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Congo red photocatalytic degradation on the copper nanoparticles deposited on carriers

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ABSTRACT

Photocatalytic removal of dyes from aqueous solutions is an important process in the context of environmental protection due to synthetic dyes are common pollutants that are difficult to biodegrade and have negative impacts on ecosystems. The aim of the present work was to compare photocatalytical properties of copper nanoparticles deposited on two inorganic carriers: gamma alumina and natural clinoptilolite type zeolite. Copper-containing samples (4.5 wt. % of Cu) were obtained by impregnation of copper nitrate and its reduction with ascorbic acid. Catalysts were characterized by means of XRD, XRF, TEM, SEM, and low temperature nitrogen adsorption/desorption. The formation of nanoparticles was confirmed by TEM images. Particles predominant dimension for both samples was 2-3 nm. However, zeolite sample possesses some bigger agglomerates of 30 nm. Based on XRD data it is suggested that nanoparticles have core-shell structure and consist of Cu⁰ core and Cu₂O shell. Photocatalytic degradation of Congo Red solutions was carried out. Both catalysts were active in decolorization and can be used as effective photocatalysts, but Cu-alumina sample activity prevails under the Cu-zeolite ones. Its better performance supposed to be connected with better sample mesoporosity and higher part of nanoparticles of 2 nm dimension.

INTRODUCTION

Organic dyes, which are widely used in the textile, paper and plastics industries, are ones of the main pollutants of natural water nowadays. Dyes such as methylene blue, crystal violet and Congo red are usually bioresistant, that is, resistant to natural degradation, because they have a stable chemical structure and a high level of chemical oxygen demand, which causes significant pollution of water bodies. The presence of these substances in wastewater leads to environmental problems, as they are toxic to aquatic organisms and carcinogenic to humans, making them dangerous for both ecosystems and human health.

Wide used methods of water treatment like as coagulation, flocculation, adsorption, and biological treatment are unsuitable for dye degradation especially in the case of high concentration of dyes. One effective approach to removing such pollutants is the use of photocatalytic materials that decompose dyes under the influence of light. It is believed that photocatalytical degradation of organic substances is the most progressive nowadays technique [1-3]. In this case, which is a

form of advanced oxidative technology, strong and non-selective hydroxyl radicals are formed, which are able to effectively decompose dyes into environmentally safe compounds such as water, carbon dioxide, and mineral salts.

One of the most widespread photocatalyst is titanium oxide [4-6]. TiO_2 is a gold standard in photocatalysis. It is highly stable, non-toxic, and inexpensive. It can primarily absorb UV light due to its wide band gap. However, other metal oxides also occupy an important place among common photocatalytic materials. For example zinc and bismuth oxides, tin and cerium dioxides, complex oxides or CdS are very popular photocatalysts [7]. The combination of ZnO with zeolite carrier showed higher effectivity of the catalyst [8] in dyes degradation as well. Another way to improve effectiveness is to use the metal additives. It could be noble or transition metals.

Copper is one of the most popular, cheap, and most effective element for improving photocatalysts. Unlike precious metals such as platinum, gold or silver, copper is an affordable alternative that radically changes the performance of basic semiconductors such as titanium dioxide [9]. In addition to the pure metal, copper oxides Cu_2O and CuO are also actively used in photocatalysis [10-13]. Being semiconductors with a narrow band gap, they are excellent absorbers of visible light. They are often combined with TiO_2 to create so-called heterojunctions, where charges are effectively separated between two materials. Numerous copper-based photocatalysts have recently been reported. They include cupric oxide (CuO) [14], cuprous oxide (Cu_2O) [15], copper monosulfide (CuS) [16], copper selenide (CuSe) [17], copper tungstate (CuWO_4) [18] and copper iron oxide (CuFe_2O_4) [19]. Most copper-based catalysts can achieve good photocatalytic efficiency when their single material is used as a photocatalyst. Many researchers have made numerous attempts to find a variety of methods for enhancing photocatalytic efficiency to improve the efficiency of single copper-based photocatalysts. The main methods include controlling size and morphology, controlling crystal surfaces, doping other elements and forming heterojunctions [11].

It is well known that the use of materials in the form of nanoparticles significantly increases their catalytic activity [20-23]. Gamma alumina and porous aluminosilicates are not semiconductors, but they have large surface area, which makes them good carriers for copper. The application of the latter in the form of nanoparticles on a significant surface will contribute to its less agglomeration and increase the efficiency as a photocatalyst. Moreover, such heterogeneous catalysts are very convenient for separation from reaction mixture and reuse.

Therefore, the aim of the paper was to obtain the copper nanoparticles on gamma alumina and natural zeolite as well as compare the photocatalytic degradation of Congo red in their presence.

EXPERIMENTAL

Synthesis of the samples

The catalyst samples were synthesized using commodity natural zeolite-containing rock (Sokyrnytsia village, Transcarpathian region, TU U 14.5.002.922540.001-2001) and gamma alumina (DSTU 8136-85, JSC "Katalizator", Kamianske, Ukraine). The chemical composition of the clinoptilolite rock tested by XRF was: SiO_2 – 75.6%; Al_2O_3 – 10.7%; Na_2O – 0.11%; MgO – 0.95%; CaO – 5.98%; K_2O – 3.67; Fe_2O_3 – 3.03%. Initial sample was crushed and the fraction 0.5-1 mm was sieved. To improve a narrow-pored natural clinoptilolite porous system, it was

previously treated by ethylenediaminetetraacetic acid (EDTA) according to the procedure described in [24] for dealumination and some pore expansion.

