

PREPARATION AND CATALYTIC ABILITY OF NOVEL
MANGANESE CARBONATE ORE/COPPER AND
COBALT OXIDE-BASED COMPOSITES FOR OZONE
DECOMPOSITION AND DISCOLOURATION OF
MALACHITE GREEN DYE

Katerina Zaharieva^{1✉}, Rositsa Titorenkova¹,
Vladislav Kostov-Kytin^{1,2}, Petya Karakashkova³,
Iliyana Yordanova³, Petya Todorova¹

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Abstract

In the present study the new manganese carbonate ore/copper and cobalt oxide-based catalysts were prepared using co-precipitation followed by calcination at 500 °C or by hydrothermal synthesis at 160 °C and then thermal treatment. The phase composition, structure, morphology, specific surface area and textural characteristics of the obtained composites were characterized by several methods as PXRD analysis, FTIR spectroscopy, SEM, nitrogen adsorption-desorption isotherms, and measurement of specific surface area. The PXRD analysis determined the average crystallite size of 10 nm for Co₃O₄ and MnCo₂O₄ and 13–23 nm for CuO phases. The synthesized composites exhibit mesoporous structure. The highest specific surface area (135 m²/g) was established for thermally treated MnCO₃ ore/cobalt oxide in comparison with

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the other investigated samples. The prepared materials were tested in two reactions – ozone decomposition and photocatalytic discolouration of Malachite Green (MG) dye as model pollutant under UV light. The results reveal that the hydrothermally treated MnCO_3 ore/cobalt and copper oxide demonstrate higher catalytic ability about removal of ozone (87% and 63%) in comparison with the composites prepared by co-precipitation and calcination – 86% and 54%, respectively. Best results for discolouration of MG dye were achieved with MnCO_3 ore/cobalt oxide-based photocatalyst (76%).

Key words: MnCO_3 ore/copper and cobalt oxide, catalyst, Malachite Green dye, ozone decomposition

Introduction. In recent years, many organic contaminants with endocrine disrupting effects and mutagenicity, toxicity, carcinogenicity have caused the heavy pollution of aquatic systems, and have to be effectively removed from water [1]. Photocatalysis has been known as a more effective method of wastewater treatment compared to conventional techniques, due to its ease of implementation and cost-effectiveness [2]. Catalytic ozone decomposition is of great importance because ozone is a toxic substance usually generated or found in human environments – offices with laser printers, photocopiers, sterilizers, and aircraft cabins. The use of catalysts based on transition metal oxides is very effective from an environmental perspective, providing a cheap and practical method for the decomposition of remaining ozone [3]. Natural ores are an attractive source due to their availability, low cost, and comparable performance to synthetic catalysts [4]. Manganese ore, as an important strategic mineral resource, is related to economic and social development and finds various applications such as magnetic materials, building materials, electrode materials, catalysts and desulphurizers, deoxidizers, alloying agents in the steel manufacturing and others [5].

LEE et al. [6] have determined that manganese ore mined in Australia possesses high catalytic activity towards ozone decomposition. The natural silicate ore supported Fe_2O_3 catalyst was synthesized by wetness impregnation method and used for catalytic ozonation of sulphamethoxazole (88.1% degradation rate after 30 min) [7]. The silicate ore supported Co_3O_4 catalyst prepared by impregnation method has been highly efficient in catalytic ozonation for tetracycline hydrochloride degradation [8]. The efficiency of the calcined magnetite from magnetite ore to catalyze the ozonation of a recalcitrant dye (RR-120) was investigated by [9]. The obtained TiO_2 -based photocatalyst from ilmenite ore from Indonesia has been demonstrated to achieve 83% photodegradation of Eriochrome Black-T dye [10]. CHEN et al. [11] prepared Bi_2O_3 photocatalyst from bismuthinite ore. The β - Bi_2O_3 possessed much higher photocatalytic ability than α - and δ - Bi_2O_3 for degradation of Rhodamine B. There is almost no research in the literature concerning preparation and catalytic behaviour of MnCO_3 ore/copper and cobalt oxide-based composites.

