11th International Conference on Renewable Electrical Power Sources

PROCEEDINGS

Editor Dr Milica Vlahović

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P R O C E E D I N G S

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FOREWORD

The conditions created by the development of technologies in which modern man lives have led to a complex and paradoxical effect: that by removing obstacles on the way to a more comfortable, simpler, faster and more efficient life and way of working, man also generates numerous misfortunes, attracting dark clouds of threats to the survival of the planet and humanity. The question that concerns and affects all of us - all people, all living beings, systems in which life takes place, large and small, strong and weak - boils down to the problem of the negative impact of man on the environment; this issue invites us to an urgent solution by looking at the causes, proposing solutions, evaluating them, changing approaches and ways of thinking, as well as drawing correct conclusions. Simply put, by adapting nature to one's own needs, man threatens and damages it. That is why, with the joint efforts of all of us, individuals, organizations and states, it is necessary to take all possible measures to immediately prevent the negative effects that are ahead of us.

The importance of renewable sources of electricity, which this international conference focuses on, is noticeable from two angles: the first - it is certain that fossil fuels as a resource will disappear and it is necessary to find alternative sources, the second - the use of renewable energy sources by its essence implies "clean" technology that significantly contributes to reducing CO_2 emissions and thus mitigating climate change and reducing pollution, while encouraging social and economic development in all spheres of life.

The 11th International Conference on Renewable Electrical Power Sources is organized by the Society for Renewable Electrical Power Sources (DOIEE) at SMEITS, with co-organizers: The Institute of Architecture and Urban & Spatial Planning of Serbia (IAUS) and the Chamber of Commerce and Industry of Serbia, with the support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The registered participants designed their papers according to the given conference topics:
- Energy sources and energy storage;
- Energy efficiency in the context of use of renewable energy sources (RES);
- Environment, sustainability and policy;
- Applications and services.

Eminent authors - scientists, teachers, experts in this field from fifteen different countries: Algeria, Belgium, Bosnia and Herzegovina, China, Croatia, Greece, Hungary, India, Portugal, Saudi Arabia, Serbia, Slovenia, Spain, the United Arab Emirates, and Ukraine, contributed to the conference through sixty-nine papers that were reviewed by the Scientific Committee of the Conference, and after the review process were accepted for presentation at the conference and for publication in the proceedings.

At the end of this short message and at the beginning of the proceedings I believe that it can be proudly said that scientists, researchers, policy makers and industry experts gathered in one place, in order to exchange experiences and knowledge with the aim of promoting scientific and professional ideas and results of research, technology improvement for the use of RES, promoting the rational use of electricity, affirming and proposing inventive solutions in the field of sustainable sources of electricity.

Belgrade, *Milica Vlahović*
November 2023

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Plenarna predavanja:

Energetski izvori i skladistenje energije:

<u>Energetska efikasnost u kontekstu primene RES:</u>

<u>Životna sredina, održivost i politika:</u>

Aplikacije:

FOTOKATALITIČKA DEGRADACIJA KONGO CRVENE BOJE KORIŠĆENJEM KOMPOZITA UIO-66 METALO-ORGANSKIH MREŽNIH STRUKTURA I METALNIH OKSIDA

PHOTOCATALYTIC DEGRADATION OF CONGO RED DYE USING UIO-66 MOF-METAL OXIDES COMPOSITES

Dimitrije PETROVIĆ[1*], Marija EGERIĆ[1], Radojka VUJASIN[1], Yi-nan WU[2,3], Fengting LI[2,3], Ljiljana MATOVIĆ[1,2], Aleksandar DEVEČERSKI[1]

