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Catalytic degradation of methylene blue in aqueous solutions over Ni- and Co- oxide systems

Research Article

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Abstract: The oxidative catalytic degradation of the cationic dye methylene blue (MB) with NaOCl in aqueous solutions was studied using individual and iron modified Ni- and Co-oxide systems as catalysts. The adsorption extent and the contribution of the uncatalyzed oxidation on the overall degree of MB were determined. The results indicate that methylene blue—a representative of a class of dyestuffs resistant to biodegradation—could be successfully decolorized and degraded using nickel and cobalt oxide catalysts at room temperature. The highest catalytic activity manifests in the Co-oxide system which is consistent with the adsorption data. The oxidative degradation reaction proceeds via first-order kinetics. Temperature has a relatively small effect on the methylene blue degradation kinetics. The results obtained reveal that the catalysts investigated are suitable for oxidative destruction of methytlene blue dye in wastewaters.

Keywords: *Methylene blue • Catalytic oxidation • Oxide systems • Adsorption • Kinetics*

1. Introduction

Water quality protection is regarded as one of the most significant problems related to environmental protection. The compounds causing water pollution are extremely various in composition and toxic effects. Among them, textile dyes, being constituents of the wastewaters from textile, pharmaceutical, food-stuff, cosmetic, paper, leather industries, *etc*., should be outlined. Most of the dyes cause water colourization at very low concentrations (even at 1 mg L^{-1}), and as a result, their uncontrolled discharge in the natural water resources creates serious ecological problems. In addition, the textile dyes negatively affect the development of aqueous organisms as well as the photosynthesis activity of the marine flora [1,2]. Their high chemical and photo resistance creates potential risk of bioaccumulation and respectively serious threats for human health through the food chain transport. For those reasons, the treatment of wastewaters containing dyes prior their disposal in the water resources is obligatory, but at the same time a complicated process.

A wide range of physical, chemical and biological methods have been developed [3-5] for the purification of wastewater containing dyes. Adsorption is regarded as one of the most effective and relatively low-cost process, which has found practical application for removal of textile dyes from wastewaters. Active carbon [6-8], clays [9,10], biosorbents [11], perlite [12-14], zeolite [15,16], *etc*. are some of adsorbents used for this purpose. However, it should be noted that adsorption methods lead only to the accumulation of the dyes on the adsorbents' surfaces, not their neutralization, which in turn requires their further degradation to non-toxic products by means of effective degradation methods. Chemical oxidation methods using chlorine, hydrogen and ozone as oxidants can overcome these disadvantages. However, the chemical method does not result in the complete mineralization of the organic pollutants [17]. Catalytic wet air oxidation processes with the usage of air or pure oxygen as oxidants have been used for removal of dissolved toxic organic pollutants from wastewaters. However, high pressures (20–200 bar) and temperatures (200– 320°C) are needed, thus increasing the treatment cost [18]. An effective and economically feasible process for the destruction of a variety of hazardous pollutants in wastewater is based on heterogeneous catalytic reactions providing complete oxidation. Using both suitable catalytic systems and reaction conditions, a high

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selectivity towards environmentally harmless products can be achieved at mild conditions (room temperature and atmospheric pressure).

Our previous studies showed that Ni- and Co- oxide systems (individual and as well as promoted with Fe and Mn) are highly effective catalysts for oxidative liquid-phase degradation of a wide range of organic and inorganic pollutants (phenol, 4-chlorophenol, methanol, benzyl alcohol, cyanides and sulfides) at ambient conditions [19-27]. The results obtained motivated us to examine the performance of these catalysts for the destruction of other water contaminants, particularly organic dyes extensively used in textile industry.

The objective of the present study is to evaluate the adsorption ability and efficiency of the individual and iron modified Ni- and Co- oxide systems for oxidative degradation of methylene blue in aqueous solutions with NaOCl.