In order to obtain copper nanoparticles both carriers were calcined at 380 °C for 2 hours. Then they were impregnated with copper nitrate solution at a moisture content of 4.5 wt. % of copper and dried at room temperature for 24 hours. Ascorbic acid was used for copper reduction [25]. To start with, the samples were suspended in water. The solid to liquid phase ratio was 1:10. Ascorbic acid was utilized in two-fold excess. Its solution was dropped with a rate of 10 ml/h via a syringe pump. The resulting mixture was stirred at 80-85°C for 5 hours. Following that, the suspension was left overnight. In the morning the samples were filtered and air-dried. The filtrate was analyzed quantitatively for Cu²⁺ ions using a photocolormetric method. The Cu content in the samples was determined based on the above analysis and XRF-ray fluorescence technique.

Methods

Textural properties were investigated utilizing low-temperature (-196 °C) nitrogen adsorption/desorption. Isotherms were measured using a Quantachrome Autosorb NOVA 1200e automatic sorbometer following *in situ* vacuumization. The alumina samples were activated at 290 °C for 6 h and the zeolite ones for 12 h. The parameters of the porous structure of the samples were calculated using the NOVWin™ software: specific surface area S^{BET} – using the multipoint BET method; specific surface area excluding micropores S^t and micropore volume V^t_{micro} – using the t-method; micropore surface – using the formula S_{micro} = S^{BET} – S^t; total pore volume V_Σ – using the volume of adsorbed nitrogen at P/P₀ > 0.99; average pore size R – assuming their cylindrical shape using the formula R = 2V_Σ/S^{BET}; pore size distribution was calculated using the BJH and DFT methods.

The samples were further investigated using transmission (TEM, JEM-1400, JEOL) and scanning electron microscopy (SEM, Phenom Pure, Thermo Scientific). For TEM the samples were previously suspended in the ethanol and impregnated on the copper grids coated with formvar carbon film.

X-ray diffraction (XRD) was performed using Mini-Flex 300/600 diffractometer (Rigaku, Japan) with Cu-Kα radiation (λ = 0.15418 nm), an operating voltage of 40 kV, and a current of 15 mA. XRD patterns of samples were analyzed in the range 2°-100° with a step of 0.02°.

X-ray fluorescence (XRF) analysis was used to determine the silver content in the obtained samples (Oxford Instruments X-Supreme 8000 analyzer, Great Britain).

The photocatalytic properties were studied using the laboratory setup (Fig. 1), which consists of a magnetic stirrer, a glass beaker of 100 cm³, and an ultraviolet mercury lamp (254 nm, 24 V). Water solutions of Congo Red (CR) dye with a concentration of 8, 15, and 25 mg/L were previously prepared. To start with, a sample of catalyst (0.01 g) was added into the dye solution. The suspension obtained was stirred on a magnetic stirrer for 5 minutes at 700 rpm. Then, an ultraviolet lamp located above the magnetic stirrer was turned on, and the rotation speed was reduced to 350 rpm. The exposure time used was from 1 to 10 min. The change in dye concentration was determined spectrophotometrically.

The photocatalytic properties of the samples were evaluated by the degree of decolorization of the Congo Red solution:

$$X = \frac{A_0 - A_x}{A_0} \cdot 100\%,$$

where A_0 – optical density of the original dye solution;
 A_x – optical density of the dye solution after photocatalysis.

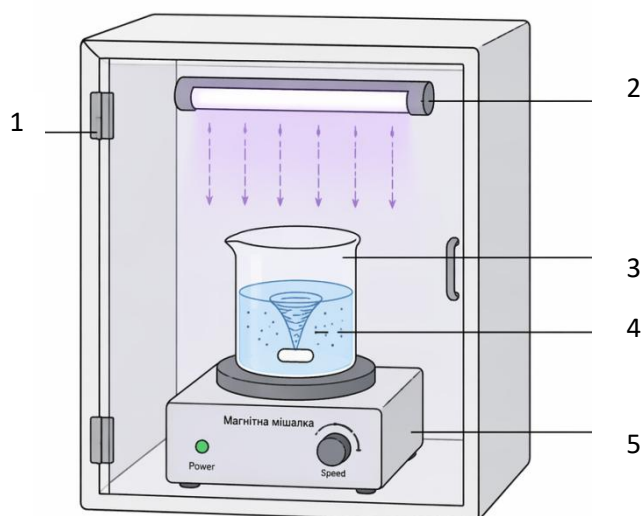


Fig. 1. Scheme of catalytic set-up: 1 – box, 2 – UV lamp, 3 – beaker, 4 – stirrer, 5 – magnetic stirrer

3 Results and discussion

3.1 Characterization of the samples

Photocolorimetric examination of the filtrates revealed a copper concentration of 4.3 wt.% in gamma alumina $\text{Cu-Al}_2\text{O}_3$ sample and 4.2 wt.% in the case of Cu-clinoptilolite sample.

The copper content in $\text{Cu-Al}_2\text{O}_3$, according to X-ray fluorescence analysis, was 4 wt.%, and 8 wt.% in Cu-Clin. The latter can be influenced by an uneven distribution of copper on the sample surface and its predominant localization on the outer surface of zeolite crystals, since this method provides surface and near-surface analysis of the chemical composition.

Low-temperature nitrogen adsorption/desorption isotherms of the starting materials and samples with copper deposited are shown in Fig. 1. The porous characteristics, calculated from the data obtained, are given in Table 1.

