catalytic efficiency of the final composites [16, 17]. And the variation of the deposition conditions and the composition of the deposition solution makes it possible to synthesize nano- and microtubes of a composition and morphology with improved characteristics [18–20].

Chemical template synthesis comprises several successive stages, namely sensitization and activation of the template and the final stage of deposition [21]. A group of authors led by F. Muench previously conducted several experimental studies on the influence of various factors on the process of chemical deposition of metals into polycarbonate TEMs. It was shown that the structure of synthesized nanomaterials was largely determined by both the conditions of processing the template at the preparatory stages and the composition of the deposition solution, in particular the nature of the introduced complexing agents [22, 23].

Cu@PET composite TeMs are both effective catalysts for various types of chemical reactions [24–27] and promising sorbents for the removal of heavy metal ions from aqueous media [28, 29]. Moreover, a formaldehyde-based deposition solution is most often used to deposit copper into TEM channels. However, in the light of the increasing strict requirements for the safety of the obtained nanomaterials, an increasing number of studies are focused on compliance with the basic principles of green chemistry, i.e. minimizing the use of toxic reagents. Alternative options for formaldehyde can be considered deposition solutions based on dimethylamine borane (DMAB), glyoxylic acid.

It was interesting to study the features of the synthesis process of composite TEMs of Cu@PET composition using glyoxylic acid as a reducing agent in a deposition solution, to investigate the catalytic properties of synthesized composite TeMs in the reaction of removal of chromium(VI) ions in aqueous solutions as well as to conduct a comparative analysis of the effectiveness of this type of TeMs with samples obtained using formaldehyde and DMAB as a reducing agent.

Experimental

Chemical reagents. Copper sulfate pentahydrate ($CuSO_4·5H_2O$), tin(II) chloride ($SnCl_2$), potassium sodium tartrate ($KNaC_4H_4O_6×4H_2O$), palladium chloride ($PdCl_2$), glyoxylic acid, sodium lauryl sulfate, ethylenediaminetetraacetic acid (EDTA), potassium dichromate, dimethylamine borane (DMAB) and carbendazim (Czm) were all purchased from Sigma Aldrich (Schnelldorf, Germany) and used without further purification. Deionized water (18.2 Mohm/cm, “Aquilon-D301” Aquilon, Podolsk, Russia) was used in all experiments.

Electroless copper deposition. The polymer template was made of PET TEM (film thickness was 12.0 microns; pore density was $4×10^7$ ion/cm^2). After the standard etching procedure in 2.2 M NaOH solution, the pore diameter of the track-etched membranes did not exceed 395.2±4.73 nm. The sensitization and activation procedure were carried out under the procedure described in [30].

Cu_Gly@PET plating solution: $CuSO_4×5H_2O$ — 7.63 g/L; EDTA — 10.26 g/L; sodium lauryl sulfate — 4.0 mg/L; glyoxylic acid — 8.14 g/L, deposition was performed at a temperature of 65 °C, the deposition time was 60 sec, the pH of the solution was 12.65 [31].

Cu_CHOH@PET plating solution: $KNaC_4H_4O_6×4H_2O$ — 18 g/L; $CuSO_4×5H_2O$ — 5 g/L; NaOH — 7 g/L, CH_2O — 0.13 M; pH = 12.45 (H_2SO_4), deposition was carried out at a temperature of 10 °C, the deposition time was 40 minutes [32].

Cu_DMAB@PET: $CuSO_4×5H_2O$ — 10 g/L; EDTA — 14 g/L; DMAB — 6 g/L, pH = 1.85, deposition was carried out at a temperature of 70 °C, the deposition time was 20 min [27].

The structure and properties of the synthesized composites were studied using a JEOL JFC-7500F scanning electron microscope (SEM). X-ray diffraction analysis of copper nanotubes in a polymer matrix was performed on a D8 Advance diffractometer (Bruker, Germany) in the angular range 2(θ) 20–90° with a step of $2(\theta) = 0.02°$, measuring time was 1 s (voltage on the X-ray tube was 40 kV, current was 40 mA). The average size of the crystallites was determined by the Scherrer equation [25].