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Apstrakt

Ovo istraživanje ima za cilj ispitivanje efikasnosti degradacije kongo crvene boje (KC) korišćenjem metalno-organskih mrežnih struktura (MOF), metalnih oksida (MeO) i njihovih kompozita. KC se često koristi u tekstilnoj industriji, a njeno ispuštanje u životnu sredinu može imati štetne efekte na život u vodenoj sredini i ljudsko zdravlje. MOF koji je korišćen u ovom istraživanju bio je UiO-66, koji ima visoku površinu i mogućnost podešavanja veličine pora, što ga čini obećavajućim kandidatom za primene u remedijaciji životne sredine. Efikasnost uklanjanja KC ocenjena je korišćenjem UV-Vis spektroskopije. Oksidi kobalta i bakra su odabrani zbog povoljnih vrednosti njihovih energetskih procepa (1.4-2.4 eV), koje se nalaze unutar energetskog opsega zračenja vidljive svetlosti, za razliku od UiO-66 čija je vrednost energetskog procepa daleko veća (3.7-4.1 eV). Rezultati su pokazali da je Cu_2O samostalno imao najmanji efekat na degradaciju KC, dok je kompozit MOF+CuO+Cu_2O imao najviši procenat degradacije KC. Kompozit je degradirao 91% KC u roku od 2 sata reakcije, dok je sam MOF degradirao samo 47%. Ovo istraživanje ukazuje na mogućnost primene MOF+CuO+Cu_2O i MOF+CuO kompozita, kao efikasnih katalizatora za degradaciju KC. Rezultati takođe sugerišu da bi MeO+MOF kompoziti uopšte, mogli biti efikasna alternativa za samostalnu upotrebu UiO-66 metalno-organskih mrežnih struktura u procesu uklanjanja boja u tretmanu otpadnih voda. Upotreba MOF-ova i njihovih kompozita sa metalnim oksidima može predstavljati obećavajući pristup za remedijaciju životne sredine tj. uklanjanje štetnih zagađujućih materija iz voda, doprinoseći očuvanju i zaštiti ljudskog zdravlja.

Ključne reči: *MOF, UiO-66; metalni oksidi; degradacija bojila; kompoziti; tretman otpadnih voda*

Abstract

This study aimed to investigate the degradation efficiency of Congo red dye using metal-organic frameworks (MOFs), metal oxides (MeOs), and their composite powders. Congo red is a commonly used dye in the textile industry and its release into the environment can have harmful effects on aquatic life and human health. MOF used in this study was UiO-66, which has a high surface area and tunable pore size, making it a promising candidate for environmental remediation applications. Removal efficiency of Congo red dye was evaluated using UV-vis spectroscopy. Cobalt and copper oxides were chosen because of their suitable band gaps (1.4-2.4 eV) which falls within the favorable band gap range for visible light absorption, contrary to the UiO-66, whose band gap is ≈3.7-4.1 eV. Results showed that Cu_2O when used alone had the weakest effect on the degradation

of the dye, while the composite of MOF+CuO+Cu_2O had the highest percentage of dye degradation. The composite degraded 91% of the dye within 2 hours of the reaction, whereas MOF alone degraded only 47% of the dye. This study showed that MOF+CuO and MOF+CuO+Cu_2O composites can be used as efficient catalysts for wastewater treatment, specifically for the degradation of Congo red dye. These findings also suggest that the MeO+MOF composites in general, could be an effective alternative to MOFs alone for the environmental remediation applications. The use of MOFs and their composites with metal oxides could provide a promising approach for the removal of harmful pollutants from wastewaters, contributing to the preservation of our environment and the protection of human health.

Key words: *MOF, UiO-66; metal oxide; dye degradation; composite; wastewater treatment*

1 Introduction

Accelerated industrial development and other anthropogenic activities have led to the widespread presence of organic pollutants in the environment [1]. Occurrence of these compounds can be attributed to the countless sources such as domestic sewage, agriculture wastewater, industry, etc. [2]. Releasing these substances into the environment may have harmful impacts not only on aquatic ecosystems but also on human health [3-7]. Dyes as an integral part of a large number of industries are one of the major contributors to this environmental problem [8]. There are over 10,000 different kinds of dyes produced and accessible worldwide at present. Despite the absence of up-to-date information on global dye production, it is estimated that annual output exceeding 700,000 tones [9]. During the dyeing, approximately 15% of the global production of dyes is estimated to be lost and released into textile effluents [10]. Leading industries that are causing these problems are textile industry, dyeing industry, paper and pulp industry, tannery and paint industry, etc. [11]. Congo red color is a direct diazo dye with the ability to dye cotton directly and because of this, it is widely used in textile industry [12]. With primary goal to dye paper products in red, congo red dye was and still is intensively used in paper industry also [13]. Due to its toxicity and potentially carcinogenic effect, attendance of congo red dye in environment is dangerous for the living world [14]. That's why removal of dyes and other pollutants is of great importance before releasing the dye wastewater into the environment. Removal methods and eliminating dye from wastewaters is the subject of research for years.