Table 1. Porous characteristics of synthesized samples and corresponding carriers

Sample	S^{BET} , m^2/g	S^{t} , m^2/g	$S^{\text{t}_{\text{micro}}}$, m^2/g	$V^{\text{t}_{\text{micro}}}$, cm^3/g	V_{Σ} , cm^3/g	$V_{\text{micro}}/$ V_{Σ} , %	R^{DFT} , nm	$R^{\text{BJH(ads)}}$, nm	$R^{\text{BJH(des)}}$, nm	R , nm
Clin	12.51	6.99	5.53	0.002	0.026	7.75	2.64	2.70	2.00	4.13
Clin-EDTA	88.21	10.50	78.10	0.036	0.061	59.00	0.97	1.52	1.98	1.38
Cu-Clin	61.88	15.71	46.17	0.021	0.059	35.59	1.17	1.51	1.98	1.91
$\gamma\text{-Al}_2\text{O}_3$	218.24	194.48	23.77	0.007	0.571	1.23	2.64	1.78	1.98	5.23
$\text{Cu-Al}_2\text{O}_3$	224.44	212.59	11.85	0.001	0.630	0.16	2.54	1.62	1.82	5.61

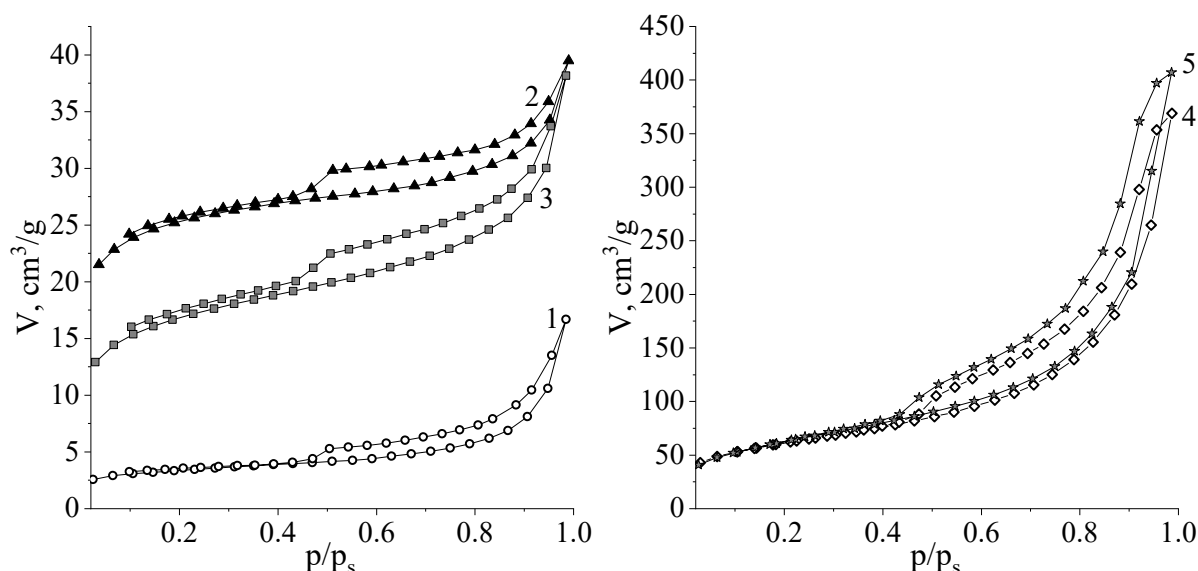


Fig. 1. Low-temperature nitrogen adsorption/desorption isotherms of carriers and copper-containing samples: 1 – Clin, 2 – Clin-EDTA, 3 – Cu-Clin-1, 4 – γ - Al_2O_3 , 5 – Cu- Al_2O_3

Industrial gamma alumina is widely used support with advanced mesoporous system with minimal number of micropores with common isotherm of IV type according to IUPAC classification [26]. It possesses a large hysteresis loop. The zeolite samples characterized by combined type I and type IV isotherm as microporous material with some mesoporous characteristics. Access of nitrogen to the micropores of zeolite is complicated by the presence of impurities. After dealumination with EDTA the BET surface area increased significantly, but preferably due to microporosity raising. The initial clinoptilolite has channels of 0.31×0.75 nm, 0.36×0.46 nm and 0.28×0.47 nm [27], the size of which is slightly expanded according to the Barrett-Joyner-Halenda pore radius data to 1.52-1.98 nm after EDTA treatment. However, apparently, copper nanoparticles still could not penetrate in such pores. It seems that EDTA leached some rock impurities and gives better entrance for nitrogen into micropore system. After copper deposition part of micropores were blocked by copper nanoparticles in the zeolite and alumina samples. As a result, S_{micro} reduced in both cases.

Copper nanoparticles were expected to be equally distributed across the whole surface of mesoporous alumina, whereas in microporous clinoptilolite, they were kept on the external surface. Furthermore, in the zeolite, they blocked the channel entrances, preventing nitrogen from entering the microporous system.

DFT-based pore size distributions for all samples are shown in Fig. 2. In zeolite rock we practically do not see microporosity at all. After dealumination the high pick of micropores near 2 nm diameter appeared and the number of mesopores of 5 nm also increased. In the case of alumina, after copper deposition the number of mesopores of 5 nm decreased but the number of pores of 7-25 nm increased.

