

ORIGINAL RESEARCH PAPER

A Comparison of the Catalytic Activity of Cu-X₂ (X=Mn, Co) Nano Mixed Oxides toward Phenol Remediation from Wastewater by Catalytic Wet Peroxide Oxidation

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Received: 2020-02-03

Accepted: 2020-04-10

Published: 2020-05-01

ABSTRACT

The catalytic wet peroxide oxidation of phenol from aqueous wastewater and COD reduction over Cu-Mn₂ and Cu-Co₂ nano mixed oxides are reported. The effects of process variables of pH, reaction time, and hydrogen peroxide dosage were investigated in the process over both catalysts. The catalysts were characterized by X-ray diffraction (XRD) and it was concluded that the mixed oxides are in the form of the spinel structure. However, a little bit CuO was found in the mixed oxides. The morphology and particle size of the catalysts were investigated by scanning electron microscope (SEM). The morphologies and particle size of the catalyst were approximately the same with an average range of 40-60 nm. The catalytic results indicated the higher activity of CuCo₂O₄ spinel. The phenol oxidation on Cu-Co₂ oxide was 82% after 40 min, whereas on the Cu-Mn₂ oxide was 78% even after 50 min. The COD reduction The higher activity and reusability of the Cu-Co₂ catalyst is attributed to the high synergistic effect between CuO particles and Cu-Co₂ spinel, promoting phenol degradation.

Keywords: Water treatment, phenolic pollution, spinel nanocatalyst, catalytic wet peroxide oxidation.

How to cite this article

Bagheri B., Hosseini SA., Mehrizadeh H. A Comparison of the Catalytic Activity of Cu-X₂ (X=Mn, Co) Nano Mixed Oxides toward Phenol Remediation from Wastewater by Catalytic Wet Peroxide Oxidation. J. Water Environ. Nanotechnol., 2020; 5(2): 139-146. DOI: 10.22090/jwent.2020.02.004

INTRODUCTION

Phenol, one of the most important aromatic compounds, is conventional pollutants, mainly from petrochemicals, chemical drugs, textile factories, refineries, and other industrial sectors [1-2]. Phenol presence in water is dangerous even at low concentrations. Many methods, such as biodegradation [3], electrochemical degradation [4], physical absorption [5], and the advanced oxidation processes (AOPs) [6] used to remove phenol from wastewater. Phenol is water-soluble and most organic solvents, such as aromatic hydrocarbons, ketones, alcohols, ethers, halogenated hydrocarbons, and acids.

Phenol is naturally present in products from coal tar and crude oil, which can be purified and

distilled through distillation, except at 170 to 230 °C or other methods, until phenolic acid Gray or pure phenol [7]. Phenol is highly carcinogenic to humans and causes significant health concerns even at low concentrations. Its toxic effects include permeating cell membranes and cytoplasmic coagulation. The standard amount of phenol in drinking

water is 0.5 mg, while the limit for effluent from industrial waste output is 1 mg.L⁻¹.

Conventional methods have been applied such as steam distillation, liquid-liquid extraction, adsorption, solid-phase extraction, wet air oxidation, catalytic wet air oxidation, and

biodegradation for removal of phenols. Advanced technologies for removal of phenols include electrochemical oxidation, photo-oxidation, ozonation, UV/H₂O₂, Fenton reaction, membrane

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processes, and enzymatic treatment [8-10].

Among the advanced oxidation processes (AOP), catalytic wet peroxide oxidation (CWPO) is recognized as a low-cost technology [10], since it operates with simple equipment and under mild conditions (e.g., at atmospheric pressure and low temperatures. So, it is a suitable method for phenol remediation. This method is usually used to remove organic pollutants from the solution and they are a remarkable subject of studies over the past three decades. The oxidation in this process is completely carried out. Hydrogen peroxide is a very powerful oxidizing agent that has been used effectively and widely for the oxidation of compounds such as phenols, cyanides, sulfur compounds, and metal ions. The main advantage of the hydrogen peroxide in the process (CWPO) is its low cost, high oxidizing capacity, ease of displacement, water solubility and the absence of toxic and coloured toxic products. This oxidizing agent is a relatively harmless substance used in the treatment of many organic and inorganic materials. Also, increasing the hydrogen peroxide can efficiently oxidize the benzene ring over a wide range of temperatures and concentrations. The mechanism of the CWPO process is that hydrogen peroxide, in the presence of a catalyst, creates hydroxide radicals that blend organic matter and disintegrate their structure. In this process like other catalytic processes, the catalyst type and its properties play a main role. Heterogeneous catalysts based on low-valence transition metals appear as a promising alternative for the catalytic wet peroxide oxidation (CWPO) of organic pollutants since oxidation efficiencies are relatively high and pH sensitivity is lower. Among the solid catalysts, spinel catalysts exhibited high catalytic activity and stability in the process [11, 12].