2. Experimental procedure

2.1. Catalyst preparation

The catalysts investigated were prepared by an oxidation-precipitation method at room temperature in accordance with procedures previously described in [28-30]. The method is based on the precipitation of hydroxides (as precursors) in a highly oxidising environment generated by NaOCl followed by heat treatment at relatively low temperatures (90-120°C). The fresh samples were characterised by means of IR, XPS, and Mossbauer spectral analyses, X-ray diffraction, thermal, and chemical analyses. The data obtained reveal that the synthesised oxide systems could be advantageous in catalytic oxidation of toxic organic and inorganic compounds in an aqueous medium.

2.2. Oxidation reaction

Oxidation reactions were performed in a laboratory scale thermostatic batch reactor equipped with a magnetic stirrer. All experiments were performed using the following procedure: 100 mL MB solution, subjected to oxidation, was poured in the reactor and the solution was left to attain the required working temperature. Then a catalyst (0.05 g) was added and after 30 min of stirring NaOCl was added (0.4 mL, 45 g L^{-1}). The catalyst fraction 0.6-1.0 mm was used to increase the catalyst surface accessible to the reaction.

The efficiency of the heterogeneous oxidation of MB over Ni-, Co- и mixed Co-Fe- oxide systems was evaluated both by the conversion degree (α, %), estimated by the following equation:

$$\alpha = \frac{Co - C}{Co} 100$$

and by the rate constant (*k*, min^{-1}), determined by the kinetic equation for a first order reaction:

$$k = \frac{1}{t} \ln \frac{Co}{C}$$

where: C_0 is the initial concentration of MB solution, mg L^{-1}; C is the solution concentration at a given moment (*t*, min) of oxidation, mg L^{-1}.

The chemical oxidation of MB model solutions was performed under similar conditions, but in the absence of catalyst in the reaction mixture.

The catalytic decomposition of NaOCl was carried out at isothermal conditions and with continuous stirring. The experiments were carried out with 100 mL NaOCl solution in concentrations of 0.0021 M and 0.05 g of the respective catalyst. Aliquots were withdrawn at regular times and were analysed iodometrically for the unconsumed NaOCl.

The adsorption experiments were performed under the following conditions:

- initial concentration of MB solutions (C_o) – 3, 5, 10, 15, 20, 35, 50 and 75 mg L^{-1}
- volume of the solution – $V = 0.025$ L
- oxide system mass – m = 0.025 g
- temperature – 25°C
- pH of the solution – 5.04; 7.25; 10.86
- stirring rate of the solution/adsorbent system – 150 rpm

After completing the adsorption process the solutions were centrifuged for 10 min at a rate of 3000 rpm for catalyst separation and the MB equilibrium volume concentration (C_{eq}) was spectrophotometrically determined. The corresponding equilibrium concentration of the dye on the surface of the oxide systems (Q_{eq}, mg g^{-1}) is calculated by the following formula:

$$Q_{eq} = \frac{C_o - C_{eq}}{m} V$$

2.3. Analytical methods and apparatus

The changes of MB concentration during the course of the investigated processes were followed by means of UV-Vis spectral analysis. The UV-Vis spectra were recorded on a Cintra 101 spectrophotometer at a wavelength λ=665 nm, corresponding to the maximum absorption of the dye. A 10 mm cell was used. In all measurements distilled water was used as a reference. The concentration of the MB solution (*C*, mol L^{-1}) in a given moment of the oxidation was determined using a calibration curve. The pH of the solutions was measured by a multifunctional INFOLAB 740 unit.

The degree of dye conversion to products of complete oxidation was estimated by the decrease in the contents of the total organic carbon (TOC) in the analysed samples. The residual TOC content in the solutions was determined by the colorimetric method using a Spectroquant® TOC cell test (Merck) and a NOVA 400 UV-Vis spectrometer (Merck, Germany).