Study of catalytic activity

The catalytic reduction of Cr(VI) to Cr(III) in the presence of methanoic acid was performed in accordance with the paper [33]: 1 mL of HCOOH (88 %) was added to 25 ml of $K_2Cr_2O_7$ (2.0×10^{-4} M) and thermostated, stirring intensively at a temperature of 30 °C for 20 minutes. After that, a 2×2 cm composite catalyst was immersed in the reaction mixture. An aliquot of the reaction mixture with a volume of 1.0 ml was taken every 1–2 minutes and measured on a Specord-250 spectrophotometer (Jena Analytical, Germany) in the wavelength range of 200-500 nm. The degree of decomposition of Cr(VI) (D%) was determined by the formula (1):

$$D=\frac{C_0-C_t}{C_0}\times 100\,\%=\frac{A_0-A_t}{A_0}\times 100\,\%, \qquad (1)$$

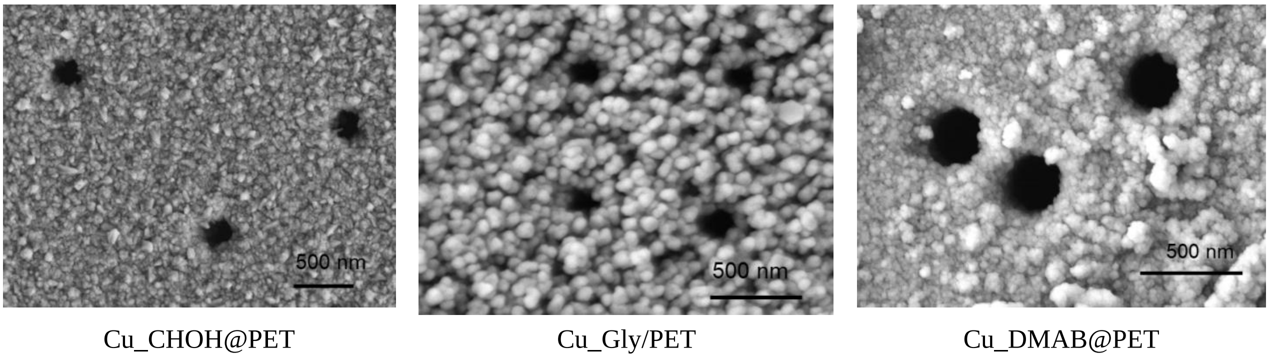
where C_0 and C_t — are the concentration values of the $K_2Cr_2O_7$ solution at the initial time and time t; A_0 and A_t — are the values of the optical density of the $K_2Cr_2O_7$ solution at the initial time and time t at 285 nm.

The effect of pH on the decomposition efficiency of Cr(VI) ions was evaluated in the range of values 1.5–7.0 (0.1 M NaOH or 0.1 M HCl) at 30 °C, other conditions were similar to those described above. The effect of temperature on the efficiency of Cr(VI) decomposition was studied in the temperature range of 20–38 °C (pH=2, Cr(VI) concentration was 2.0×10^{-4} M).

Results and Discussion

Classical chemical processes of copper plating [34, 35] are widely used in the production of various types of nanoscale materials [36]. In previous studies, various types of reducing agents such as formaldehyde [35], ascorbic [37, 38] or glyoxylic [31, 39, 40] acid, hydrazine hydrate [41], hypophosphite [42], dimethylamine borane [43, 44], etc. were used in copper deposition solutions. At room temperature, the reduction reaction of copper(II) ions is possible only when using formaldehyde as a reducing agent, but its high toxicity limits the use of this composition for coatings used in pharmaceuticals and biomedicine [45]. The use of hypophosphite or hydrazine is possible only at elevated temperatures, which limits their widespread use in practice.

Figure 1 shows electron micrographs of the synthesized composite TeMs. In these SEM images, besides the nanochannels that are still visible in places, the accumulation of nanoparticles (NPs) is clearly visible as an abundant phase covering the entire surface of PET TeMs and the interior of the nanochannels.



Cu_CHOH@PET Cu_Gly/PET Cu_DMAB@PET

Figure 1. SEM images of the surfaces of synthesized composites

As can be seen from the XRD patterns of synthesized composite membranes in Figure 2, characteristic peaks consistent with the metallic copper, and PET template are apparent in the diffractograms of the Cu_CHOH@PET as well as Cu_Gly/PET samples; Cu_DMAB@PET composite has an additional peak revealed to the Cu_2O phase.

Table 1 presents the data of X-ray phase analysis of composites obtained using various reducing agents. The quantitative phase composition was determined using the Rietveld method, which is based on estimating the areas of diffraction peaks by approximating them and determining convergence with reference values for each phase [29]. As can be seen from the data presented, when using DMAB–based deposition solutions, the formation of two phases is observed — pristine copper (0) and copper (I) oxide. In other cases, monophase copper microtubes with a degree of crystallinity of 72.8 and 61.7 %, respectively, are formed for deposition solutions based on formaldehyde and glyoxylic acid. The sizes of copper crystallites of the order of 19.4±4 nm were calculated according to the Scherrer equation for Cu_CHOH@PET samples, for Cu_Gly@PET KTM was of the order of 25 nm.

