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Study of the applicability of ACdSe (A – Co, Ni) thin films as catalysts for heavy metal capture

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ABSTRACT

Expansion of the possibilities of using photoactive thin films with a unique combination of optical and morphological characteristics as a basis for creation of highly efficient catalysts for the aqueous media purification is one of the promising research areas in modern materials science, which has both fundamental significance and potential for practical application. This study examines the prospects for using modified thin CdSe films by substituting nickel or cobalt for cadmium and selenium as a basis for creating highly efficient catalysts for the aqueous media purification from heavy metals such as arsenic, manganese and iron. A rather inexpensive electrochemical synthesis method was proposed as a method for obtaining thin films, in which the substitution effect is achieved by addition of nickel or cobalt sulfates to the electrolyte, which allows obtaining films with an equally probable distribution of elements in the composition of the synthesized films. Optical spectroscopy methods were used as methods for characterization of the initial samples, which made it possible to establish the dependences of the change in the band gap and absorption bands on the composition of the synthesized films, as well as to anticipate the influence of morphological features on optical absorption. During the conducted studies it was established that partial substitution of nickel and cobalt for cadmium and selenium in the composition of films results in growth in the adsorption efficiency of heavy metals, alongside operation stability maintenance of modified films during cyclic tests. At the same time, enhancement of the adsorption efficiency of heavy metals for modified films is due to both an alteration in the optical properties of the films and morphological features associated with the specific surface area growth due to a reduction in the grain size and a more developed surface.

1. Introduction

The problem of water pollution with heavy metals and organic dyes that are highly resistant to standard decomposition methods is one of the key environmental problems in the world that requires solutions and the attention of not only environmentalists but the entire world [1–3]. The proposed disposal methods are currently either expensive or not highly effective due to several reasons, including both the electronic properties that ensure energy output processes and the morphological features that play an important role in determining the specific surface area and adsorption capacity [4–6]. One of the potential solutions to this problem is the use of thin films based on oxide or chalcogenide compounds [7–9], which have fairly high band gap values, the value of which plays an important role in determining the efficiency of decomposition during photocatalysis, as well as the adsorption capacity of materials, the use of which allows the extraction of heavy metals from aqueous media, thereby reducing the concentration of pollutants. At the same time, a significant disadvantage limiting the widespread use of these types of films for the purification of aquatic environments is their low resistance to mechanical damage, which limits their use in conditions where films can be subject to mechanical influences [10–12]. In this case, mechanical influences such as friction or bending can lead to cracking of the

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surface due to mechanical influences and stresses, which will also negatively affect the optical and electronic properties of thin films [13,14]. It is important to highlight that the properties of thin films are partly determined by the substrate on which they are synthesized, which ensures the adhesive strength and adhesion of the films to the substrate [15,16]. The use of polymer substrates allows obtaining sufficiently flexible films that are resistant to bending and also have good adhesive strength, provided by good adhesion of the film to the surface of the polymer substrate. However, the use of polymer substrates imposes certain restrictions on the methods of film modification, in particular, restrictions associated with thermal annealing of films used to stabilize defects in films and increase their degree of structural ordering, the value of which plays a very important role in determining the potential for application and further use of films. In this regard, the solution to increasing the degree of structural ordering can be considered the effect of partial substitution, the use of which allows changing not only the structural features of the synthesized films, but also making significant changes to their optical and electronic properties [17–20]. At the same time, the use of such elements as nickel, cobalt or iron to replace elements in chalcogenide structures allows for significant adjustments to their electronic, structural, optical and strength properties, which in this case can be considered as an opportunity to create highly effective films for catalysts that, in addition to good adsorption efficiency indicators, are also resistant to external mechanical influences that arise as a result of testing and operational processes.

The main objective of this study is to determine the efficiency of using modified ACdSe (A - Ni, Co) as a base for catalysts used to capture and adsorb heavy metals from aqueous media in order to reduce their concentration. The main focus of the research is on studying the effect of concentration dependences of the content of heavy metals during their adsorption using films of different compositions, as well as establishing the relationship between catalytic activity and strength parameters that determine the number of cyclic tests. At the same time, the use of the method of modification of films by adding nickel and cobalt to them due to changes in the electrolyte solution when adding fairly inexpensive and accessible nickel or cobalt sulfates to it allows obtaining films with a controlled content of elements in the composition, as well as the degree of structural ordering. Moreover, the use of polymer films as substrates allows obtaining films with good adhesion strength indicators, due to the good compatibility of the films with the substrate, the use of which allows obtaining films of uniform thickness and composition. At the same time, the proposed electrochemical deposition method for obtaining films with different elemental composition, the change of which is due to the use of different electrolyte solutions, is one of the inexpensive and accessible methods for producing films both in laboratory conditions and when scaling up for industrial production in the case of high efficiency of the proposed compositions. It is worth noting that this modification method is not the only effective way to increase the efficiency of the adsorption capacity of catalysts, but the proposed method is one of the inexpensive ways to change the properties of thin films that does not require additional effects or manipulations with materials. In addition to the catalytic properties of these films, much attention to such structures is shown by microelectronic devices with the possibility of using them as various sensors. At the same time, the determining role in the efficiency of using films in various areas is played by the methods of their production [21–23], which determine the potential for further use, as well as the possibilities of scaling the technology of film production.

2. Materials and methods of research

Thin films of the ACdSe type were chosen as objects for the study, where cobalt and nickel were chosen as components of dopant A, the addition of which made it possible to increase the resistance of the films to mechanical damage, as well as to make changes in the morphology and optical properties of the films. Previously, a number of studies have shown that the addition of elements such as iron [24], cobalt [25], and nickel [26] to the composition of CdSe films leads to a change in the morphological, structural, and optical properties due to the effect of partial substitution of cadmium or selenium by these elements, which leads to an increase in their stability and an increase in efficiency when used as catalysts for the decomposition of organic dyes.