Different treatments technologies of such a waste waters were investigated, such as biological, chemical and physical. Biological methods are ecologically friendly and application is widely spread in industry. However, process itself is difficult to control and biodegradable potential of some types of organic matter may be very low [15]. Chemical treatments are on the other hand simple, but they poses several disadvantages like high sludge generation [16]. Furthermore, overabundant chemical usage may cause a secondary pollution [17]. Among mentioned, adsorption is considered to be effective treatment process. Because of it's own cost effectiveness and ecological acceptability, adsorption is the most commonly utilized physico-chemical method for eliminating dissolved organic compounds from wastewater [18]. However, results of adsorption methods are considered non-destructive since contaminants are transferred from the liquid phase onto a solid surface, which may require additional treatment [19]. Other physical processes for wastewater treatment like filtration is considered to be effective but expensive, while sedimentation itself is not a sufficient treatment process [20,21].

Hence, the use of photocatalysis as a treatment method exhibits significant promise in decomposing organic pollutants [22,23]. Photocatalyst is chemical treatment method and it implies catalyst material and light energy to generate highly reactive oxidizing species that can degrade or transform pollutants in water or air through photocatalytic reactions [24]. Unlike other chemical treatments it is environmentally friendly and process cost is low [25]. Furthermore, photocatalysis can degrade a wide range of organic pollutants, making it a versatile tool for water and wastewater treatment applications [26-31]. However, the implementation of photocatalytic in large-scale industrial applications is currently limited, as there are still certain drawbacks that need to be addressed. These drawbacks encompass various aspects, such as catalyst preparation, carrier construction, and

the design of photocatalytic water treatment reactors, indicating a need for further development. [32]. Most commonly used photocatalysts are semiconductors such as TiO_2, ZnO, WO_3, ZnS, CdS, SnO_2, etc... These photocatalysts demonstrated that they are effective in breaking down various types of pollutants to either less toxic chemicals or CO_2 and H_2O [33]. This is due their ability to generate charge carriers upon exposure to a sufficient amount of light energy, in addition to their exceptional stability in various conditions and biocompatibility [34]. However, other metal oxides are having these properties too and these characteristics enabled their use as a photocatalyst [35,36].

In the past few years, there has been a significant focus on the exploration of novel materials that exhibit photocatalytic activity. In recent years, metal-organic frameworks (MOFs) have garnered significant interest as a new type of porous material with distinctive properties and diverse applications. Due to their exceptional features, including their sizable surface area, customizable pore size, and capacity to integrate a wide range of functional groups within their framework, make them suitable for photocatalysts. [37]. Significant strides have been made by researchers in developing MOFs with improved photocatalytic properties for diverse applications, including degradation of organic pollutants, with MOFs like MIL-125-NH_2 and UiO-66, displaying remarkable photocatalytic activity for organic dye degradation under visible light irradiation. [38]. Regrettably, most MOFs have failed to achieve photocatalytic activity levels that are satisfactory and comparable to some commercial standards. To address this issue, it is possible to immobilize other semiconductor functional materials possessing photocatalytic activity onto the MOF substrate, which can result in improved catalytic activity and stability [39]. Utilizing metal oxide for photodegradation is considered a highly beneficial approach, as it enables the direct degradation of organic pollutants [40].

Cobalt oxide has garnered substantial attention in research as a highly effective photocatalyst for degrading a wide range of organic dyes [41-44]. Cobalt oxide stands out due to its favorable characteristics, including its cost-effectiveness, stability in both acidic and alkaline environments, exceptional catalytic capabilities, and its optical band gap energy falling within the range of 1.5 eV to 2.6 eV. Consequently, it remains also a promising candidate for the advancement of photocatalysts in the realm of water splitting [45].

Similar to cobalt, copper possesses a combination of properties that make it a promising and effective photocatalyst for the degradation of organic dyes in wastewater treatment and environmental remediation processes. Its stability, cost-effectiveness, and ability to harness solar energy for catalysis make it an attractive choice in the quest for sustainable and efficient dye degradation solutions [46].

While metal oxide catalysts hold great promise, their widespread industrial application is impeded by formidable challenges such as particle aggregation, limited recyclability, and the risk of catalytic deactivation [47]. To address these challenges, conventional practice involves immobilizing metal nanoparticles onto or within support materials [48]. A prevalent approach involves employing porous materials characterized by distinct pore features. In doing so, the division between the external and internal pore structures enables the selective control of the molecules that can access and subsequently interact with the nanoparticles [49]. Porous materials also have the advantage of confining and protecting the nanoparticles, thus facilitating their recovery from the bulk solution and preventing particle aggregation. In this context, the regular porosity of MOFs together with the possibility to tailor their pore size, shape and chemical functionality makes them an excellent substrate to support active metal nanoparticles for heterogeneous catalysis [50].