The transformation of MB dye in the course of the oxidation process was also monitored by high-performance liquid chromatography. Analyses were performed with a Knauer Series HPLC system equipped with a Smartline PDA 2800 detector. The separation of the compounds in the analysed sample (10 μL) was obtained through a Purospher ^{R}star RP-18e column (250 mm × 4.6 mm i.d.; silica particle size 5 μm). The column was eluted in isocratic mode with a mixture of 1% methanol-water 60:40 (v/v) with a flow rate of 1 mL min^{-1}. Detection was performed at 285 nm.

3. Results and discussion

The heterogeneous catalytic processes take place on the catalyst surface following the preliminary adsorption of the reagents to this surface. The oxidation reactions in liquid phase can be accompanied by the simultaneous occurrence of non-catalytic, chemical oxidation of the substrate in the bulk solution. Thus, three simultaneous processes, *i.e.*, adsorption of MB dye on the catalyst surface, catalytic oxidation and chemical oxidation of MB in the presence of oxidant may occur during the MB liquid-phase oxidation which contribute to the total degree of its degradation. In order to clarify the role of each one of these processes three types of experiments were carried out.

3.1. Chemical oxidation

Sodium hypochlorite is a strong oxidizer ($\varphi^{o} = 1.49$ V), and for that reason it is widely used for decolourisation of wastewaters generated from the textile industry. It has been established that the efficiency of the chemical oxidation of MB is low (15-20%) at low concentration of the reagent (to 1 g L^{-1}), and a contact time of 30 minutes is required. For preliminary assessment of the impact of catalyst addition to the dye-NaOCl system, chemical oxidation of MB solutions with NaOCl was carried out. The results obtained show that complete decoulorisation of MB *via* chemical oxidation with NaOCl at 298 K and pH=11, without catalyst, was achieved for about 20 hours at an initial concentration of the MB solution of 50 mg L^{-1} and for about 30 hours in the presence of 12 mg L^{-1} Co.

3.2. Adsorption of MB on the catalyst investigated

Preliminary experiments on the kinetics of the adsorption process revealed that adsorption equilibrium was achieved by the 30th minute.

The adsorption experiments indicated that the pH of the initial MB solutions has a significant effect on the adsorption capacity of the catalyst samples. The adsorption process in alkaline medium (pH=10.86) is the most efficient, and as the pH of the solution is decreased, the amount of the adsorbed dye on the catalyst surface is strongly reduced. This tendency is most pronounced in the case of the Co-oxide system—its adsorption capacity is decreased ~4 fold during the proceeding of adsorption in neutral or acidic media while in the case of Co-Fe the reduction is ~2 fold (Fig. 1).
o-fresh (a) and Co-Fe-fresh (b)

The results obtained are in a good agreement with the values of pzc of the oxide systems: NiOx-fresh – 7.97; for CoO$_x$-fresh – 7.32; for Co-Fe-fresh – 7.89. At pH=10.9 the surface of catalysts becomes negatively charged due to the protonation of the surface OH$^-$ groups according to the following reaction:

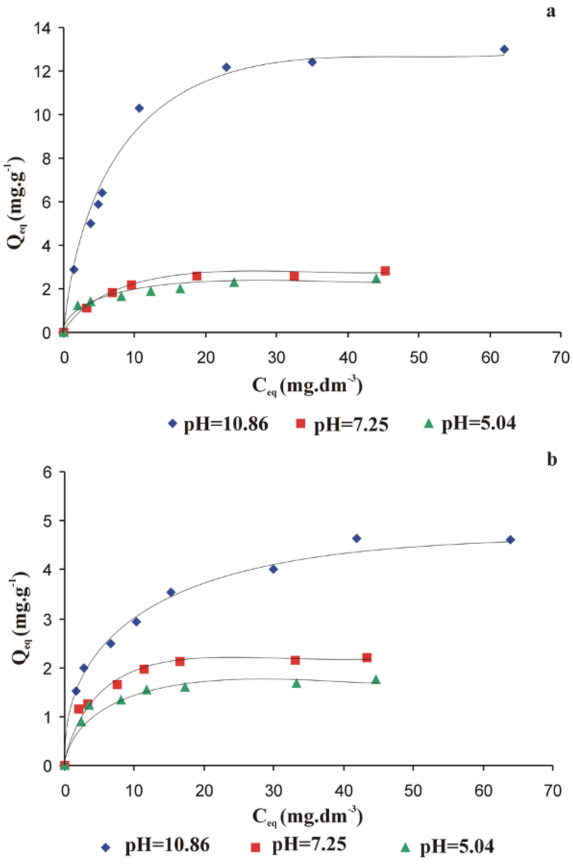

Figure 1. Effect of pH on the adsorption of MB over Co-fresh (a) and Co-Fe-fresh (b) C.

$$S\text{–}OH + OH^{-} \leftrightarrow SO^{-} + H_2O$$

Since MB is a cationic dye, a strong electrostatic attraction with the negative surface easily takes place:

$$SO^{-} + MB^{+} \leftrightarrow SO^{-}MB^{+}$$

The adsorption isotherms of MB on the three catalytic samples at pH=10.86 are shown in Fig. 2. As can be seen from this figure, the amount of dye adsorbed on the Co-oxide is greatest—about 3 times higher compared to that of Co-Fe and Ni. This difference could be explained by the higher number of effective adsorption centers on the surface of Co-fresh in comparison with that of Co-Fe-fresh and Ni-fresh. This, in turn, supposes a higher activity of the cobalt catalyst with respect to the heterogeneous oxidation of the MB dye.

It is also seen from Fig. 2 that adsorption isotherms are non-linear and seem to be approaching their maximum values. Adsorption isotherms were analysed by the most frequently used Freundlich and Langmuir isotherm models. Adsorption data were fitted to the linear form of both isotherms as shown in Fig. 3.

Evidently, the adsorption of MB on the catalysts investigated closely follows the Freundlich model as revealed by the high correlation coefficient values (R^2>0.99). The Freundlich empirical constants K_F and n, being indicative of the extent of adsorption and the degree of non-linearity between bulk and surface concentration, respectively, are presented in Table 1.

The results from the adsorption experiments allow the determination of the most favourable value for pH of the MB initial solutions which guarantees the proceeding of heterogeneous-catalytic oxidation of the dye: pH=11.

3.3. Heterogeneous catalytic oxidation

The kinetic studies were performed on model MB solutions at two different initial concentrations - 12 and 50 mg L^{-1} at an equal ratio of C_o/C_{cat} = 0.1. The amount of the added oxidant for the two experiments was in conformity with the stoichiometric one necessary for the complete oxidation of MB. On the one hand, this allows establishing whether the oxidation process is carried out on the surface of the oxide catalysts, and on the other, to determine the diffusion limitations for its proceeding.

The change in MB concentration in the course of the oxidation process was evaluated by following the decrease in the absorbance maximum at 665 nm in the UV-Vis spectra of the reaction mixture. The spectra obtained for the kinetic oxidation of the dye over the investigated Co, Co-Fe and Ni-oxide systems, under the following conditions: C_o=12 mg L^{-1}; pH=11; C_{cat}=0.5 g L^{-1}; T=298 K, are presented in Fig. 4.

It is seen from the presented UV-Vis spectra that under the experimental conditions used, the low-temperature liquid-phase oxidation of MB proceeds with the participation of the Co-, Ni- and Co-Fe- oxides systems. The oxidative degradation of MB in the presence of Co-oxide system is most effective. The intensity of the band at 665 nm decreases with the time during the catalytic oxidation, but new absorbance maxima have not been observed. This is an indication

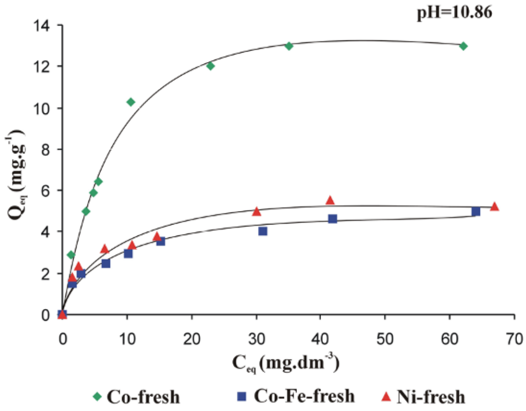

Figure 2. Isotherms of methylene blue adsorption onto catalysts under study at pH 10.86