The main objectives of the present study are the synthesis of novel manganese carbonate ore/copper and cobalt oxide-based composites and a comparison of their

catalytic activity for two environmentally important reactions – ozone decomposition and UV-initiated discolouration of Malachite Green dye.

Experimental. Synthesis of MnCO_3 ore/copper or cobalt oxide-based composites. The MnCO_3 ore/copper or cobalt oxide-based composites were prepared using 0.15 M aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Valerus Co.) or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Valerus Co.) at constant stirring for 10 min. After that the 3 g thermally treated (500 °C) MnCO_3 ore (mineral name rhodochrosite) from Obrochiste deposit, Bulgaria was added to the solution of nitrate precursor at constant stirring for 10 min. The precipitant 2 M NaOH (Valerus Co.) was added drop by drop in the mixture of aqueous solution of nitrate precursor and manganese carbonate ore until pH reached 10 at continuous stirring. After precipitation the suspension was ultrasonically treated for 10 min and then it was stirred for one hour. The precipitate was filtered and washed with distilled water several times. The obtained precipitate was dried at 50 °C and calcined at 500 °C for 3 h in air media. The obtained samples were denoted CuT and CoT.

The samples CuH and CoH were obtained as the resulting mixture from 3 g MnCO_3 ore and nitrate precursor (aqueous solutions of 0.15 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2 M NaOH were transferred into an autoclave at 160 °C for 8 h. The so-obtained precipitates were washed and dried up in an oven, after which they were treated at 500 °C for 3 h in air media.

Physicochemical characterization. The powder X-ray diffraction (PXRD) analysis was performed on an X-ray powder diffractometer “Empyrean” within the range of 2θ values between 3° and 100° using Cu $K\alpha$ radiation ($\lambda = 0.154060$ nm) at 40 kV and 30 mA. The presence of phases was established using High Score Plus, Version 4.9 (4.9.0.27512) software. The average crystallite size (D) of cobalt and copper phases were determined using the Powder Cell software [12]. Infrared spectra were taken on a Bruker Tensor 37 spectrometer (FT-IR) in the region 4000–400 cm^{-1} , using KBr pellet technique. Low-temperature adsorption of nitrogen (–196 °C) was applied to study specific surface area and pore structure of the samples using a Quantachrome Nova 1200e apparatus. The specific surface area was calculated according to BET method (Brunauer–Emmett–Teller theory). The pore size distribution was determined using BJH method based on the isotherm desorption branch. Total pore volume (V_t) and average pore diameter (D_{av}) were calculated according Gurvich rule at a relative pressure $P/P_0 \sim 0.99$. Before measurement samples were degassed for 20 h at 110 °C. The surface morphology of the samples was investigated with scanning electron microscope (JEOL SEM JSM-6390, Japan); accelerating voltage of 20 keV. Samples were coated with thin layers of carbon.

Ozone decomposition study. The ozone conversion was examined by observing changes in ozone concentration. The experiment was carried out in a glass tube reactor containing 0.2 g of catalyst. Ozone was generated by passing dried oxygen (99.99% purity) through a 4–9 kV discharge in a self-made tubular

ozone generator. An ozone-oxygen mixture, with an initial concentration of up to 13 000 ppm, was passed through the reactor at a flow rate of approximately 6.0 L/h at room temperature. The ozone concentrations at the inlet and outlet of the reactor were measured using a BMT 964 UV absorption-type of ozone analyzer.

The time-conversion degree dependence has been measured in the course of 180 min time interval over the studied samples. The activity of the catalysts was calculated on the basis of the following equation:

$$\text{O}_3 \text{ conversion} = \frac{C_0 - C}{C_0} \times 100\%,$$

where C_0 and C are inlet and outlet concentrations of ozone, respectively.