Cobalt oxide and copper oxide manifest distinct phases, including Co_3O_4, Co_2O_3, CoO, CuO, and Cu_2O. Each of these phases, when combined with a MOF, has been employed in the degradation of Congo red. The primary objective of this research is to create a composite material comprising of UiO-66/cobalt oxide, and UiO-66/copper oxide, aiming to enhance photocatalytic activity while maintaining satisfactory stability for the degradation of organic pollutants.

2 Experimental

2.1 Materials and characterization

The chemicals used were of high quality, meeting reagent grade standards, and were obtained from commercial suppliers. Congo red was utilized as a representative of an azo anionic dye. UV-Vis diffuse reflectance spectra were captured within the 200–800 nm wavelength range using a Thermo scientific MULTISKAN GO UV/Vis spectrometer. pH measurements of the Congo red dye solution were conducted employing a pH meter Hanna. The initial pH of the solution was determined prior to the commencement of the experiment, followed by subsequent measurements after the reaction (final pH).

2.2 Preparation of MeO/MOF composite

An exceptionally straightforward synthesis approach was employed to fabricate composites by combining Metal-Organic Frameworks (MOFs) and Metal Oxides (MOs) in varying ratios. Simply MeO and MOF were homogenized with an agate mortar and pestle. This method was deliberately chosen due to the common observation that the production of MOF composites often leads to the degradation of their microstructure and/or morphology, consequently resulting in diminished material performance [51]. By utilizing the proposed procedure, we aimed to mitigate potential adverse effects on the MOF's inherent characteristics and ensure the preservation of its superior properties.

2.3 Photocatalytic activity evaluation

To evaluate the photocatalytic performance of the photocatalyst, the degradation of Congo red (CR) was investigated under visible-light illumination. This study utilized a custom-designed photoreactor equipped with a 20W COB LED 770lm lamp, to provide the necessary irradiation. Throughout the reaction, the reactor's temperature was regulated at 25 °C, ensuring a controlled and consistent operating condition. For each experimental trial, a 0.005 g portion of the sample was combined with 10 mL of CR solution. The resulting suspension was then exposed to visible-light irradiation. After a 2-hour exposure, the suspension was carefully collected and subsequently centrifuged to eliminate the generated products. The absorbance value of the dye at a wavelength of 500 nm (CR) was determined using a Thermo scientific UV/Vis. An additional control experiment was conducted using the same procedures, but without the inclusion of any photocatalyst.

The following equation was employed to compute the efficiency (EF) of dye degradation.

$$\%Degradation = \mathrm{EF} = \left(\frac{Co - C}{Co}\right) x100$$

Here, C_0 represents the initial dye concentration, and C corresponds to the final concentration after a defined time interval.

3 Results

The research entailed an exploration of the influence of a metal oxide catalyst on the degradation process of CR dye. This investigation was conducted by monitoring the degradation of the dyes over a specified duration, during which 0.005 g of the catalyst was introduced under carefully defined reaction conditions. The efficiencies of dye degradation were assessed by altering both the type of metal oxide in the catalyst and the ratio of metal oxide to MOF.

As illustrated in Figure 1, the impact of metal oxides on the degradation of CR dye is evident, when compared with the degradation of the pure CR dye after the same irradiation period.