Thin film samples were obtained by electrochemical deposition by varying the electrolyte composition to obtain structures based on cadmium-selenium compounds with nickel or cobalt. To synthesize CdSe thin films, an electrolyte solution of 0.5 M $CdSO_4 \cdot 8H_2O$ and 5 mM SeO_2 was used. To obtain thin films of the ACdSe (A – Co, Ni) type, 0.5 M $CoSO_4 \cdot 7H_2O$ or 0.5 M $NiSO_4 \cdot 7H_2O$ were added to the initial electrolyte solution [27]. The synthesis was carried out at a potential difference of 1.5 V in a three-electrode cell with a copper cathode and anode in the form of metal plates with an area of 4 cm^2 and an AgCl electrode used as a reference electrode. The deposition was carried out on polymer substrates made of polyethylene terephthalate (PET), 12 μm thick, onto which a gold layer of about 30 nm thick was previously applied by magnetron sputtering, which served as a conductive layer for activating the nucleation processes of grains forming thin films on the surface of the dielectric substrate. The deposition time was 10 min, as a result of which, according to the assessment by the side cleavage method, films of about 1 μm thick were obtained.

The use of this method of film production at the selected value of the difference in applied potentials makes it possible to obtain films with a hexagonal type of crystal structure, characteristic of the CdSe phase of the spatial syngony P63mc(186). In this case, the main differences when adding nickel or cobalt sulfates to the electrolyte solution are associated with a change in the parameters of the crystal lattice of these films, due to differences in the ionic radii of the dopant elements and the cadmium and selenium they substitute, as well as the structural ordering degree, the growth of which for film samples with dopants is about 10–12 % compared to the value for CdSe films obtained without a dopant (the structural ordering degree for CdSe films is about 43–44 %).

Determination of optical characteristics in order to detect changes in the band gap width, as well as optical absorption of films depending on their type, was performed using the method of measuring UV–Vis spectra using a SPECORD 200/210/250 PLUS dual-beam spectrophotometer (Analytik Jena, Jena, Germany). Measurements were carried out in the wavelength range from 200 to 1000 nm, with a step of 1 nm, which made it possible to estimate the value of the fundamental absorption edge, as well as the transmittance and absorption capacity of the obtained films.

The morphological features reflecting the change in grain shape and size with a change in the composition of the electrolyte solution used for film synthesis were studied using the scanning electron microscopy method implemented using a TM3030 microscope (Hitachi, Tokyo, Japan). The elemental composition was determined using the energy-dispersive analysis method implemented using a special attachment built into this microscope. The uniformity of the element distribution in the composition was confirmed by the mapping results reflecting the isotropy of the element distribution in the films with a change in the electrolyte composition.

Tribological tests for the purpose of establishing the resistance of the film surface to mechanical impacts were carried out using the “ball-disk” scheme, the value of the applied load on the friction body was 50 N, the sliding speed was 0.2 m/s, the number of test cycles was 20,000. The microhardness of the studied film samples was assessed using the indentation method, implemented using the Duroline M1 microhardness tester (Metkon, Bursa, Turkey). Adhesive strength, characterizing the adhesion of films to the substrate under external influences, was measured by the action of an indenter along the film surface at a constant speed and variable load. These tests were carried out using the Unitest SKU UT-750 (Unitest, USA) installation. All tests to determine the critical load, as well as wear resistance for all films, were carried out under the same conditions in order to determine the effectiveness of the proposed modification method.

The efficiency of using synthesized films as absorbents of heavy metals – manganese, iron and arsenic – was determined using model solutions with certain concentrations of these elements dissolved in them. The initial concentration of elements in the model solution was 10, 20 and 50 mg/dm^3. The concentration of these elements was assessed by determining the optical density of the solution at different time intervals, which allowed us to assess the kinetics of the absorption capacity of the selected films depending on their type. For the measurements, film samples with an area of 2 x 2 cm^2, which were placed in a model solution and subsequently removed from it at the end of the measurement cycles, were used. The choice of sample area is determined by the size of the cell for electrochemical deposition, which was used to obtain the films. It should be noted that this method allows you to obtain films of any area, the only limitation is the cell size. The absorption efficiency of heavy metals from aqueous solutions was assessed by comparison with the concentration in the initial model solution kept for a similar measurement time in order to exclude effects associated with agglomeration or a decrease in concentration due to precipitation.

3. Results and discussion

3.1. Characterization of synthesized samples

Fig. 1 shows the results of a comparative analysis of changes in the transmission spectra characterizing the transmission and absorption capacity of the films, as well as its variation in the case of a change in the composition of the films obtained by adding nickel or cobalt sulfates to the electrolytes. Analysis of the transmission spectra shown in Fig. 1 for the samples under study depending on changes in the electrolyte solutions indicates that the addition of nickel and cobalt leads to a decrease in the transmission capacity of the films, expressed in a decrease in the transmission intensity in the range of 400–700 nm due to the presence of an absorption band. Such alterations in the optical spectra can be explained by structural features of the resulting films associated with the partial substitution of cadmium and selenium with nickel and cobalt, leading to the formation of additional absorption bands in the structure due to the properties of these elements (the presence of absorption bands is characteristic of cobalt structures, which was shown in the works [28, 29]. According to the presented inserts in Fig. 1, reflecting the morphological features of the studied films, the addition of nickel or cobalt sulfates to the electrolyte solution leads to the formation of films from grains whose size is significantly smaller than in the case of CdSe films, which contributes to changes in the specific surface area, which has a direct correlation with the grain size. Moreover, the addition of cobalt sulfate results in more pronounced changes in the morphological features of the synthesized films, which can also cause a change in the absorption capacity of the films, and changes in the optical density observed in the transmission spectra in Fig. 1.