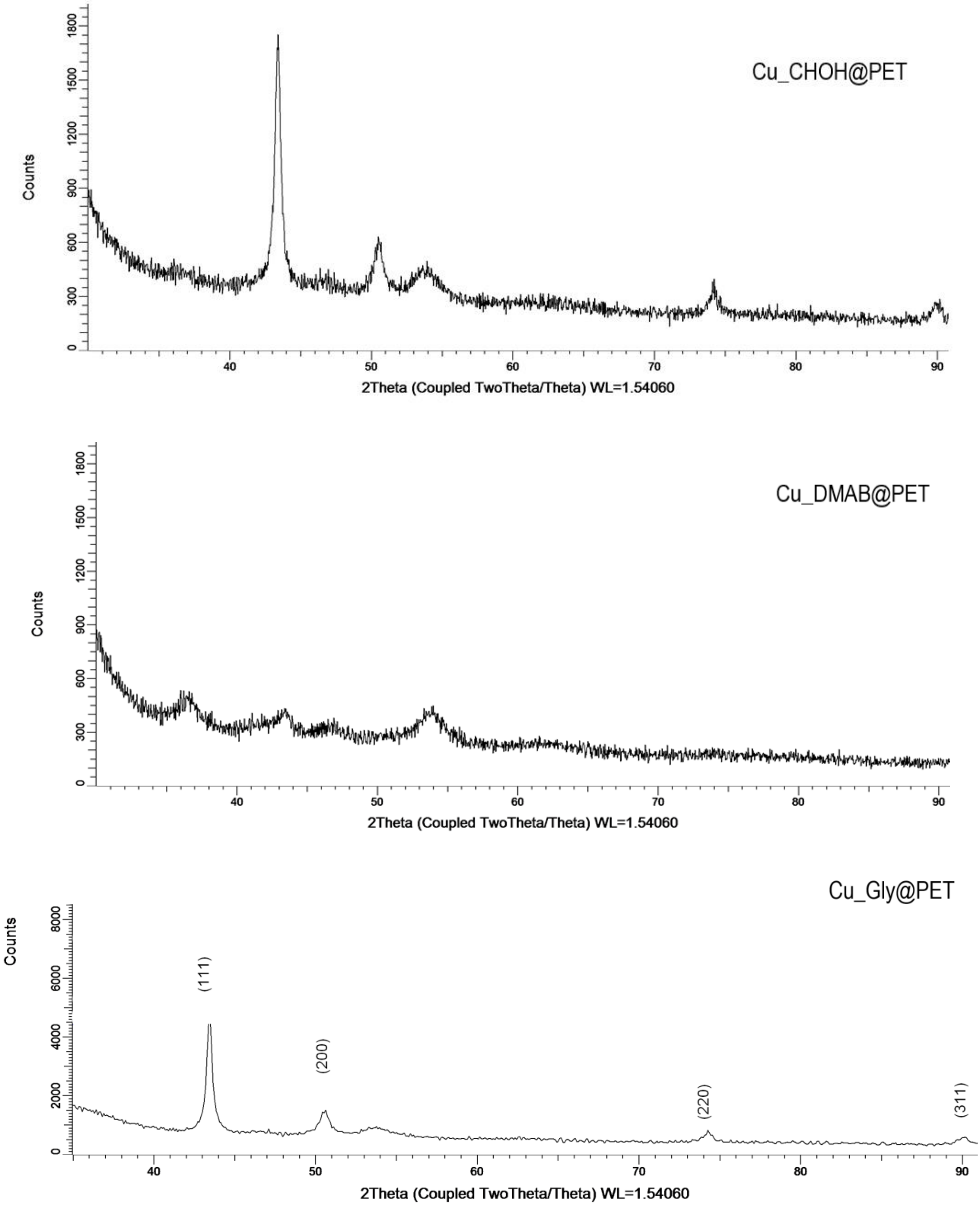


Figure 2. X-ray diffraction (XRD) patterns of composite membranes

Table 1

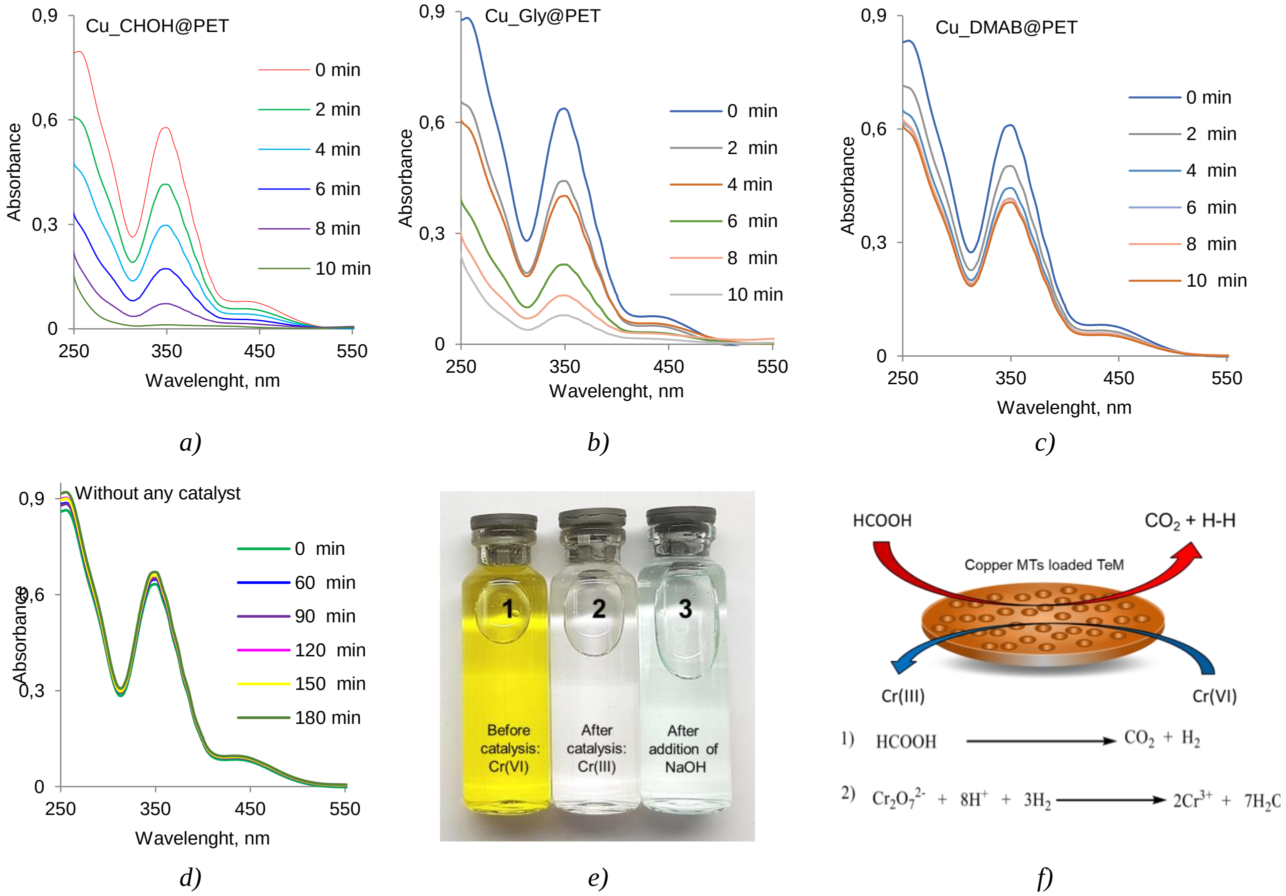
Changes in the crystal structures of the composites according to XRD data

Composite	Phase/ phase content %	Symmetry group	(hkl)	2θ°	d, Å	Average L, nm	FWHM	Cell parameter, Å	Crystallinity degree, %
Cu_DMAB@PET	Cu_2O/ 37.4	Pn-3m(224)	211	53.64	1.707	65.6±16	1.775	4.205	67.0
			220	62.37	1.488		0.122		
			221	66.61	1.403		0.187		
	Cu/ 62.6	Fm-3m(225)	111	43.49	2.079	58.2±30	0.438	3.598	
			200	50.70	1.799		0.113		
			200	50.79	1.796		0.277		
			220	74.63	1.271		0.189		
			311	90.27	1.087		0.066		
Cu_Gly@PET	Cu/ 100	Fm-3m(225)	111	43.60	2.075	24.7±7	0.349	3.603	61.7
			200	50.71	1.808		0.571		
			220	74.09	1.279		0.366		
Cu_CHOH@PET	Cu/ 100	Fm-3m(225)	111	43.48	2.08	19.4±4	0.404	3.604	72.8
			200	50.41	1.81		0.655		
			220	74.24	1.28		0.513		
			311	89.94	1.09		0.715		