The paper aims are to evaluate the activity of two mixed oxides of copper with cobalt and manganese (Cu-Mn and Cu-Co mixed nano oxides) as novel nanocatalysts in catalytic wet peroxide oxidation of the phenol from wastewater and reduction of COD contents. In the study, some process variables such as the effect of hydrogen peroxide oxidation, pH reaction, and reaction time are studied at the same value of catalyst dosage and initial phenol concentration. The catalysts were synthesized by the conventional sol-gel auto combustion method and characterized by XRD and SEM.

MATERIALS AND METHOD

The used materials were copper and manganese nitrates, H₂O₂, citric acid monohydrate, phenol (C₆H₅OH) and MnO₂. All materials with a purity of 98% were supplied by Merck company.

CATALYST SYNTHESIS

The conventional sol-gel method was used to synthesize the catalysts. In summary, 0.01 mol of copper nitrate and 0.02 mol from cobalt nitrate (for Cu-Co₂ oxide) and 0.02 mol Manganese nitrate for Cu-Mn₂) were dissolved in 100 mL distilled water and mixed at 70 °C for 20 minutes. Then 5 of citric acid is added to the solutions. The temperature increased to 100 °C and gradually increase to 200 °C to burn the gel and turn to powder. The resulted powder was ground and calcined at a temperature of 700 °C for 6 hours.

CATALYST CHARACTERIZATION

The catalysts were characterized by XRD and SEM. The characteristic structure of the catalysts was resulted by XRD using Philips PW1800 diffractometer and Cu K_α radiation.

The morphology of the mixed oxides was determined via scanning electron microscopy (SEM) by Tescan instrument with pre-coating samples with gold.

CWPO process

The catalytic wet oxidation tests were carried out in a 500 mL batch reactor. In all tests, the concentrations of the catalyst and phenol in the wastewater were 0.5 g.L⁻¹, and 100 ppm, respectively. In all studies, the reaction temperature was the same. To study the effect of other process variables, different values of hydrogen peroxide, reaction time, and pH were considered under continuous stirring at 500 rpm. The concentration of the remained phenol after the reaction was detected and measured by a UV-Vis spectrophotometer (PG Instrument 80). The COD (dichromatic closed reflux method) was measured according to the standard methods book [13].

During all the oxidation reactions, 5 mL aliquots were mixed with 0.1 g of manganese oxide for 15 min to eliminate the residue of hydrogen peroxide, and filtered before measuring the residual phenol concentration.

The percentages of phenol and COD removed

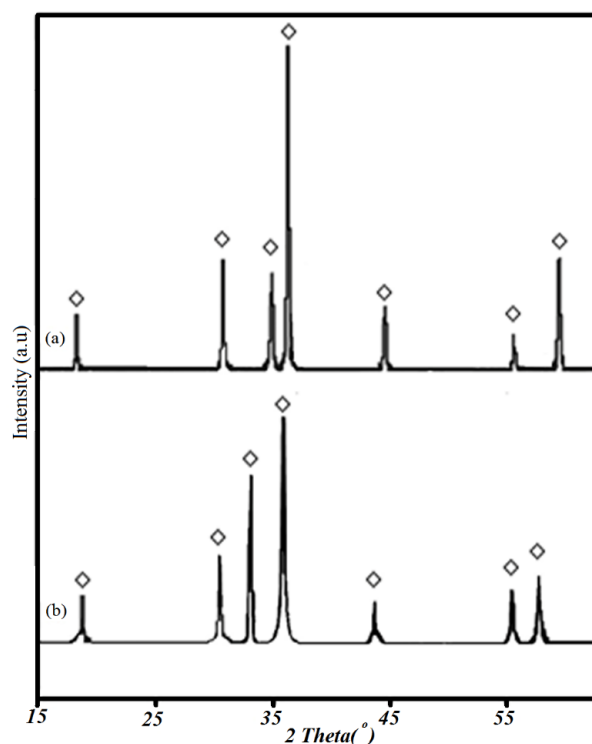


Fig.1. XRD pattern of the Cu-Co (a) and Cu-Mn (b) mixed catalysts

were calculated using the following equation (Eq. 1):

$$R = \frac{[input] - [output]}{[input]} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