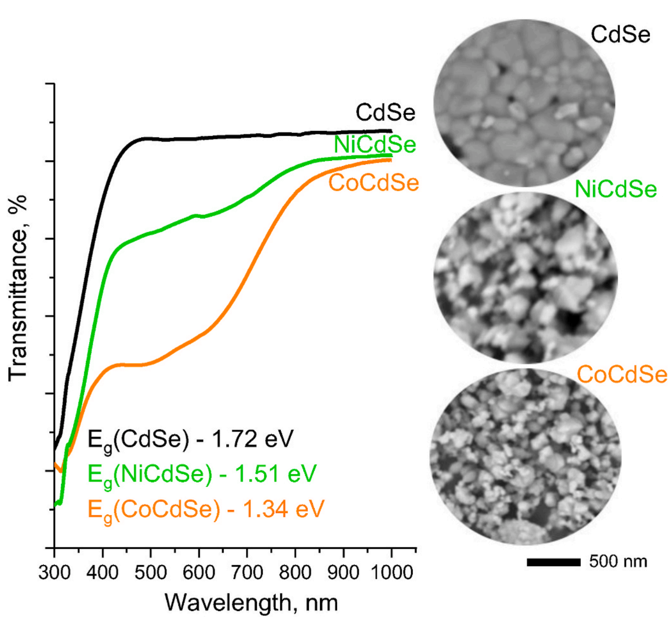


Fig. 1. Results of optical transmission spectra of the studied films contingent upon the dopant type, and the insets show the results of morphological features that determine changes in transmission capacity in the visible light region.

According to the measurements, it was found that the addition of nickel and cobalt to the CdSe films leads to a decrease in the band gap from 1.71 eV for CdSe films to 1.51 eV and 1.34 eV for NiCdSe and CoCdSe films. Such changes are due to the effects of substitution of cadmium by nickel and cobalt, which leads to a change in the electronic structure of the films and, as a consequence, a decrease in the band gap. Such effects are due to the effects associated with the formation in the structure of films of an exchange sp-d interaction between localized electrons in d-orbitals and zone electrons, which in turn leads to a decrease in the band gap.

In this case, the decrease in the band gap indicates the formation of exchange interaction mechanisms caused by the effect of partial substitution of cadmium ions with nickel or cobalt ions, while substitution with cobalt results in more pronounced changes, which indicates a positive effect of addition of cobalt on the optical and electronic properties of the synthesized films. Also, such clearly expressed changes can be caused by the fact that with partial replacement of cadmium with cobalt, the structure of the resulting films has higher indices of structural ordering, caused by the fact that during the electrochemical synthesis of these films, the addition of cobalt to the electrolyte leads to acceleration of the processes of reduction of metal ions from the electrolyte solution, with the subsequent construction of a more ordered structure due to binding elements in the form of cobalt particles. It should be noted that the addition of nickel or cobalt to the electrolyte leads to a change in the optical transmission spectra associated with a decrease in the transmission intensity in the visible and IR ranges, indicating an alteration in the optical density of the material and a rise in the absorption efficiency in the range of 400–700 nm, which can also contribute to a change in the catalytic and adsorption capacity of the films.

Table 1 reveals the results of the elemental composition of the films under study, reflecting the effect of substitution of cadmium and selenium by nickel or cobalt in the structure of the synthesized films. The data were obtained using the method of evaluating the obtained energy-dispersive spectra, the measurement error was determined by evaluating

Table 1
Elemental analysis data of the studied films.

Element, at. %	Film type		
	CdSe	NiCdSe	CoCdSe
Cd	46 ± 3[a]	40 ± 1	38 ± 2
Se	54 ± 2	42 ± 2	43 ± 1
Ni	–	18 ± 1	–
Co	–	–	19 ± 1
Distribution of elements in the composition of films	Homogeneous, isotropic	The distribution of nickel in the films is homogeneous and isotropic.	The distribution of cobalt in the composition of films is typical for core-shell structures, where the shell is cobalt combined with a low content of cadmium and selenium.
S_{BET}, m/g^2	0.026	0.037	0.052

[a] The results of the elemental composition of the films were obtained from different places (at least 10–15 points on the surface of the sample) in order to average the values and determine the isotropy of the elemental composition.

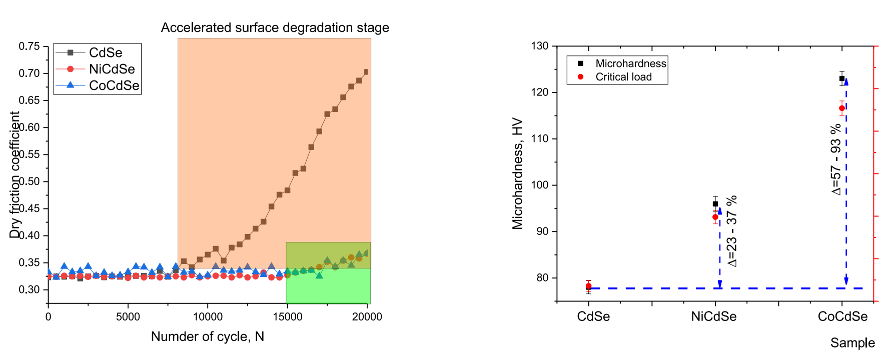
the distribution of elements in different areas of the film samples under study. The general trend of the distribution of elements and their ratio in CdSe films indicates that the use of the proposed synthesis conditions allows one to obtain films with an equally probable distribution of elements, the ratio of which is approximately equal to each other. Addition of nickel sulfate to the electrolyte leads to the formation of nickel in the film composition of about 18 at. %, while the concentration of cadmium changes to a lesser extent than in the case of selenium, which indicates that nickel replaces selenium in the film composition to a greater extent, and the nickel content in the film composition is approximately 1/5 of the total elemental composition. In the case of using cobalt sulfate to modify the films, the cobalt content in the film composition is about 19 at. % (as in the case of nickel, the total content is 1/5 of the total composition), while the analysis of changes in the cadmium and selenium ratio in the film composition indicates that cobalt substitution is equally probable in both cadmium and selenium. It is important to mention that the distribution of cobalt in the composition of the synthesized films is characteristic of the formation of grains of the core-shell type, where the shell is cobalt combined with a low content of cadmium and selenium, which is in good agreement with the results of work on the electrochemical synthesis of similar structures [25,30]. The value of the specific surface area of S_{BET} was estimated by the Brunauer-Emmett-Teller adsorption method. The results are presented in Table 1.