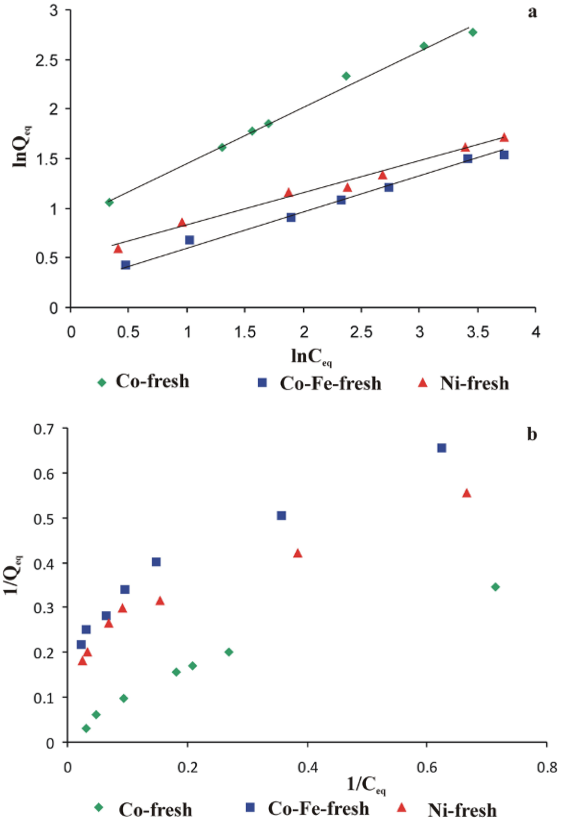

Figure 3. Freundlich (a) and Langmuir (b) plots of isotherms for methylene blue adsorption onto the investigated oxide systems (pH=10.86)

Table 1. Values of the Freundlich constants

Catalyst	K_F	n
Co - fresh	2.45	0.57
Co-Fe – fresh	1.65	0.32
Ni - fresh	1.33	0.34

of the achievement of complete MB degradation. In addition, a shift of the absorbance maximum to shorter wavelengths (hypsochromic effect) is not observed, which shows that N-demethylation of MB auxochromic groups does not take place during the catalytic oxidation. A similar effect was observed by other authors studying the photocatalytic oxidation of MB in the presence of TiO_2 [31].

The kinetic curves for the oxidation of model solutions of MB at pH=11 and temperature 298 K in the presence of the synthesized catalytic samples are shown in Fig. 5.

The data obtained show that the oxidation process is most effective in the presence of the Co-oxide catalytic system. Complete oxidation of MB at 298 K in the presence of Co-oxide system at C_o=50 mg L^{-1} is achieved by the 25th minute from the beginning of the process (α~100%). This result is in agreement with the expected higher activity of the cobalt catalyst with respect to the heterogeneous oxidation of the dye, as suggested by the adsorption experiments. The Fe Co-oxide modified system demonstrates a weaker activity in comparison with that of Co-fresh—the decolourisation of the dye is achieved by the 40 minute. The weakest catalytic activity is displayed by Ni-fresh, although its adsorption capacity is similar to that of Co-Fe-fresh. It has been found that the degradation degree in the presence of the Ni- oxide system is only 76% achieved by the 60th minute, which remains constant as the oxidation process proceeds. It was established that this is due to the oxidant consumption. Adding extra NaOCl to the reaction mixture causes further oxidation of MB and decolourisation is achieved after 60 more minutes. These results suggest that in the presence of Ni-catalyst only part of NaOCl contributes to the MB oxidation, *i.e.*, in the presence of Ni-fresh catalyst two simultaneous reactions occur—catalytic decomposition of NaOCl releasing molecular oxygen and heterogeneous-catalytic oxidation of MB.