The catalytic activity of composite TeMs was investigated by converting toxic Cr(VI) to Cr(III) in the presence of formic acid as a reducing agent at 38 °C. $K_2Cr_2O_7$ was selected as a chromium source. The Cr(VI) reduction process was monitored using UV-visible spectroscopy. Figures 3*a-c* show the optical density spectra of solutions containing Cr(VI) after the addition of catalysts. First of all, it should be noted that the reduction of Cr(VI) in the presence of formic acid and without the addition of a composite catalyst does not lead to an effective spectral change in the absorption of Cr(VI) (Fig. 3*d*). The intensity of the characteristic absorption peak at 352 nm for $Cr_2O_7^{2-}$, which is caused by the charge transfer transition of ligand (oxygen) to the metal (Cr(VI)), decreases over time confirming the rapid reduction of Cr(VI). Thus, the reduction efficiency of Cr(VI) after 10 minutes of reaction was about 98 % for composites of the Cu_Gly@PET and Cu_CHOH@PET composition. This indicator was only about 37 % after 10 minutes for Cu_DMAB@PET composite TeM samples. Visually, there is a change in the solution’s color from yellow to colorless within 10 minutes, which indicates an effective conversion of Cr(VI) (yellow) to Cr(III) (colorless). The presence of Cr(III) ions as a reaction product is confirmed by the addition of an excess of sodium hydroxide solution, and the appearance of a green color characteristic of hexahydroxochromate (III) (Figure 3*e*) [46].

It is believed that the adsorption of both chromate and hydrogen donor (formic acid) on the surface of nanoscale catalysts leads to the redox decomposition of formic acid into carbon dioxide and hydrogen, which leads to the reduction of Cr(VI) to Cr(III) by proton transfer (Figure 3*f*).

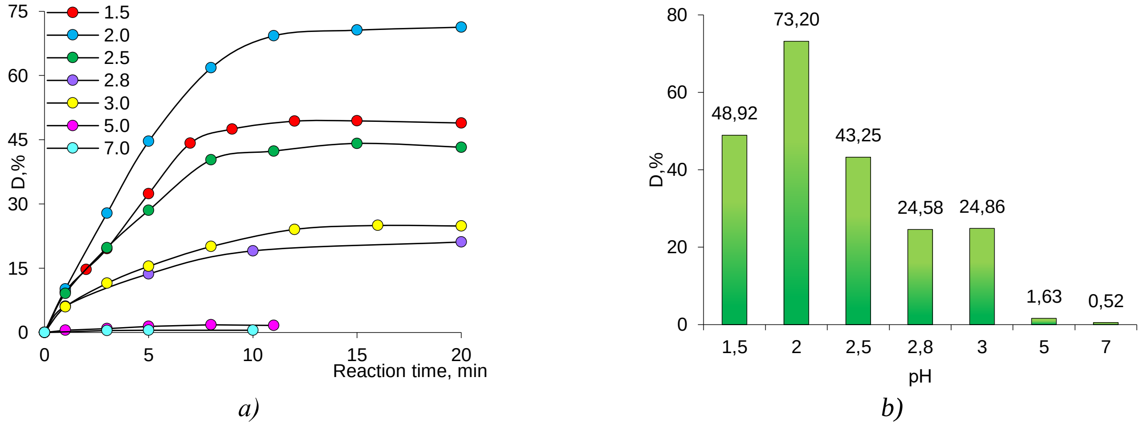
Initially, the effect of the pH of the initial solution on the effectiveness of the studied catalysts in the decomposition reaction of Cr(VI) chromium ions (Figure 4) was studied. The studies were carried out for a series of Cu_Gly@PET samples. From the presented graphical data, it is obvious that the efficiency of the reduction of chromium ions Cr(VI) significantly decreases with an increase in pH from 2.0 to 7.0. The results showed that the low pH was favorable for the adsorption and decomposition of formate and dichromate reagents. For one part, the addition of dilute hydrochloric acid provides the required level of acidity of the reaction mixture and promotes the transfer of hydrogen atoms. For the other part, a low pH is most favorable for formate and dichromate reagents, which both have a negative charge and are adsorbed on a composite catalyst. In addition, it should be noted that at all studied pH levels, Cu_Gly@PET porous composite catalysts retain good catalytic reduction activity and physical and chemical stability. It was previously shown that due to the prolonging effect of catalytic agents and the strong binding force existing between ions, the surface acidity of catalysts increased at low pH values and, as a result, an increase in catalytic properties was observed [7]. Considering the results obtained, all further studies and tests were carried out in solutions with a pH value of 2.0.



a) *b)* *c)*

d) *e)* *f)*

Figure 3. UV-vis absorption spectra of Cr(VI) ion reduction reaction in the presence of various types of composites as a function of time (*a*–*c*) without any catalyst and (*d*) and the image of the initial feed solution of Cr(VI) ions before and after catalysis and after the addition of excess NaOH (*e*) and the proposed mechanism of Cr(VI) reduction up to Cr(III) in the presence of Cu@PET composite catalyst (*f*)