Fig. 2a demonstrates the results of tribological tests of the films under study, reflecting changes in the dry friction coefficient, a rise of which indicates degradation of the film surface during long-term mechanical impacts. The general appearance of the presented dependencies is characterized by a fairly low value of the dry friction coefficient (about 0.3–0.35), which indicates a fairly low surface roughness capable of providing significant resistance to the movement of the indenter. The presence of alterations in the dry friction coefficient within the permissible errors (about 0.01–0.03) indicates a low degradation rate of the film surface under external influence during a sufficiently large number of cycles, which also characterizes the resistance of the films to external mechanical effects that create friction during interaction. In the case of CdSe films, when the number of cycles reaches about 7000–8000, the dry friction coefficient growth is observed, which indicates deterioration of the surface due to degradation and the creation of additional obstacles that increase friction. It should be noted that the maximum value of changes in the dry friction coefficient after 20,000 cyclic tests compared to the initial value is more than twice as high, which indicates strong surface degradation and loss of wear resistance under long-term exposure. In the case of addition of nickel and cobalt films to the CdSe composition, despite the observed morphological changes caused by the formation of smaller grains compared to unmodified films, the difference in the dry friction coefficient in the initial state is insignificant. At the same time, for modified films, the degradation resistance growth is observed. This is expressed in a longer number of test cycles during which no elevation in the friction coefficient is observed, and the observed changes after 15,000 test cycles are no more than 10–15 % of the initial value, which indicates a positive influence of the substitution effect on degradation resistance enhancement.

Fig. 2b demonstrates the results of the evaluation of the microhardness values (data obtained using the indentation method) and the adhesive strength (expressed in the value of the pressure applied to the indenter during movement, which results in the film being torn off from the substrate). According to the data presented, the addition of nickel and cobalt to the film composition leads to a significant growth in the resistance of the films to external influences, in particular to mechanical pressure applied during indentation, as well as in the case of scratch tests aimed at studying the adhesive strength. In this case, the hardening effect is caused by several factors, including a change in grain size, which allows for an increase in dislocation density, which results in emergence of the dispersion hardening effect, as well as changes in the structural ordering degree, the change of which leads to a reduction in the composition of disordered inclusions in the films, which play a negative role in determining the strength properties [31,32].

3.2. *Results of catalytic reactions of heavy metal adsorption using thin films*

Fig. 3 illustrates the results of experiments on the adsorption of pollutants (iron, manganese and arsenic) for all the studied films (unmodified CdSe and modified), with variations in the concentration of the pollutant in the model solution (from 10 to 50 mg/dm^3). The results are presented as a dependence of the change in the pollutant concentration during the test time, the maximum value of which was 60 min, during which, in the case of using NiCdSe and CoCdSe films, the achievement of maximum adsorption efficiency was observed, expressed in a reduction in the pollutant concentration in the model solution to almost 0. The general form of the presented dependences of the change in the value of the pollutant concentration in the model solution on time can be described by linear dependences indicating a sufficiently fast adsorption rate, the value of which for modified films is preserved in the case of variation in the dye concentration. It should be noted that in the case of CdSe films, the maximum decrease in the pollutant concentration in the model solution after 60 min of testing is about 55–60 %, and an increase in the pollutant concentration in the model solution leads to the adsorption efficiency decrease. In the case of pollutant concentrations in the model solution of 10–20 mg/dm^3 after 40 min of testing, the adsorption efficiency reduction, expressed in a decrease in the trend of pollutant concentration reduction over the course of the experiment, is observed. At the same time, at low pollutant concentrations in the model



a) b)

Fig. 2. Results of measurements of strength parameters of the studied films: a) results of tribological tests (The highlighted areas indicate the main changes in the dry friction coefficient in the case of the original CdSe films (orange area) and modified ones (green area)); b) results of measurements of hardness and adhesive strength. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

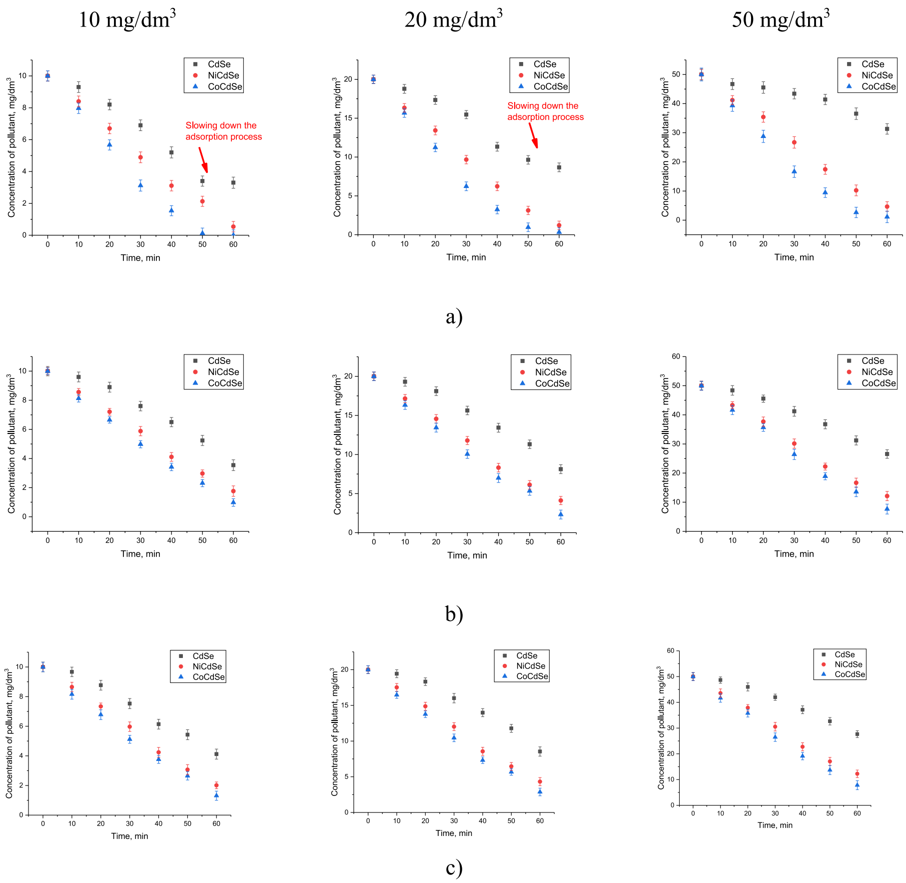


Fig. 3. Assessment results of the pollutant concentration change in a model solution with variation in pollutant concentration in the case of: a) iron adsorption; b) manganese adsorption; c) arsenic adsorption.