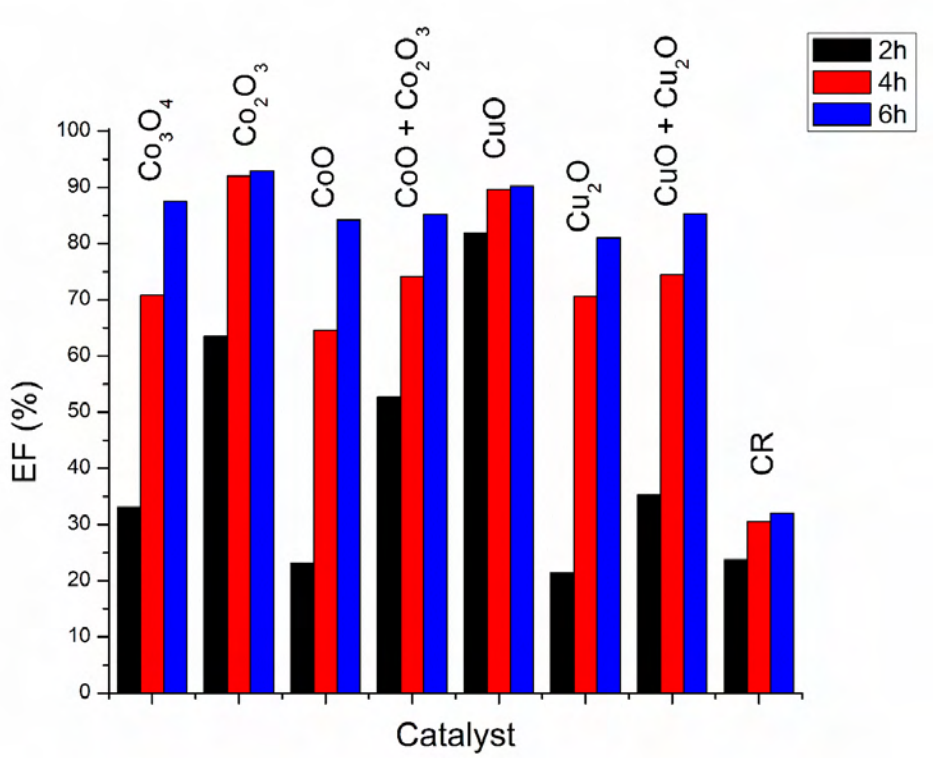

Figure 1. Impact of metal oxides on the CR degradation, compared to the pure CR

The maximum CR degradation efficiency of the metal oxide after a 2-hour irradiation period was achieved by copper in the form of CuO. The catalytic activity decreases in the following order, as illustrated in Table 1, showcasing the comparative effectiveness of various metal oxides in degrading CR dye.

Table 1. Comparative Effectiveness of Metal Oxides in CR Dye Degradation After 2 Hours

Metal Oxide	*CuO*	*Co_2O_3*	*CoO/Co_2O_3*	*Cu_2O/CuO*	*Co_3O_4*	*CoO*	***CR***	*Cu_2O*
CR degradation (%)	81.9	63.6	52.7	35.3	33.1	23.1	23.7	21.4

As one can see, after 2h of irradiation, CuO is the best catalyst by far, followed to some extent by Co_2O_3, while other oxides show much lower activity.

Table 2. Comparative Effectiveness of Metal Oxides in CR Dye Degradation After 6 Hours

Metal Oxide	*Co_2O_3*	*CuO*	*Co_3O_4*	*Cu_2O/CuO*	*CoO/Co_2O_3*	*CoO*	*Cu_2O*	***CR***
CR degradation (%)	93	90.5	87.2	85.3	85.2	84.3	81	32

After 6h of irradiation, all oxides reach high values of efficiencies (>80%). Co_2O_3 even surpasses CuO activity by little and Co_3O_4 activity is also very close to theirs.

Another noteworthy observation: after 2h of irradiation, CoO and Cu_2O have almost no influence on the decomposition speed of CR, but after the 4h and 6h of irradiation, their catalytical behavior is obvious. In other words, all oxides (investigated in this work) are catalyst for CR decomposition, it is just that some are slower/faster than others.

Figure 2 summarizes results that have been previously shown for metal oxides only and for MeO+MOF (50:50 wt% ratio) catalyst mixtures after 2 h or irradiation.