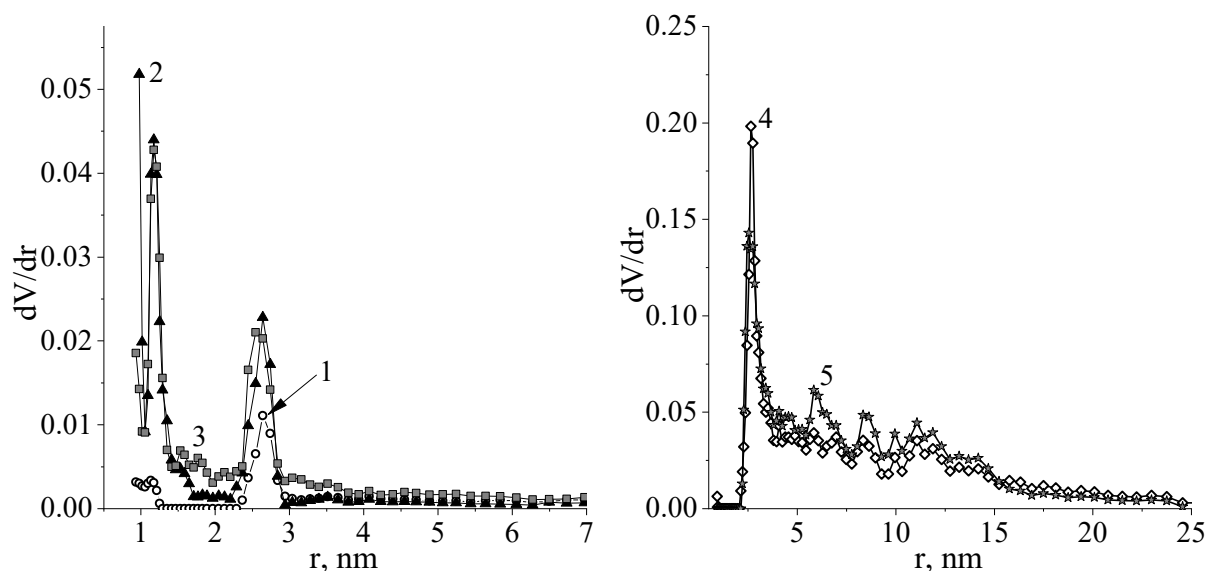
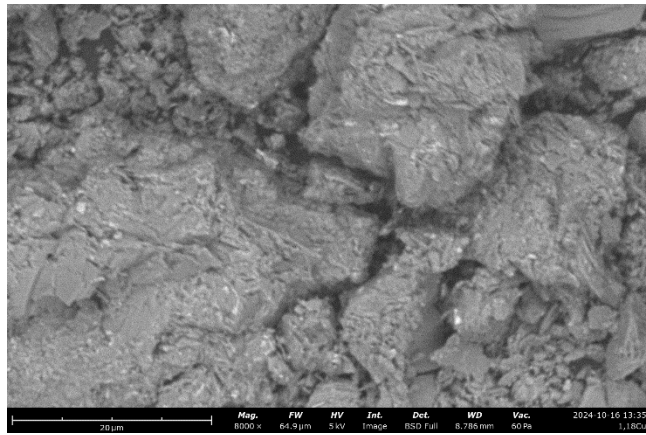


Fig. 2. DFT pore size distribution for zeolite- and alumina-based samples: 1 – Clin, 2 – Clin-EDTA, 3 - Cu-Clin, 4 – γ - Al_2O_3 , 5 - Cu- Al_2O_3

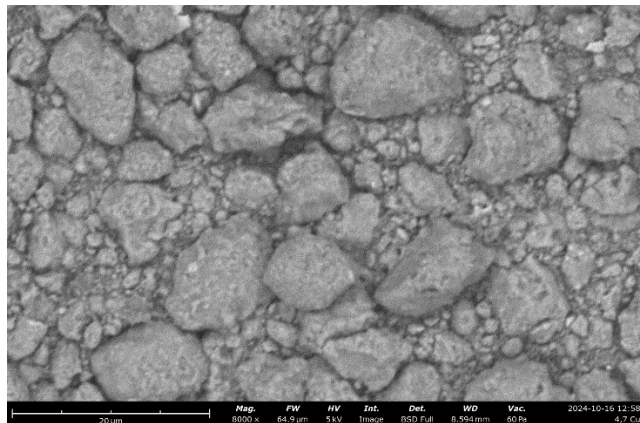
SEM analysis of zeolite and alumina samples (Fig. 3) revealed that Cu-Clin contains heterogeneously sized fragmented particles with sharp edges and irregular boundaries. Particles agglomerate significantly when smaller fractions are concentrated on the surface of larger conglomerates. In general, the observed image is consistent with a crushed natural mineral [28]. The Cu- Al_2O_3 sample has a more homogenous structure, with rounder granules [29]. The particles have a comparatively smooth surface and a more consistent size distribution than the clinoptilolite sample.

High-contrast inclusions (white speckles) of submicron size may be found on the surfaces of both samples particles. The latter enhanced brightness as compared to the main matrix shows a local concentration of metal components. On clinoptilolite, white inclusions appear to be randomly scattered particles of varied shapes. On alumina, brilliant spots appear as tiny inclusions inside the matrix structure. Copper is dispersed inhomogeneously in the first sample, with the metal phase localized as distinct agglomerates around the corners and edges of the major particles. This morphology could suggest that copper is deposited mostly on surface defects. In the second sample, the deposited copper has a wider dispersion. The metal inclusions are smaller and more uniformly dispersed on the granules surfaces.

The picture looks to be the product of a zeolite microporous structure and an alumina mesoporous system. Nanoparticles were only formed on the exterior surface due to the existence of micropores, which are too tiny to allow copper precursors to spread throughout the structure. This resulted in the formation of enormous surface agglomerates of copper, which may be seen as bright massive inclusions on particle edges. A developed mesopore system allows copper to penetrate deeply into the carrier's volume. This led in a high metal dispersion: a large percentage of the copper is trapped inside the pore space, while the rest emerges on the surface as tiny, uniformly dispersed point inclusions.



a



b

Fig. 3. SEM images: a – Cu-Clin, b – Cu-Al₂O₃

The TEM study of copper-containing samples (Fig. 4) on copper grids coated with formvar after ultrasonic dispersion in alcohol shows that the primary sizes of copper nanoparticles were always between 2 and 5 nm. However, in the case of zeolite, smaller particles with a diameter of 1 nm and individual huge agglomerates up to 40 nm are also detected, while in the case of alumina, larger ones are not presented (only some of 5-10 nm). In Figure 5 the nanoparticles distribution on both samples is shown.