solution (10–20 mg/dm^3) in the case of CoCdSe films, maximum efficiency is achieved with a test time interval of 50 min.

The assessment results of the adsorption efficiency using the synthesized films depending on the pollutant concentration in the model solution in the form of comparison diagrams are presented in Fig. 4. These diagrams were constructed based on the data in Fig. 3 obtained after 60 min of testing. The results reflect the dependences of the change in efficiency with an increase in the pollutant concentration, indicating the potential for using these films as catalysts in environments with different pollutant contents, including quite high values. The results of the assessment of the adsorption efficiency depending on the type of pollutant, presented in Fig. 4, were obtained by comparatively assessing the values of the change in the optical density of the model solution in the initial state (before filtration) and after 60 min of exposure of the films used as catalysts to the model solution.

As can be seen from the presented data of comparative diagrams of adsorption efficiency in the case of CdSe films, an increase in the pollutant concentration in the model solution leads to an adsorption efficiency reduction by more than 15–20 %, which indicates a fairly low efficiency of using these films as adsorbents at high concentrations of pollutants. It should be noted that the efficiency value of about 55–65 % is maintained for all types of heavy metals sorbed from model solutions

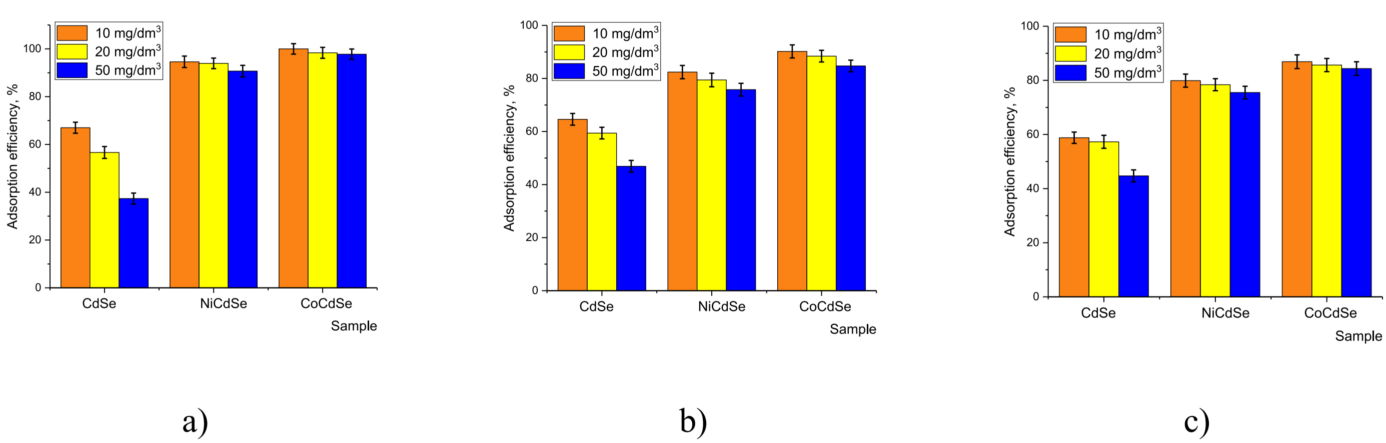


Fig. 4. Evaluation results of the efficiency of purification of model solutions using thin films of different composition as catalysts: a) during iron adsorption; b) during manganese adsorption; c) during arsenic adsorption.

for CdSe films, while for modified films the highest adsorption efficiency is observed in the case of experiments on purification of model solutions from iron, and in the case of manganese and arsenic the efficiency decreases somewhat, especially for NiCdSe films, and is about 85–90 %, while for CoCdSe films the efficiency is more than 90 % for the adsorption of manganese and arsenic and more than 97 % for the adsorption of iron. It is important to highlight that for modified films, changing the pollutant concentration in the model solution does not lead to a significant decrease in the adsorption efficiency, as was observed for CdSe films. At the same time, higher efficiency indicators for CoCdSe films in comparison with NiCdSe films can be explained both by the morphological features of the synthesized films, expressed in smaller grains, and by the presence of a wide absorption band, promoting more effective adsorption on the surface of particles.