Photocatalytic tests. The photocatalytic discolouration of Malachite Green dye as a model contaminant with an initial concentration of aqueous solution of the dye–5 ppm has been investigated. The prepared manganese carbonate ore/copper and cobalt oxide-based composites as photo-catalysts were used. Polychromatic UV-A lamp (Sylvania BLB, 18 W) with an emission maximum at 365 nm was used. The photocatalytic tests were carried out in semi-batch slurry reactor using 0.075 g photocatalyst and 75 ml of dye solution under constant stirring and air flowing. In order to reach the adsorption-desorption equilibrium state the studied systems were left in the dark for about 30 min before switching on the UV illumination for 2 h and 30 min. The powder was separated from the aliquot solution by centrifugation. After that the change of absorbance during the photocatalytic tests was monitored by UV-Vis absorbance spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm ($\lambda_{\text{max}} = 618 \text{ nm}$ for MG). The degree of dye degradation was calculated using the dependence:

$$\text{Degradation} = \frac{C_0 - C}{C_0} \times 100\%,$$

where C_0 and C were initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval.

Results and discussion. PXRD patterns of the prepared manganese carbonate ore/copper or cobalt oxide-based composites are displayed in Fig. 1A. The presence of newly formed tenorite phase CuO (Ref. Code: 04-005-4872) and possibly bixbyite (Mn_2O_3) (Ref. Code: 01-075-1573) has been detected. Additionally, glauconite ((K,Na)(Fe,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂) (Ref. Code: 00-058-2025) has also been identified in some of the samples. This aluminosilicate is known to belong to the natural ore phase composition and it has survived the applied thermal and hydrothermal treatment of the MnCO_3 ore/CuO samples. The performed Powder X-ray diffraction studies of the other two prepared samples indicate the existence of Co_3O_4 (Ref. Code: 01-080-1533); manganese cobalt oxide (MnCo_2O_4)

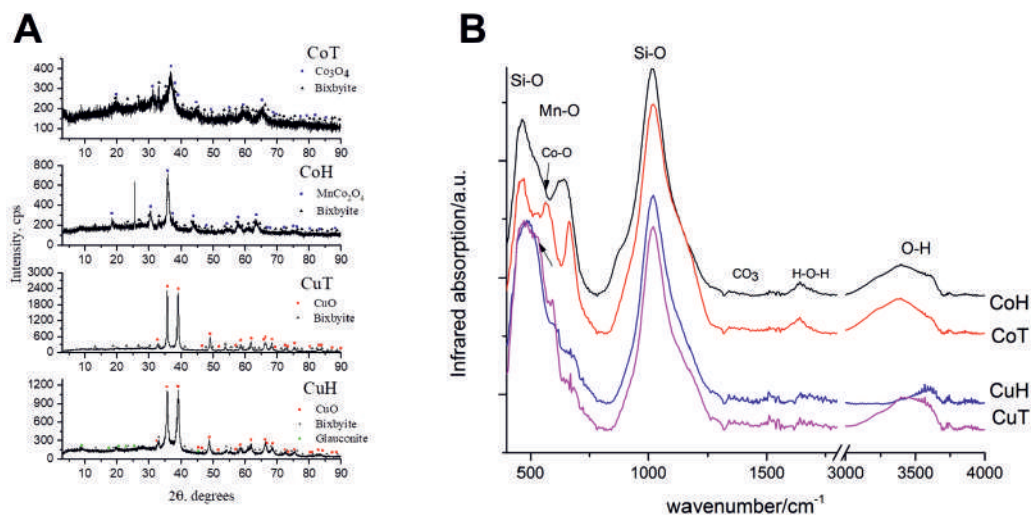


Fig. 1. A) PXRD patterns and B) FTIR spectra of synthesized manganese carbonate ore/copper or cobalt oxide-based composites

(Ref. Code: 01-084-0482) and bixbyite. Average crystallite size of 13 nm and 23 nm (CuO), 10 nm (Co_3O_4), and 10 nm (MnCo_2O_4) in the hydrothermally and thermally treated materials has been determined, respectively.