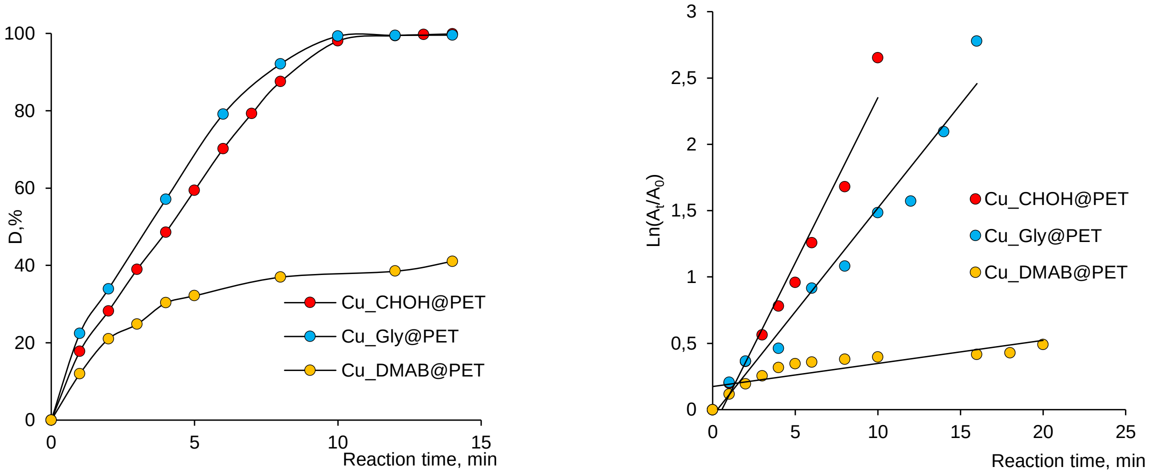


a) *b)*

Figure 4. Variations in Cr(VI) ions degradation degree (*D*, %) as a function of pH for Cu_Gly@PET ZnO@PET composite membrane (*a*) and corresponding values of D parameter (*b*)

Figure 5a shows the graphical dependences of the change in the D value as a function of the reaction time for all three types of catalysts under study. As can be seen from the presented data, composites obtained using DMAB as a reducing agent have the least activity in the decomposition reaction of Cr(VI) ions, which is most likely due to the presence of the copper(I) oxide phase in the composite [27]. The Cr(VI) chromium ion decomposition reaction proceeds according to the Langmuir-Hinshelwood mechanism and has a pseudo-first order [35], which makes it possible to calculate the rate constant by changing the concentration of the key component (Fig. 5*b*). The calculated value of the reaction rate constant k_a for composites of the

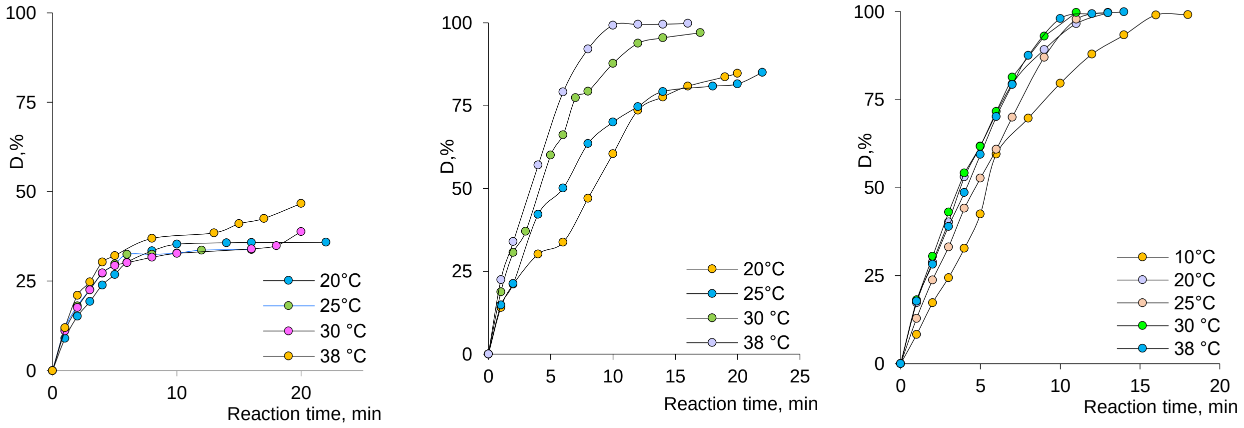
Cu_DMAB@PET composition (0.017 min^{-1}) is more than 9 times less than that of composites obtained using glyoxylic acid (0.156 min^{-1}) and more than 15 times less than the k_a value of Cu_CHOH@PET samples (0.249 min^{-1}).



a) *b)*

Figure 5. The variation in the degree of Cr(VI) degradation (*D*, %) as a function of irradiation time in the presence of different composite catalysts (*a*), and Langmuir–Hinshelwood plots for photodegradation of Cr(VI) catalyzed by different composites (*b*)

The effect of temperature on the efficiency of composites in the Cr(VI) ion removal reaction was studied in the temperature range of 20–38 °C, which also allowed us to evaluate a number of such thermodynamic characteristics of catalysts as activation energy, enthalpy and entropy of activation according to the methods described in paper [27]. The change in the efficiency of Cr(VI) decomposition at different temperatures is shown in Figure 6. As can be seen from the presented data, catalysts based on Cu_CHOH@PET effectively remove chromium ions Cr(VI) even at low temperatures, which is very important for the further use of catalysts in technological processes.