Fig. 5 demonstrates the results of tests of the synthesized films when used as catalysts in cyclic (sequential) tests in the case of model solutions with a pollutant concentration of 10 mg/m^3. The obtained dependences of the change in the adsorption efficiency value reflect the degradation of the catalysts caused by a decrease in the structural and optical properties of the films, which occur due to the interaction of the film surface with the pollutant during the adsorption process, as well as the model aqueous solution, which results in initialization of oxidation processes. As can be seen from the data presented, the repeated use of the synthesized films as catalysts for the adsorption of heavy metals does not lead to a decrease in the adsorption efficiency after 2 and 3 consecutive cycles, with the efficiency indicators remaining at the same level as after the first test cycle. The adsorption efficiency reduction, indicating degradation of the films when used as catalysts, is observed after three cycles of consecutive tests. According to the presented data, after 4 consecutive test cycles, a decrease in efficiency is observed, and the nature of the changes has a different trend for the studied films, which indicates that the degradation processes are different for different films. In the case of CdSe films, the maximum value of the adsorption efficiency degradation is about 14–15 % after 5 consecutive test cycles, while the substitution of cadmium and selenium with nickel or cobalt results in degradation resistance growth in comparison with CdSe films by more than 6.5–7 times (the maximum value of the decrease in adsorption efficiency is about 2–2.5 % after 5 consecutive cycles). Such an effect can be explained by higher indices of structural parameters (structural ordering degree) which cause a lower rate of film degradation. It should also be noted that the change in grain sizes for modified films causes the presence of a larger number of dislocations and grain boundaries, in comparison with CdSe films, which helps to restrain the mechanisms of oxygen diffusion deep into the films, due to the creation of additional obstacles on the path of the introduced ions, which have a sufficiently high mobility and the ability to create additional deformation distortions in the structure due to the introduction into the interstices of the crystal lattice, thereby deforming it, and also creating complex or cluster defects, the presence of which leads to film degradation. In the case of modified films, the dispersion hardening effect (associated with a reduction in grain size and an elevation in dislocation density), the migration rate is significantly reduced, which is confirmed by low degradation rates of the pollutant adsorption efficiency. It should also be noted that changing the pollutant type does not have a significant effect on the degradation rate (the difference in the maximum reduction in ΔAE is no more than 0.1–0.2 % when changing the pollutant type during adsorption after 5 consecutive cycles).

3.3. Determination of the influence of the number of heavy metal adsorption cycles on the change in optical (band gap) and strength parameters

Graph 6 illustrates the dependences of the change in the band gap value of the studied films contingent upon the number of cycles of cyclic tests aimed at studying the preservation of the stability of the adsorption efficiency of heavy metals using films during repeated use. Analysis of the obtained data on the changes in the value of E_g depending on the number of test cycles revealed that the least stable preservation of the bang gap is exhibited by CdSe films, for which the shifts of the fundamental absorption edge are observed after 2–3 cycles, and the maximum change after 5 test cycles is more than 3.8–4.1 %. In this case, the change in the E_g value for NiCdSe and CoCdSe films after 5 test cycles is about 2.5–2.8 % and 1.9–2.1 %, respectively, which indicates that partial substitution makes it possible to increase the stability of film degradation by inhibiting the effects associated with corrosion and the introduction of oxygen, the appearance of which in the film composition leads to a shift in the fundamental absorption edge and, as a consequence, an increase in the E_g value. It should also be noted that the change in the bandgap width after 5 cycles for the studied films is not so significant in comparison with the value of the decrease in the adsorption capacity efficiency of the films, especially for CdSe films, from which it can be concluded that the adsorption efficiency reduction is more influenced by changes associated with morphology and degradation of strength characteristics caused by oxidation processes than by the fundamental absorption edge shift.

One of the important parameters determining the potential for using films as catalysts is not only their adsorption efficiency, but also the maintenance of this parameter over several cycles of successive tests, as well as the relationship between the decrease in adsorption efficiency as a result of cyclic tests and strength, structural and optical parameters. Fig. 7 reveals the assessment results of the change in strength parameters (microhardness and adhesive strength) after 1, 3 and 5 test cycles,

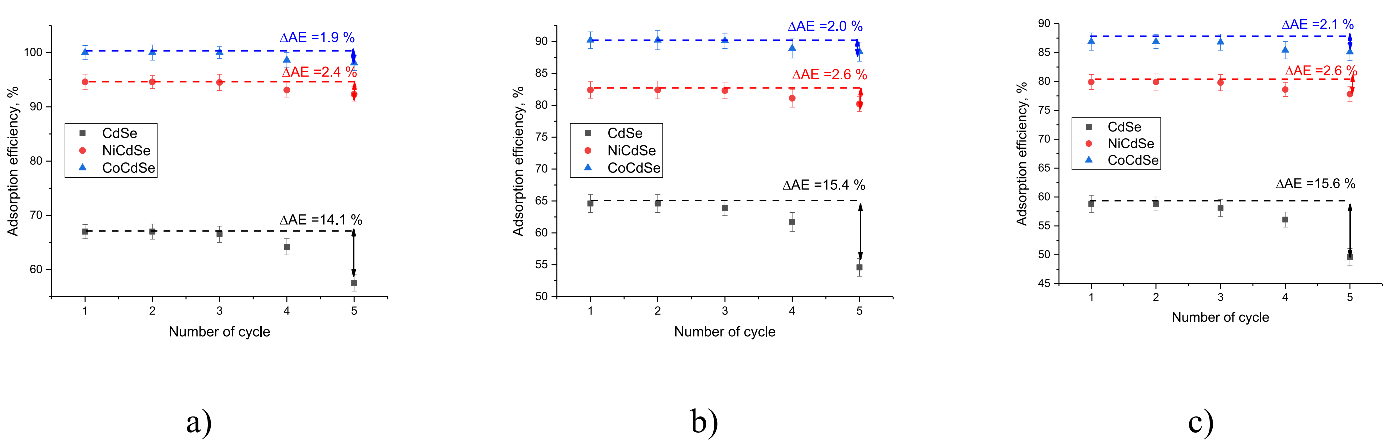


Fig. 5. Assessment results of changes in the adsorption capacity efficiency of thin films with an increase in the number of consecutive test cycles: a) during iron adsorption; b) during manganese adsorption; c) during arsenic adsorption.