The reliability of this supposition was confirmed by the results from the studies of the kinetics of the heterogeneous catalytic decomposition of NaOCl over the synthesized oxide systems (Table 2). It was found that the activity of the samples changes in the following order: Ni- fresh > Co–fresh > Co-Fe-fresh. The catalytic decomposition of NaOCl has the highest rate in the presence of the Ni-oxide system. Under the experimental conditions used 91% of NaOCl were decomposed after 35 minutes. The lowest activity in the investigated process is manifested by the Co-Fe- oxide system—$\alpha_{90'}$=71%. The results obtained fit with the data well for the efficiency of the oxide systems related to the oxidation of the MB dye.

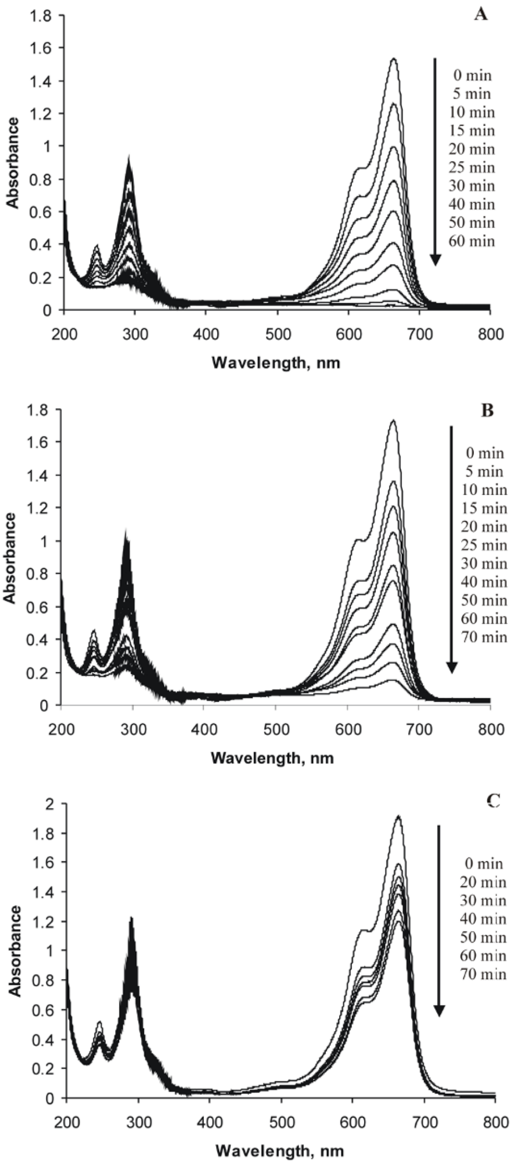

Figure 4. UV-Vis spectral changes for MB degradation by using different catalysts (A) Co-fresh; (B) Co-Fe-fresh; (C) Ni-fresh

The results of the kinetic studies show that the liquid-phase oxidation of MB in the presence of Ni-, Co- and Co- Fe-oxide systems obey the kinetic regularities for first order reaction with respect to MB, which is supported by the linear pattern of the lnC_o/C = f (t) dependences (Fig. 6).