The Cu-Clin sample consists of massive, dense aggregates. They have a "monolithic" look, with clear edges [30]. Figure 3b depicts a dark, spherical region located on top of the zeolite crystals. Smaller black inclusions are visible against the mineral backdrop, however they are irregularly dispersed on the zeolite carrier. The Cu-Al₂O₃ sample has a porous spongy structure, similar to aluminum oxide, resulting in branching nanostructures or tiny flakes [31]. Small contrasting areas of deposited copper can be observed evenly throughout the matrix.

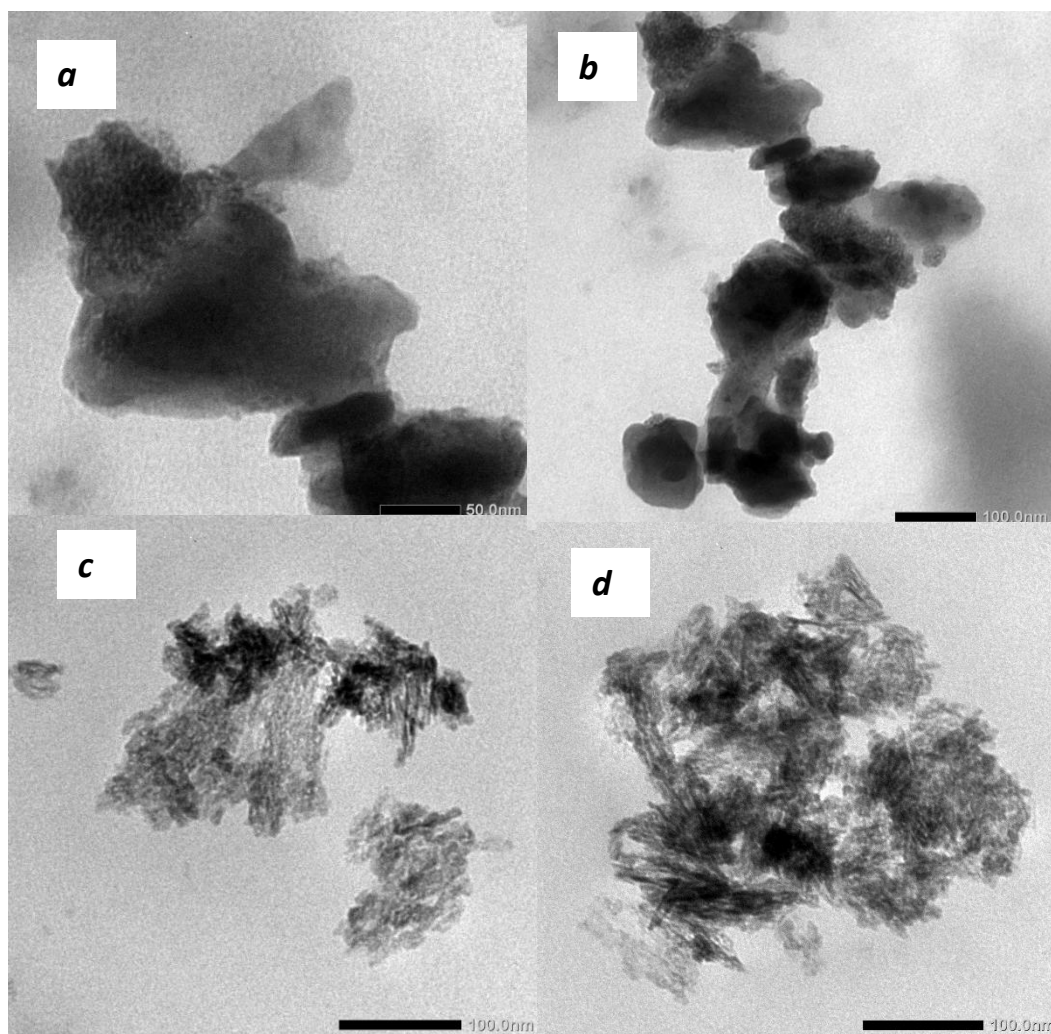


Fig. 4. TEM images: a, b - Cu-Clin; c, d - Cu-Al₂O₃

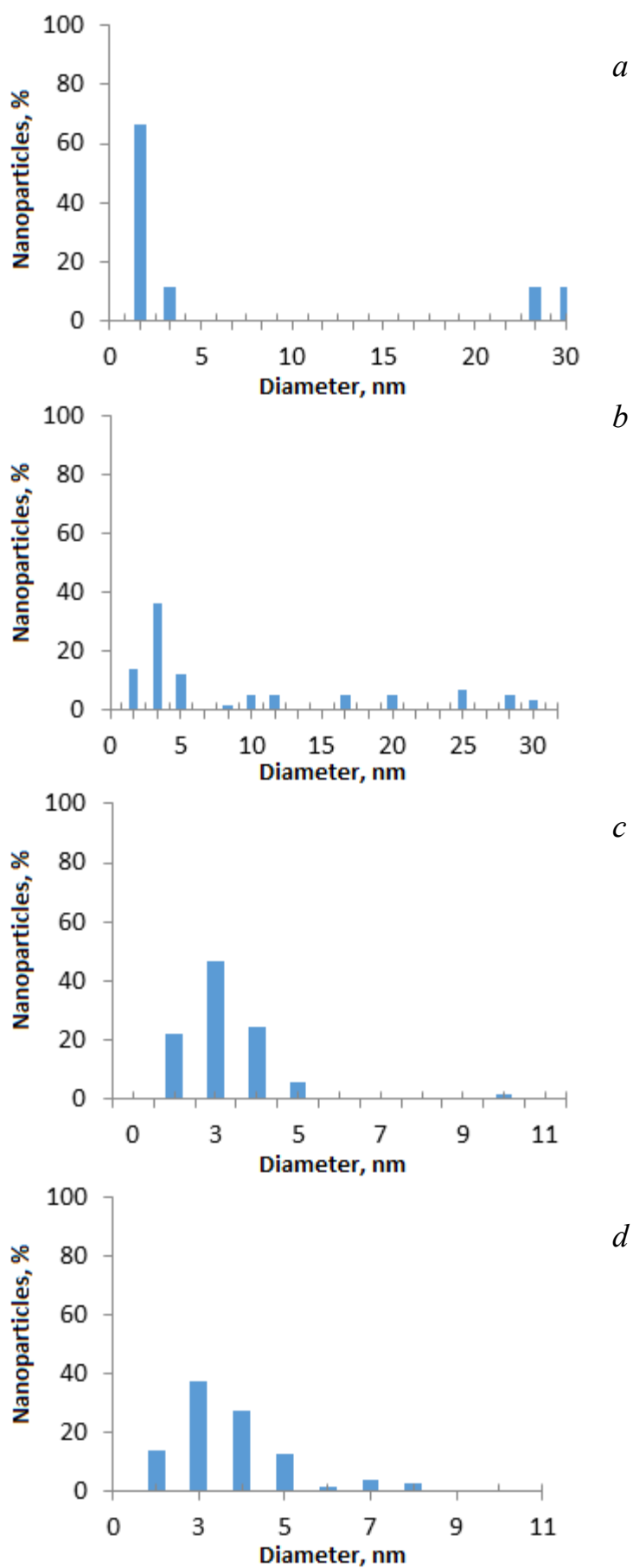


Fig. 5. Particles size distribution from TEM images: a, b - Cu-Clin; c, d - Cu-Al₂O₃

Nanoparticles in the 2.5–3 nm range are the dominant species in both samples. However, the nanoparticles on the aluminum oxide surface exhibit a narrower size distribution (2.5–5 nm), with only a small fraction (up to 10%) reaching sizes of up to 10 nm. In contrast, for the zeolite — evidently due to its greater surface heterogeneity and lower specific surface area — larger agglomerates (up to 30 nm) are formed, accounting for up to 30% of the total species.

Following copper application and reduction, both diffractograms shown in Fig. 6 reveal peaks confirming the existence of face-centered cubic structures of metallic copper (43, 50, 74°, JCPDS no. 04-0836) with various intensities. They are strongest for Cu-alumina and weaker for Cu-zeolite.