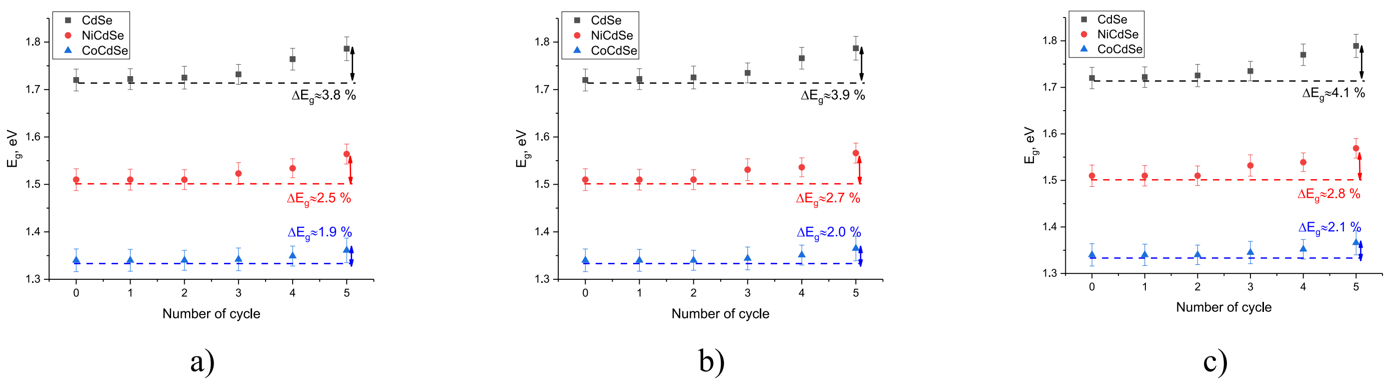


Fig. 6. Results of changes in the band gap value of the studied films contingent upon the number of test cycles: a) during iron adsorption; b) during manganese adsorption; c) during arsenic adsorption.

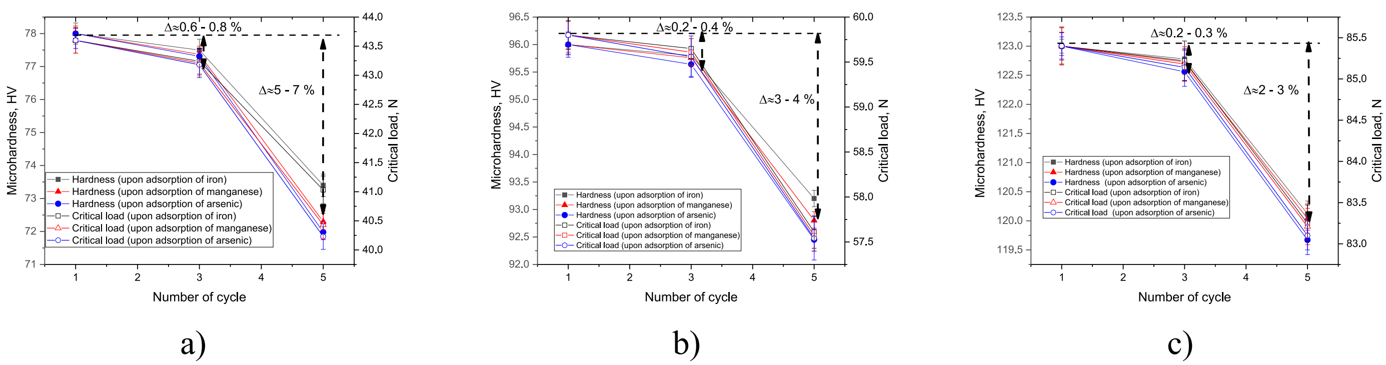


Fig. 7. Results of changes in the strength parameters of the studied films in the case of cyclic tests for maintaining the efficiency of catalytic activity: a) CdSe films; b) NiCdSe films; c) CoCdSe films.

reflecting the degradation of strength parameters, as well as the degradation rate caused by the processes of destructive change in films associated with both adsorption processes and oxidation processes initiated during long-term exposure to the environment. The general appearance of the presented changes in microhardness and adhesive strength with a rise in the number of test cycles indicates a decrease in strength characteristics due to degradation and oxidation processes (the introduction of oxygen from aqueous solutions into films with the subsequent creation of deformed inclusions). Moreover, the nature of the observed changes is different depending on the type of films, which indicates the influence of the substitution effect not only on the adsorption capacity of films in the case of their modification, but also an increase in resistance to degradation during repeated use of films. In this case, small grain sizes resulting from the addition of nickel or cobalt sulfates to the electrolyte and, as a consequence, leading to the occurrence of the effect of dislocation hardening, create barrier obstacles that enhance not only stability and adhesion to the substrate surface, but also resistance to oxidation processes. At the same time, an increase in the number of test cycles leads to a more pronounced change in strength parameters, which indicates an acceleration of the processes of destruction of the film surface, due to the accumulation of deformation distortions in the structure caused by oxidation.

Inhibition of oxidation processes due to the substitution effect in this case plays a very important role in determining the service life, due to the fact that when the adhesive strength decreases as a result of long-term testing, the effect of peeling of films from the substrate and their fragmentation in the aquatic environment may occur, which in turn can lead to contamination of the aquatic environment not only with heavy metals, which were already present in it, but also with the material of the films in the form of particles or larger inclusions.

Fig. 8 demonstrates the results of a comparative analysis of changes in tribological tests of the studied films depending on the number of test cycles, reflecting the degradation of the film surface as a result of adsorption processes. The data are given for films after 1, 3 and 5 consecutive test cycles, reflecting the degradation kinetics associated with softening processes, the results of which were presented in Fig. 7.

The obtained dependences of the change in the dry friction coefficient for the studied films with a change in the type of pollutant showed a similar trend of decreasing wear resistance as in the case of a change in strength parameters, which indicates a small contribution of the type of sorbed element to the rate of degradation of the films, which in this case depends on the time spent in the environment, as well as the terms of its operation. In turn, the observed decrease in wear resistance, expressed in an increase in the coefficient of dry friction, indicates a decrease in the strength properties of films used repeatedly (for 3 and 5 cycles), which can result in their accelerated degradation under mechanical impact. Moreover, the presence of the dispersion hardening effect in modified films results in significant growth in the wear resistance of films, and the value of changes in the dry friction coefficient with a change in the number of test cycles in the case of modified films is no more than 10–15 % in comparison with the observed trend of changes in the dry friction coefficient of films not tested as catalysts.

4. Conclusion

According to the test trials of the studied samples for wear resistance under mechanical friction, it was found that the replacement of cadmium and selenium with nickel and cobalt leads to an increase in wear resistance, as well as an increase in resistance to tearing off from the template surface. It should be noted that the highest resistance indicators are shown by films with the addition of cobalt in comparison with unmodified CdSe films.