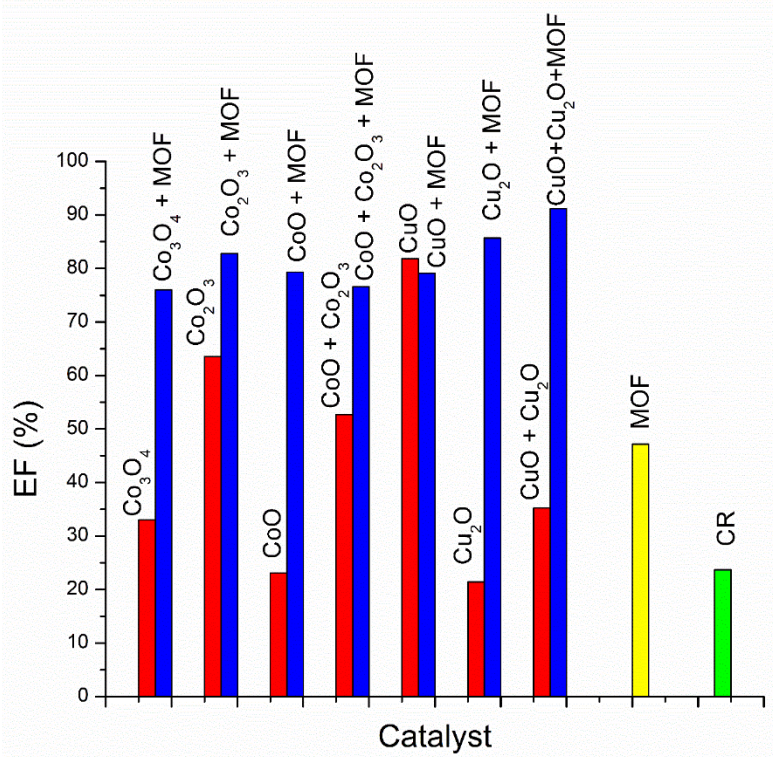

Figure 2. Impact of MeO/MOF (50:50) on the CR degradation after 2h, compared to the pure MeO, MOF and CR

For MeO+MOF samples irradiated for 2h, catalytic activity decreases in following order, as represented in Table 3.

Table 3. Comparative Effectiveness of MeO/MOF (50:50) in CR Dye Degradation After 2 Hours

Metal Oxide	*Cu_2O/CuO-MOF*	*Cu_2O-MOF*	*Co_2O_3-MOF*	*CoO-MOF*	*CuO-MOF*	*CoO/Co_2O_3-MOF*	*Co_3O_4-MOF*	*MOF*	*CR*
CR degradation (%)	91.2	85.7	82.8	79.3	79.1	76.6	76	47.2	23.7

Upon examining the graph, it becomes evident that the introduction of MOF notably enhanced catalytic performances of all oxides. Efficiency values for MeO+MOF samples are far higher than values obtained for pure MeOs, pure MOF and pure CR after the 2h of irradiation, unequivocally indicating that MeO+MOF composite powders are better photocatalysts than individual components. The only exception to this general observation is CuO, which evidently retains its catalytic activity unaffected by the presence of MOF. Efficiency values for pure CuO and CuO+MOF exhibit minimal disparity, measuring at 81.9% and 79.1%, respectively.

It can also be observed that presence of the MOF influenced the catalytic activity of oxides in a manner such that now oxides who weren't showing high activities while used alone, now shows higher photocatalytical activities when in contact with MOF, while some oxides who were among the best catalyst while being alone – now shows lower activity when in contact with MOF.

Examples: Pure CuO was the best catalyst for the CR decomposition after the 2h of irradiation, but when mixed with MOF – it is now at the $4^{th}/5^{th}$ place as a MeO/MOF composite. Pure Cu_2O who was the worst catalyst for the CR decomposition after 2h of irradiation, is now at the $1^{st}/2^{nd}$ place in the catalytic activities order of the MeO/MOF composites.

At the two-hour mark, the CuO+Cu_2O/MOF composite displayed exceptional performance, achieving a remarkable 91.2% efficiency in CR degradation. This MeO/MOF composite, outperformed the pure metal oxide counterpart by an impressive 56% and pure MOF by an 44% within

the same time frame. The composite Cu_2O/MOF exhibited the second-highest performance, with a CR degradation efficiency of 85.7%.

4 Conclusion

Photocatalytic activity of some cobalt and copper oxides and their composite powder mixtures with UiO-66 MOF on the degradation of a Congo red dye were investigated. Our findings demonstrated that the addition of MOF, with a 50:50 MeO/MOF ratio, significantly improved the catalytic performance of most metal oxides, with CuO being an exception. Notably, CuO+Cu_2O/MOF composite exhibited exceptional efficiency, outperforming both pure metal oxides and MOF individually. In summary, the study highlights the potential of metal oxide/MOF composites, particularly Cu_2O/MOF and CuO+Cu_2O/MOF, as promising photocatalysts for the degradation of organic dyes like Congo red. These findings contribute to the ongoing efforts to develop efficient and sustainable wastewater treatment methods to mitigate the environmental impact of industrial pollutants.

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