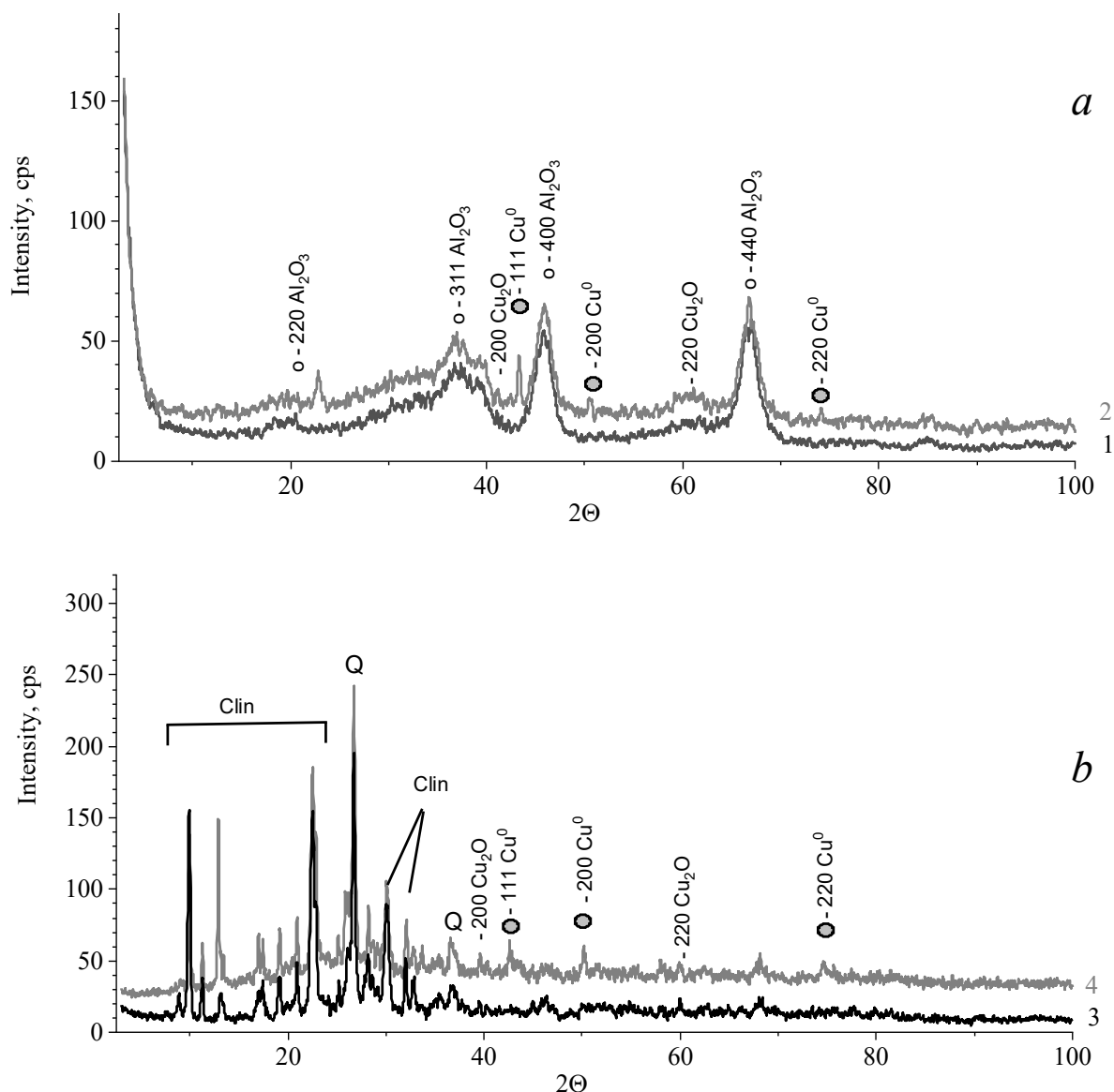


Fig. 6. XRD patterns: a - Al₂O₃, b - clinoptilolite; 1 - Al₂O₃, 2 – Cu-Al₂O₃, 3 – clinoptilolite, 4 – Cu-Clin. Clin – clinoptilolite, Q – quartz

Cu-containing samples diffraction patterns also show tiny reflections at 42.3 and 61.4 2θ, which may indicate a low level of Cu₂O (JCPDS 05-0667) in the samples. Unfortunately, the major line of Cu₂O at 36.4 ° overlapped with strong gamma alumina and quartz signals. Thus, the diffraction image reveals the existence of a small quantity of oxidized copper. The "shell-core"

structure is thought to be generated by combining a metallic copper core with a thin cuprous oxide shell due to the susceptibility of copper to easy oxidation by atmospheric