Cu_DMAB@PET Cu_Gly@PET Cu_CHOH@PET

Figure 6. Variation of Cr(VI) degradation degree with irradiation time at different temperatures in the presence of composite membranes

From the presented data, it can be said that for all catalyst systems, there is a general tendency to increase in the amount of degradation with increase in temperature, and after a certain period, the degradation reaches almost equilibrium at all temperatures. The highest activity in the degradation of Cr(VI) over the entire temperature range was demonstrated by the Cu_CHOH@PET catalysts, which catalyzed the degradation of almost all the contaminant in the medium after 15 minutes at 10 °C. Since, Cu_CHOH@PET catalysts demonstrate undeniable catalytic activity even at very low temperatures (e.g. 10 °C); the developed membrane catalysts seem suitable to be used for wastewater treatment without preheating, especially considering their ease of use.

Table 2

Thermodynamic parameters of the Cr(VI) decomposition reaction in the presence of the copper loaded composite catalysts

Composite catalyst	E_A, kJ/mol	ΔH, kJ/mol	ΔS, J/(mol×K)
Cu_CHOH@PET	10.8	13.21	–163.1
Cu_Gly@PET	35.96	38.47	–83.65
Cu_DMAB@PET	37.00	97.19	–58.05

Given the positive $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ values in Table 2, it appears that endothermic interactions and a decrease in entropy occur at the solid-liquid interface during the degradation process of Cr(VI) ions on the surface of the studied composite TeMs.

Table 3 presents the data on the efficiency of Cr(VI) ions degradation in the presence of different types of nanocatalysts. Note that the direct comparison of the *D* values as well as corresponding k_a is hardly possible, because such parameters as irradiation conditions (lamp capacity and type), amount of the loaded catalyst, and pollutant concentration in tests exert a considerable effect on degradation efficiency value. Nevertheless, it can easily be said that our results compete closely with the existing alternatives and that the obtained composite membranes prepared with formaldehyde and glyoxylic acid are promising objects, considering particularly their practicality and high surface areas.

Table 3

Catalytic activity of nanocatalysts in the reaction of the Cr(VI) ions reduction

Catalyst	Testing conditions				*D*, %	k_a, min^{-1}	E_A, kJ/mol	Ref.
	Cr(VI) concentration, ppm	Amount of catalysts, mg	Pollutant volume, ml	Lamp type				
Biogenic Pd NPs	250	0.043	0.1	Visible	95.5	0.0971	–	[47]
TiO_2 nanotubes	100	–	100.0	Sunlight	37.0	0.0249	–	[8]
Pd NPs/Fe_3O_4@ nanocellulose	354	10.0	25.0	Sunlight	98.6	–	–	[33]
$Cu_{1-x}Fe_xS$ (x = 9 %) NPs	100	2.4	40.0	UV-light	100	0.093	43.0	[48]
Cu_CHOH@PET	58.8	2.68	25.0	Sunlight	99.88	0.249	10.8	This work
Cu_Gly@PET		0.7			99.56	0.156	35.96	
Cu_DMAB@PET		2.0			41.04	0.017	37.00	

Conclusions

In this paper, we demonstrate the possibility of obtaining composite catalysts based on track-etched membranes and tubular microstructures of copper using various reducing agents of copper deposition solutions (formaldehyde, glyoxylic acid, dimethylamine borane). It was found with the help of X-ray diffraction that copper(I) oxide phase was formed in the composition of synthesized copper microtubules when using DMAB as a reducing agent, while in other cases single component copper microstructures were formed. It was shown that all synthesized samples effectively removed chromium ions Cr(VI) in a wide range of pH values and at various temperatures including low ones. When studying the kinetic parameters of the reaction, it was found that the reaction rate constant k_a of Cu_DMAB@PET composites (0.017 min^{-1}) was more than 9 times less than that of composites obtained using glyoxylic acid (0.156 min^{-1}) and more than 15 times less than the k_a value of Cu_CHOH@PET samples (0.249 min^{-1}).

Analysis of the calculated activation energy values showed that the most effective catalyst could be considered composite TeMs samples obtained using formaldehyde as a reducing agent.