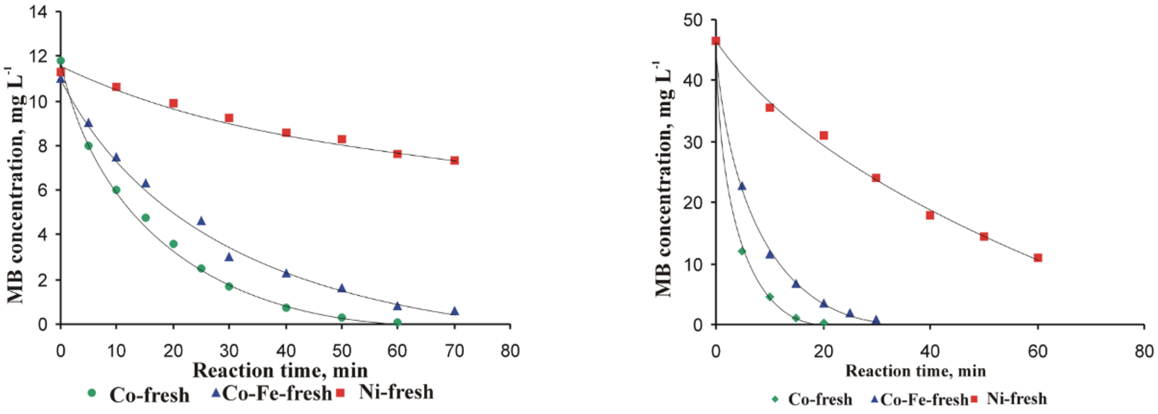

Figure 5. Kinetics curves of MB oxidation for different initial concentration.

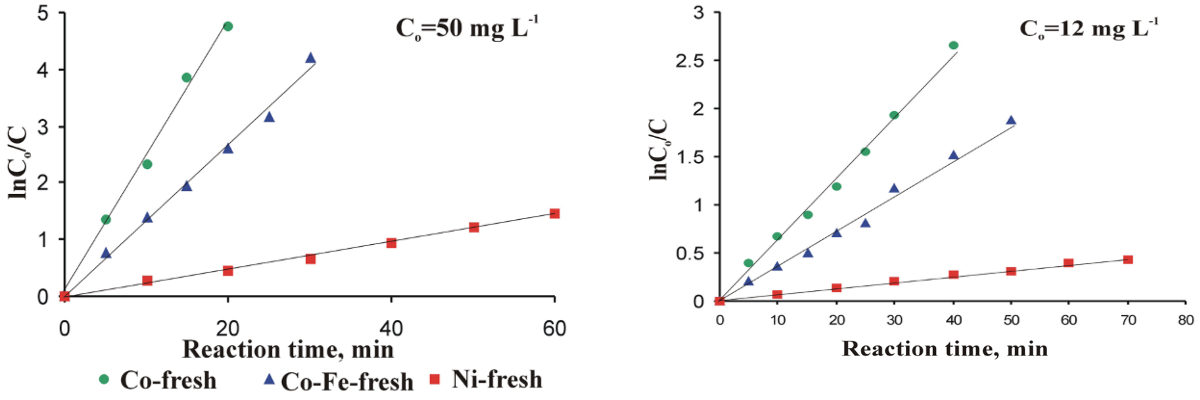

Figure 6. First-order fit of MB liquid-phase oxidation in the presence of Ni-fresh, Co-fresh and Co- Fe-oxide system.

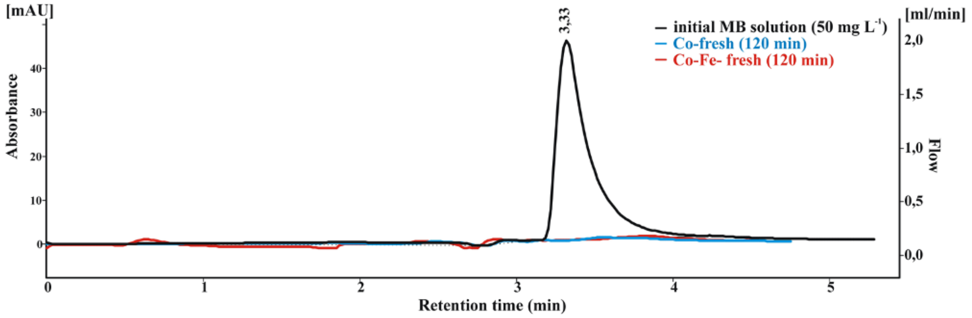

Figure 7. HPLC chromatograms of MB (50 mg L^{-1}) before and after catalytic oxidation over Co-fresh and Co-Fe-fresh catalysts.