oxygen. Cu_2O nanoparticles shown high activity as photocatalyst in CR degradation [32], which depends on their morphology. In [33] employed Cu_2O nanowhiskers to photodegrade *p*-chloronitrobenzene.

The results of photocatalytic investigations are shown in Figure 7. The $\text{Cu-Al}_2\text{O}_3$ sample demonstrates high level of dye degradation (98-99 %) with all three dye solutions (Figure 7a). In the case of Cu-zeolite sample, the lowest concentration of dye (8 mg/L) could be destroyed practically totally, but the catalyst effectiveness decreases when concentration rises.

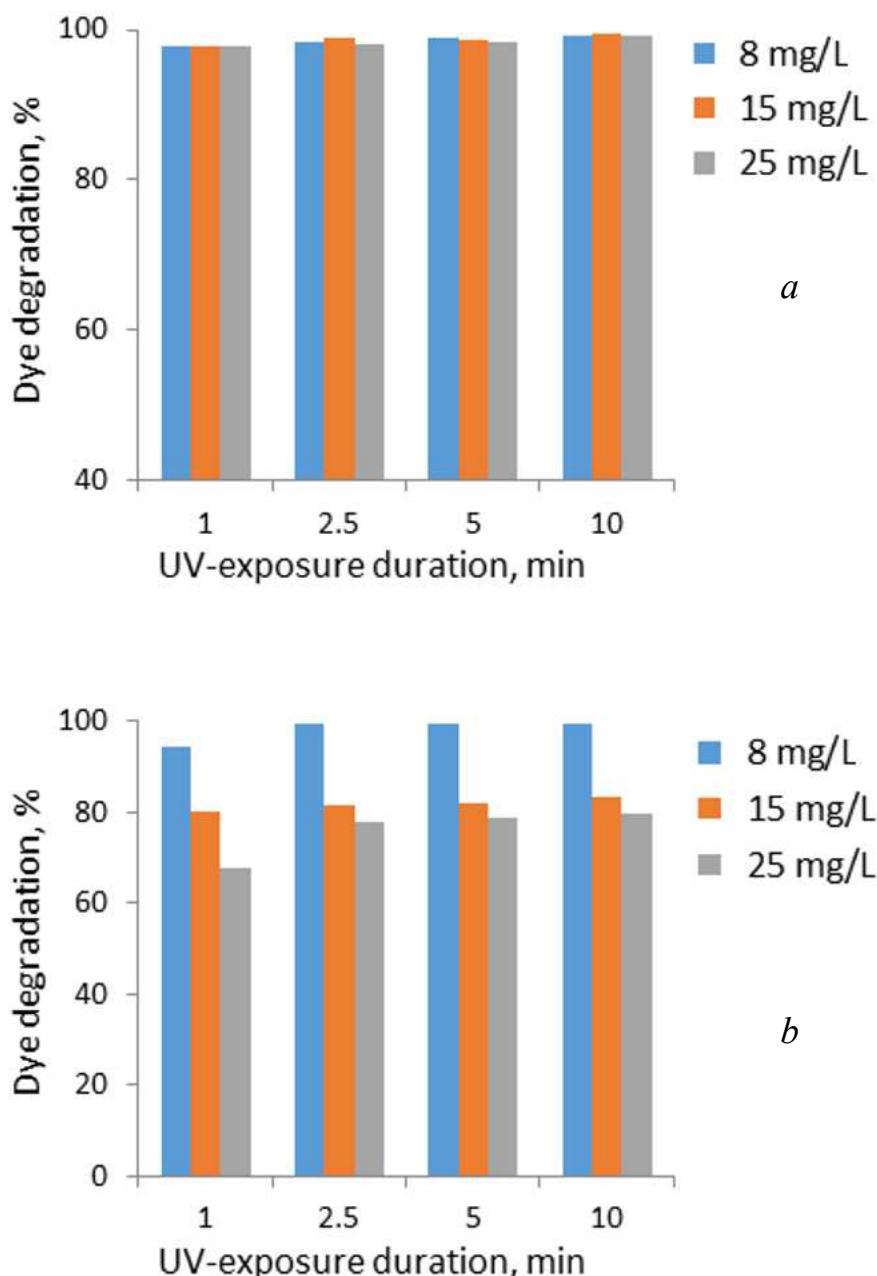


Fig. 7. Congo red solution decolorization on copper-based samples: a – $\text{Cu-Al}_2\text{O}_3$, b – Cu-Clin