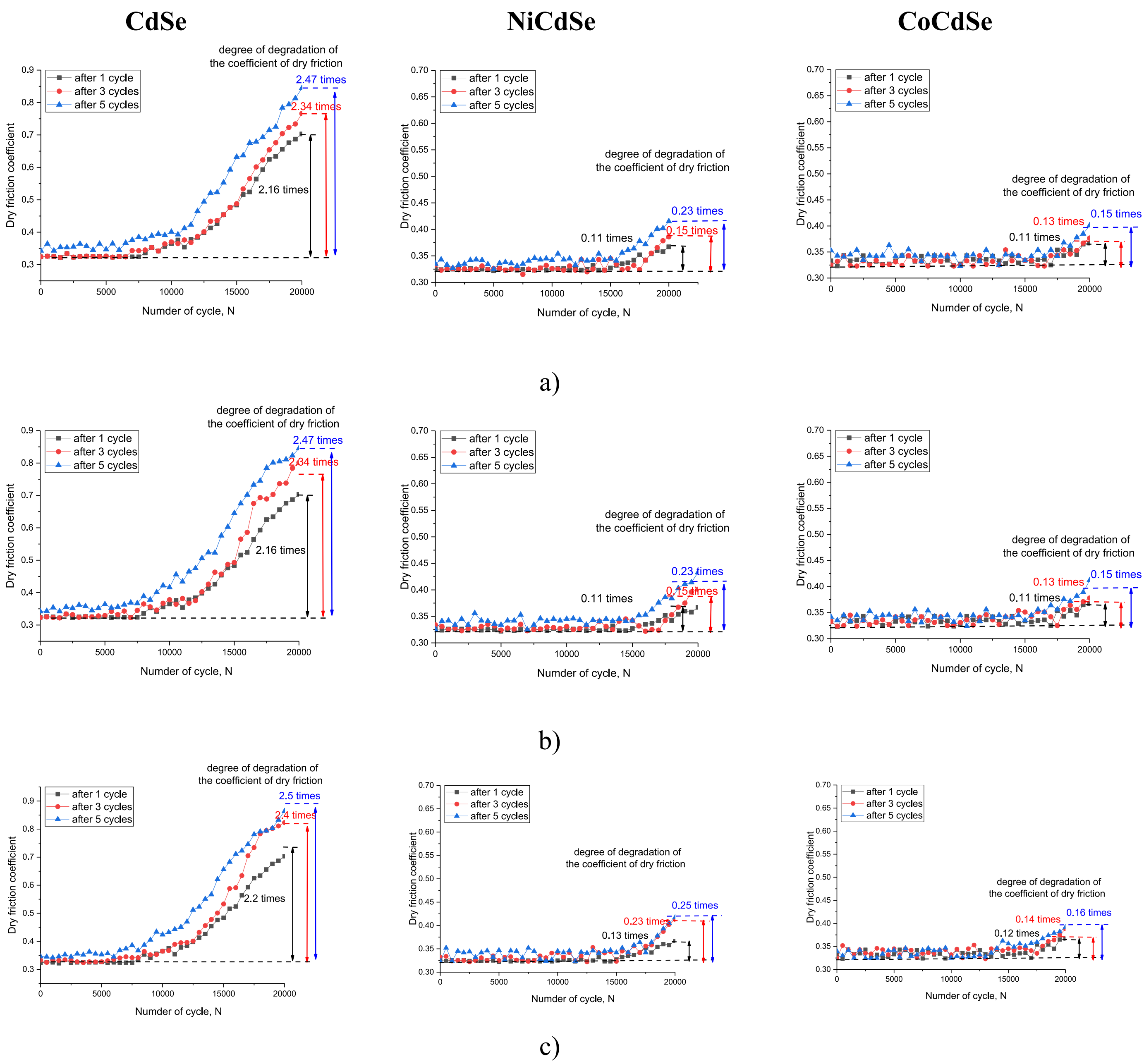


Fig. 8. Results of tribological tests of the studied films after cyclic tests for maintaining the efficiency of catalytic activity: a) during iron adsorption; b) during manganese adsorption; c) during arsenic adsorption.

The use of modified NiCdSe and CoCdSe thin films as catalysts makes it possible to achieve adsorption efficiency of about 85–95 % with 60 min of adsorption reactions, while the efficiency of CdSe films was about 55–60 % in the case of low pollutant concentrations in the model solution.

It should be noted that a rise in the pollutant concentration in the model solution from 10 to 20 mg/dm^3 leads to a slight reduction in the adsorption efficiency for modified films, while an elevation in the concentration to 50 mg/dm^3 results in the adsorption efficiency reduction for CdSe films by approximately 15–20 %, depending on the type of pollutant being sorbed.

The results of cyclic tests revealed the effectiveness of film modification by partial substitution, which is expressed in maintaining high adsorption indices during a larger number of cycles in comparison with CdSe films. At the same time, the degradation resistance growth during cyclic tests in this case for modified films is due to dispersion hardening associated with the effect of small grains. It should also be noted that the greatest contribution to the reduction in adsorption efficiency when analyzing changes in optical properties, as well as assessing strength parameters, is made by changes associated with the degradation of the film surface due to oxidation processes and distortion of the crystalline structure, expressed in a destructive reduction in strength parameters.

Summarizing the obtained results, it can be concluded that the use of the proposed method for enhancement of the adsorption efficiency of heavy metals from aqueous media by partial substitution of nickel or cobalt for cadmium and selenium in the composition of films obtained by electrochemical deposition is very promising in terms of creating an inexpensive technology for creating highly effective catalysts for cleaning aqueous media from pollutants.

Institutional review board statement

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CRediT authorship contribution statement

Aliya Zh Omarova: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Artem L. Kozlovskiy:** Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Gulnaz Zh Moldabayeva:** Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

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.

Data availability

No data was used for the research described in the article.

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