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Хром(VI) иондарын каталитикалық жою үшін Cu@ PET құрамды композитті тректі мембраналарын қолдану

Бұл зерттеу жұмысында формальдегид (Cu_CHOH@PET), диметиламинборан (Cu_DMAB@PET) және глиоксил қышқылы (Cu_Gly@PET) сияқты әртүрлі құрамды тұндыру ерітінділерін және әртүрлі түрдегі тотықсыздандырғыштарды пайдалана отырып, мыс микротүтікшелері негізінде композитті тректі мембраналарды алу ерекшеліктері зерттелді. Композиттердің құрылымы мен құрамы порометрия, сканерлеуші электронды микроскопия және рентгендік фазалық талдау арқылы зерттелді. Тотықсыздандырғыш ретінде диметиламинборанды пайдаланған жағдайда алынған композиттер мыстан (0) (62,6 %) және мыс (I) оксидінен (37,4 %) тұратындығы, басқа жағдайларда монокомпонентті мыс микротүтікшелері алынғаны көрсетілген. Каталитикалық белсенділік хром (VI) иондарының тотықсыздану реакциясының мысалында зерттелді. Монокомпонентті композиттерді қолданған жағдайда хром иондарын жою тиімділігі 95–99 %-ға дейін жетеді, ал Cu_DMAB@PET композиттерінің құрамында оксидтік фазаның болуы катализаторлардың белсенділігін айтарлықтай төмендетеді және ұқсас жағдайларда реакция жүйесінен ластаушы заттардың 41%-ы ғана жойылады. Cr(VI) тотықсыздану реакциясының псевдо-бірінші ретті болатыны және Ленгмюр-Хиншельвуд механизмі бойынша жүретіні көрсетілген. Cu_DMAB@PET үлгілері үшін реакция жылдамдығы константасының есептелген мәні (0,017 мин$^{-1}$) Cu_Gly@PET үлгілерінен (0,156 мин$^{-1}$) 9 есе аз және Cu_CHOH@PET композиттерінің k_a мәнінен (0,249 мин$^{-1}$) 15 есе аз. Зерттелетін композиттердің каталитикалық қасиеттеріне температураның әсері 10–38 °C температура аралығында зерттелді; активтену энергиясы, активтену энтальпиясы және энтропиясы сияқты термодинамикалық сипаттамалар есептелді. Ең төменгі активтену энергиясы Cu_CHOH@PET үлгілері үшін алынғаны анықталды.

Кілт сөздер: композитті тректі мембраналар, катализаторлар, мыс микротүтікшелері, хромды жою, темплатты синтез, химиялық тұндыру.

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Применение композитных трековых мембран состава Cu@PET для каталитического удаления ионов хрома(VI)

В данном исследовании нами изучены особенности получения композитных трековых мембран на основе микротрубок меди с использованием различных составов раствора осаждения и различных типов восстановителей, таких как формальдегид (Cu_CHOH@PET), диметиламинборан (Cu_DMAB@PET), глиоксиловая кислота (Cu_Gly@PET). Структура и состав композитов исследованы методами порометрии, растровой электронной микроскопии и рентгенофазового анализа. Показано, что в случае использования диметиламинборана в качестве восстановителя полученные композиты состоят из оксида меди(I) (37,4 %) и меди(0) (62,6 %), в остальных случаях были получены монокомпонентные медные микротрубки. Каталитическую активность исследовали на примере реакции восстановления ионов хрома(VI). Показано, что в случае применения монокомпонентных композитов эффективность удаления ионов хрома достигает 95–99 %, в то время как наличие оксидной фазы в составе Cu_DMAB@PET композитов значительно снижает активность катализаторов и при аналогичных условиях из реакционной системы удаляется лишь 41 % загрязнителя. Показано, что реакция восстановления Cr(VI) имеет псевдо-первый порядок и протекает по механизму Ленгмюра-Хиншельвуда.

Рассчитанное значение константы скорости реакции для образцов Cu_DMAB@PET (0,017 мин$^{-1}$) более чем в 9 раз меньше аналогичного показателя для образцов Cu_Gly@PET (0,156 мин$^{-1}$) и более чем в 15 раз меньше чем величина k_a композитов состава Cu_CHOH@PET (0,249 мин$^{-1}$). Влияние температуры на каталитические свойства исследуемых композитов изучали в интервале температур 10–38 °C; были рассчитаны такие термодинамические характеристики как энергия активации, энтальпия и энтропия активации. Установлено, что минимальное значение энергии активации было получено для образцов Cu_CHOH@PET.

Ключевые слова: композитные трековые мембраны, катализаторы, микротрубки меди, удаление хрома, темплатный синтез, химическое осаждение.

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