The recorded FTIR spectra of synthesized composites are illustrated in Fig. 1B. The silicate phase dominates the spectra with intense peaks in the range 900–1050 cm^{-1} and at around 460 cm^{-1} , due to Si–O stretching and bending vibrations, respectively. The detected hydroxyl groups at 3400–3600 cm^{-1} and water molecules at 1640 cm^{-1} confirm the presence of a phyllosilicate mineral such as glauconite. The absorption peaks of the other identified oxide phases are less intense and overlap in the lower frequency range 500–700 cm^{-1} . The manganese oxide phase is present in all samples, so the spectral differences should be due to the presence of tenorite (CuO) or cobalt oxide (Co_3O_4). Infrared spectrum of Mn_2O_3 reveals a broad absorption centred around 500 cm^{-1} . Most likely, the absorption peak at 528 cm^{-1} can be due to the contribution of Cu–O bending vibrations in tenorite, while the peaks at 563 cm^{-1} can be attributed to Mn–O, Cu–O or Co–O stretching [13].

Low-temperature nitrogen adsorption was performed to evaluate the texture parameters of the studied samples. The adsorption–desorption isotherms and the pore size distributions of manganese carbonate ore/copper or cobalt oxide-based materials are presented in Fig. 2A.

Adsorption–desorption isotherms of all studied samples are from II type according to the IUPAC classification with H3 type hysteresis, indicating slit-shaped pores between rigid particles. The heterogeneous distribution of pores with a content of mesopores was determined. The textural parameters of the materials are