The rate constants of the oxidation process at two initial concentrations of MB solution were determined from the slope of the kinetic curves. The values of the rate constants related per unit mass of the catalyst do not differ significantly (Table 3). This indicates that the oxidation process is carried out on the surface of the catalytic systems and there are no diffusion limitations for its proceeding.

Considering that the Co-oxide system exerts the highest catalytic activity in the oxidation reaction, the effect of temperature treatment of the sample on its catalytic behavior has been studied. For this purpose, the oxidation reactions were carried out in the presence of Co-400 at an initial MB concentration of 12 mg L^{-1}. It was found that the investigated catalytic sample demonstrates markedly lower activity than the fresh one. Thus, at 298 K for 50 minutes the colour removal was only 23%, while in the presence of Co-fresh, this value increased to 96%. The reason for the observed difference in the activity is probably due to change in the composition and structure of the catalyst as a result of its treatment at 400°C which affects also its catalytic behavior.

Table 2. First-order rate constants of catalytic decomposition of NaOCl over the investigated catalytic samples

Catalyst	κ [s^{-1}]
Co- fresh	0.825×10^{-3}
Co-Fe- fresh	0.408×10^{-3}
Ni- fresh	1.150×10^{-3}

Table 3. First-order rate constants for the MB oxidation process

Catalyst	C_o=12 mg L^{-1}		C_o=50 mg L^{-1}	
	k [s^{-1}]	k [s^{-1} g^{-1}]	k [s^{-1}]	k [s^{-1} g^{-1}]
Co - fresh	1.050×10^{-3}	0.0827	4.067×10^{-3}	0.0813
Co-Fe – fresh	0.617×10^{-3}	0.0485	2.233×10^{-3}	0.0447
Ni - fresh	0.105×10^{-3}	0.0085	0.40×10^{-3}	0.0080

Table 4. Degree of MB mineralization over studied catalysts

Catalyst	α_{TOC} [%]
Co- fresh	35.6
Co-Fe- fresh	30.6
Ni- fresh	28.4

3.4. Study on the mineralization degree of MB dye

The oxidation degradation of MB may lead to a wide range of intermediates with toxic effects. Several reaction schemes of the process have been proposed for their formation. The mineralization degree of MB under the conditions of catalytic degradation was estimated by determining the content of total organic carbon in the treated samples and by HPLC analysis.

The data for the reduction degree of TOC (α_{TOC}, %) in the presence of the synthesized catalytic samples are shown in Table 4.

The results obtained show that the catalytic oxidation of MB over the investigated oxide systems results in low mineralization degree. These data do not correlate with the UV-Vis spectral results. The absence of absorption maxima in the range 200-800 nm in the UV-Vis spectra of the discolored solutions is supporting evidence for the complete degradation of the aromatic moiety of MB molecule. The most likely reason for this discrepancy is the non-applicability of the used tests for TOC determination in complex matrixes. On the other hand, the data of the HPLC analyses confirm the absence of aromatic structures in the treated samples (Fig. 7).

4. Conclusions

In this work, the adsorption and catalytic degradation of the methylene blue in aqueous solution over individual and iron modified Ni- and Co-oxide systems was investigated. The most effective adsorption process takes place in alkaline medium (pH=10.86), which can be explained by the electrostatic interaction of dye cationic species with the negatively charged catalyst surface. The Freundlich isotherm model represents the experimental results well. The contribution of the non-catalytic oxidation process to the overall degree of methylene blue degradation is negligible. The catalytic performance of the Co-oxide system towards dye degradation is found to be much better than that of Co-Fe-oxide and Ni-oxide system. In fact, at pH=11 and catalyst loading 0.5 g L^{-1}, complete color removal in the presence of Co-oxide system is attained in 25 min. UV-Vis spectra of the discolored solutions and HPLC analyses indicate that the aromatic structure of the MB molecule is completely destroyed.

Acknowledgements

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