With a purpose to improve the level of dye degradation on zeolite sample without significant exposure time raising the bigger weight of catalyst was used. In Figure 8a the difference in catalyst

performance on 15 mg/L dye solution at 0.01 and 0.02 g of catalyst is shown. In the last case, the appropriate degradation level could be achieved at 10 min. It is increasing from 90 to 98 % in 10 min. In case of CR concentration of 25 mg/L we obtained high levels of degradation only at 0.05 g of catalyst (Fig. 8b).

Therefore, varying the weight of Cu-zeolite catalyst practically complete degradation of CR solutions of 8-25 mg/L could be achieved.

Why Cu-Al₂O₃ sample is more active than Cu-zeolite? Both samples have similar predominant size of copper nanoparticles. In [34] experimentally it has been concluded that photocatalytic activity bears a close relationship with exposed crystal planes, surface area, and particle size of Cu₂O. In our case we have similar particles size, but different BET surface of the samples. We supposed that, first of all, different activity is connected with porous structure of the carriers. Alumina has substantially bigger BET surface area and bigger mesopores size in comparison with clinoptilolite. There is diffusion limitation for CR molecules (0.9x22 nm) penetration into the porous structure of clinoptilolite. It seems as EDTA modification was not successful for significant mesoporosity improving. Maybe it would be better to use strong mineral acids like HCl or HNO₃, which as a rule leads to better pores expansion [30]. From other side, Cu-Clin zeolite sample possesses above 30 % of copper nanoparticles agglomerates up to 30 nm. Consequently, such larger nanoparticles may exhibit lower activity [22, 23], which is one of the reasons for the lower performance observed with the zeolite sample.

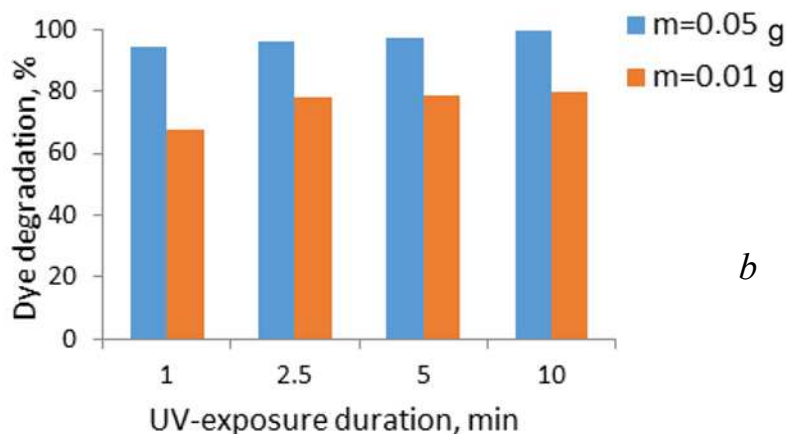
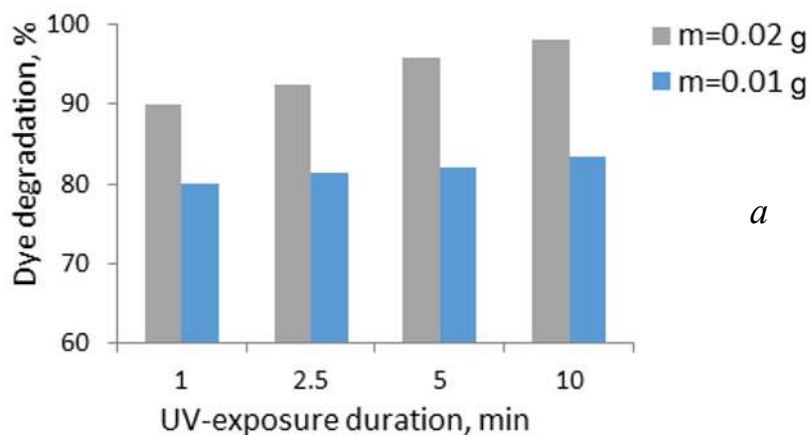


Fig. 7. Congo red solution decolorization on Cu-Clin: a – 15 mg/L, b – 26 mg/L

If comparing the results obtained with ZnO-zeolite composites activity in CR decolorization [8], it can be noted that on 8 mg/L solution the performance of both zeolite-containing samples are similar in spite of different content of active ingredient and different types of zeolites. In this work it is only 4.5 wt.% of copper and it was 20 % of ZnO in [8].

CONCLUSIONS

High active copper nanoparticles based photocatalysts were synthesized. The formation of nanoparticles was confirmed by TEM. The particle diameter of 2-3 nm was comparable for both samples, but zeolite sample possesses some bigger agglomerates. According to porous peculiarities of samples it could be concluded that in case of zeolite only outer surface with copper nanoparticles work in the reaction.

From XRD data it could be suggested that nanoparticles have core-shell structure. They consist from a bulk Cu⁰ core and a thin Cu₂O shell. Both samples were active in decolorization of solutions and might be utilized as photocatalysts, although the Cu-zeolite sample inferior to Cu-gamma alumina. It is assumed that its superior activity is due to the sample high mesoporosity and high content of 2 nm nanoparticles. It is shown that the efficiency of zeolite samples increases when the catalyst loading increases.

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