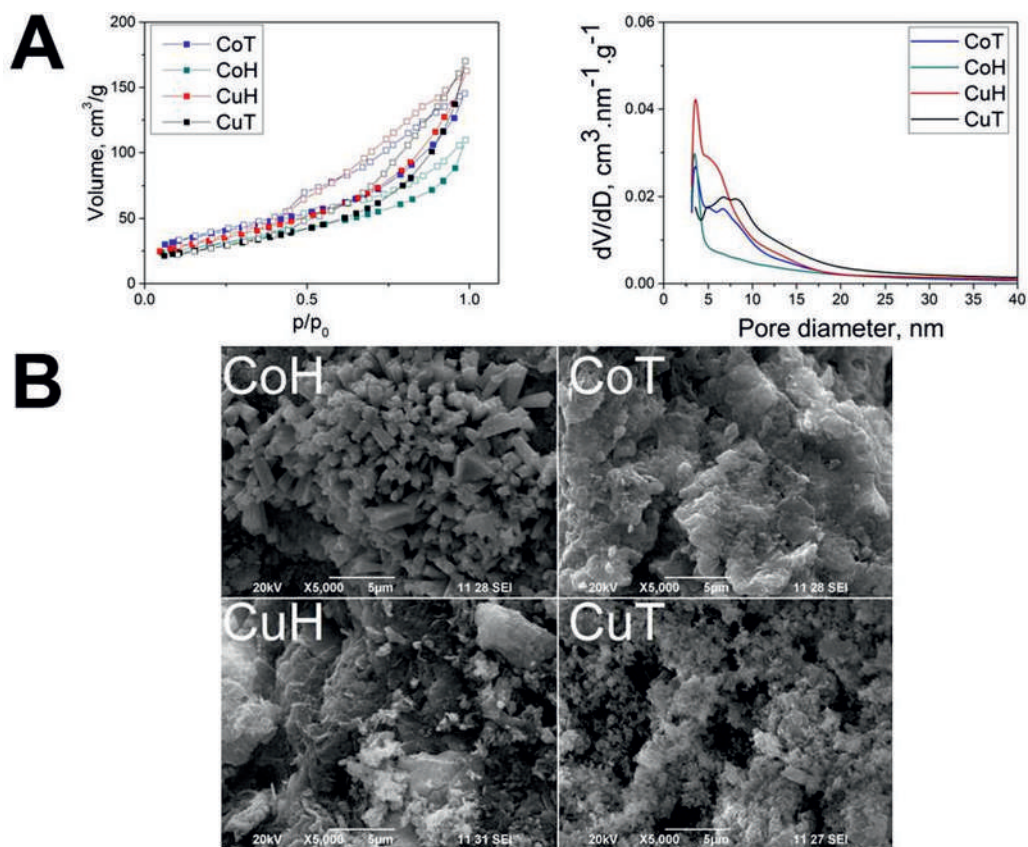


Fig. 2. A) Nitrogen adsorption-desorption isotherms and pore size distribution and B) SEM images of the synthesized manganese carbonate ore/copper or cobalt oxide-based materials

presented in Table 1. The CoT composite possesses the highest specific surface area ($135 \text{ m}^2/\text{g}$) in comparison to those of the other samples. The volume (V_t) and average diameter (D_{av}) of the prepared MnCO_3 ore/copper oxide materials are higher than that of the MnCO_3 ore/cobalt oxide-based composites (Table 1).

T a b l e 1

Textural characteristics of the investigated catalysts: specific surface area (S_{BET}), total pore volume (V_t) and average pore diameter (D_{av})

Sample	$S_{BET}, \text{m}^2/\text{g}$	$V_t, \text{cm}^3/\text{g}$	D_{av}, nm
CuT	98	0.26	11
CuH	119	0.25	8.5
CoT	135	0.22	6.7
CoH	104	0.17	6.7

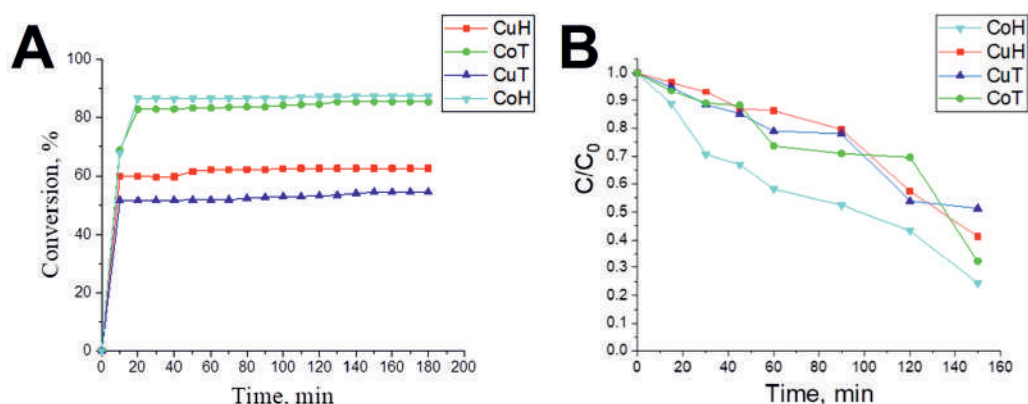


Fig. 3. A) Ozone conversion reaction and B) Concentration ratio C/C_0 of MG as a function of UV irradiation time using manganese carbonate ore/copper or cobalt oxide-based catalysts

SEM images (Fig. 2B) of the prepared composites provide notion for the morphological peculiarities and give evidence of the porous structure of the investigated materials. In the case of CoH sample, the aggregation of small rod like structured particles is observed.

The investigated manganese carbonate ore/copper and cobalt oxide-based catalysts manifest catalytic activities in the reaction of ozone decomposing, following the sequence of $\text{CoH} > \text{CoT} > \text{CuH} > \text{CuT}$ (Fig. 3A). The results demonstrate that the catalysts prepared through hydrothermal synthesis exhibit higher catalytic abilities. Specifically, the manganese carbonate ore/cobalt and copper oxide-based catalysts synthesized hydrothermally achieved ozone removal efficiencies of 87% and 63%, respectively. The composites treated only thermally demonstrated slightly lower efficiencies – 86% for manganese carbonate ore/cobalt oxide-based catalyst and 54% for CuT. The hydrothermally synthesized manganese carbonate ore/cobalt oxide-based catalyst achieved the highest conversion degree for ozone, showing its potential as an effective catalyst for ozone decomposition. The hydrothermal treatment produces a more optimal texture of the catalyst in terms of the achieved porosity providing more sites for the formation of oxygen vacancies, as manifested by the higher ozone conversion as compared to the thermal treatment, which can cause particle agglomeration of lower porosity [14, 15]. DAAWE et al. [15] established that Mn species may enhance catalytic ability by generating oxygen vacancies. The activity of the manganese carbonate ore/cobalt oxide-based composites is higher than that of the manganese carbonate ore/copper oxide, which may be attributed to greater content of adsorbed oxygen species, and stronger metal-oxygen bond energy [16, 17].

The concentration changes of MG dye in a photocatalytic discolouration process under UV illumination using synthesized composites based on MnCO_3 ore/copper and cobalt oxide as photocatalysts are presented in Fig. 3B. The re-

sults show that materials CoH (76%) and CoT (68%) have the best photocatalytic performance, whereas the discolouration degree after 150 min of CuH (59%) and CuT (49%) is lower. The enhanced photocatalytic ability could be due to the combined effects of several factors – large specific surface area, small crystallite size, and mesoporous structure [18,19]. Moreover manganese, cobalt and copper species in the catalysts for ozone decomposition and photocatalytic dye discolouration due to their easily variable valence states (Mn^{2+} , Mn^{3+} , Mn^{4+}), $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Cu}^+/\text{Cu}^{2+}$ facilitate the electron transfer. This leads to the formation of highly reactive radicals, such as $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$ which are involved in the photocatalytic discolouration of dyes and the ozone degradation. These species can also create oxygen vacancies on the catalyst surface. The combination of Mn with Co and Cu leads to a synergistic effect reflected in enhanced catalytic ability [15,20].

Conclusion. Novel composite catalysts based on MnCO_3 ore/copper and cobalt oxide were prepared and applied towards two environmentally important processes – ozone decomposition and photocatalytic Malachite Green dye discolouration. The prepared mesoporous materials possesses slit-shaped pores. The highest degree of ozone conversion during the reaction was achieved using hydrothermally synthesized MnCO_3 ore/cobalt oxide-based catalyst (87%). It remains almost constant until the end of the catalytic tests. The photocatalytic tests for discolouration of MG dye determined that the hydrothermally treated photocatalysts exhibit higher photocatalytic activity. The MnCO_3 ore/cobalt oxide-based composite also demonstrates a higher photocatalytic activity towards discolouration of MG dye (76%) in comparison with the other synthesized photocatalysts. The natural manganese carbonate ore is suitable for preparation of promising eco-friendly composite catalysts due to its stability and low cost.

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¹*Institute of Mineralogy and Crystallography “Acad. I. Kostov”,
Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 107, 1113 Sofia, Bulgaria*

e-mail: zaharieva@imc.bas.bg, rositsatitorenkova@imc.bas.bg,
vkytin@abv.bg, petia.todorova@imc.bas.bg

²*National Centre of Excellence Mechatronics and Clean Technologies,
8 Kliment Ohridski Blvd, 1756 Sofia, Bulgaria*

³*Institute of Catalysis, Bulgarian Academy of Sciences,
Akad. G. Bonchev St, Bl. 11, 1113 Sofia, Bulgaria*
e-mails: petia.karakashkova@gmail.com, yordanova@ic.bas.bg