The X-ray diffraction pattern of Cu-Mn and Cu-Co mixed oxides is shown in Fig.1. It has resulted from Fig.1a that the Cu-Co mixed oxide is comprised of a mixture of $Cu_{0.15}Co_{2.84}O_4$ spinel (a $Cu_xCo_{3-x}O_4$ spinel-type) and some CuO [11]. The X-ray pattern of copper-manganese mixed oxide (Fig.1b) showed the tetragonal phase in the form of $CuMn_2O_4$ and CuO. Through the peak of 36.7° and using the Debye-Scherrer formula, the mean crystallite size of the Cu-Mn and Cu-Co mixed oxides was estimated to be 50 and 55 nm, respectively.

The scanning electron image of the mixed oxides is shown in Fig. 2. Generally, the morphology of both catalysts is similar. The images reveal that the catalysts are comprised of granule particles agglomerate to some extent. It is clear that the particle size is below 100 nm and most of the

particles are at the range 40-60nm.

The stated before, the studies of phenol oxidation in aqueous solutions by catalytic wet peroxide oxidation were conducted at the constant reaction temperature, catalyst amount, and phenol concentration. To find the optimum temperature for the reaction, the reaction was performed at different temperatures. We found the temperature of $50^\circ C$ as optimum value and applied it in all tests.

Massa et al. investigated the catalytic wet peroxide oxidation of phenol solutions over CuO/CeO₂ systems at $70^\circ C$ [14]. Catrinescu et al. reported the temperature of $50^\circ C$ as the optimum temperature at catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite [15]. Zazo et al. also reported the temperature of $50^\circ C$ as the optimum value for Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst [16].

The studies include the investigation of the effect of three effective factors on the process including the volume of H₂O₂ (mL), reaction time (min), and pH of the solution. The effect of each factor was studied and optimized by one factor at a time method. For each catalyst, four tests were

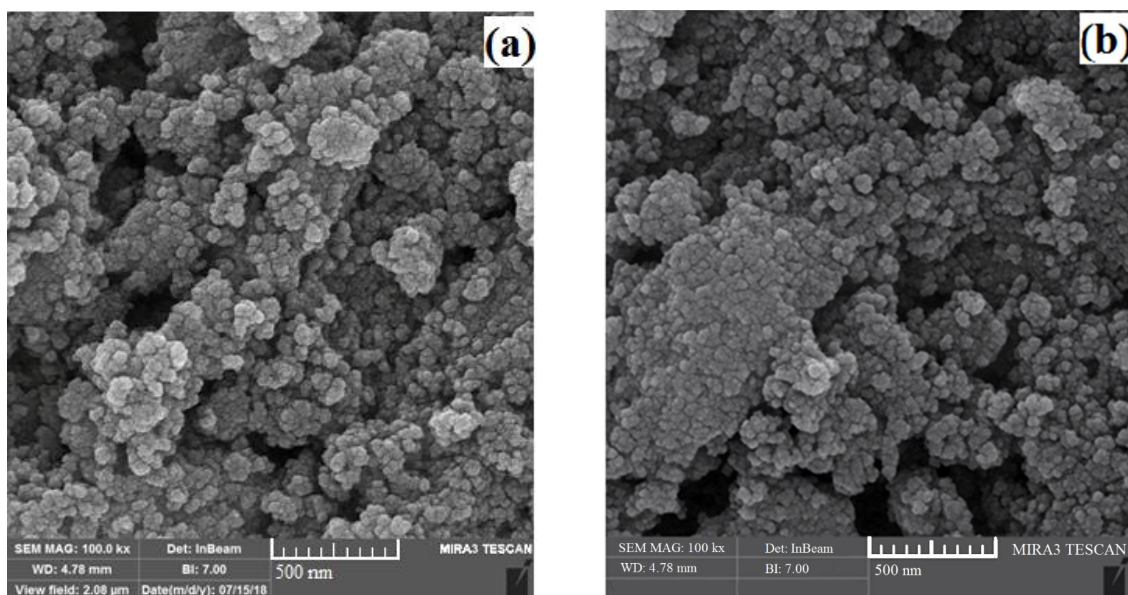


Fig. 2. SEM image of Cu-Co (a) and Cu-Mn (b) mixed oxide

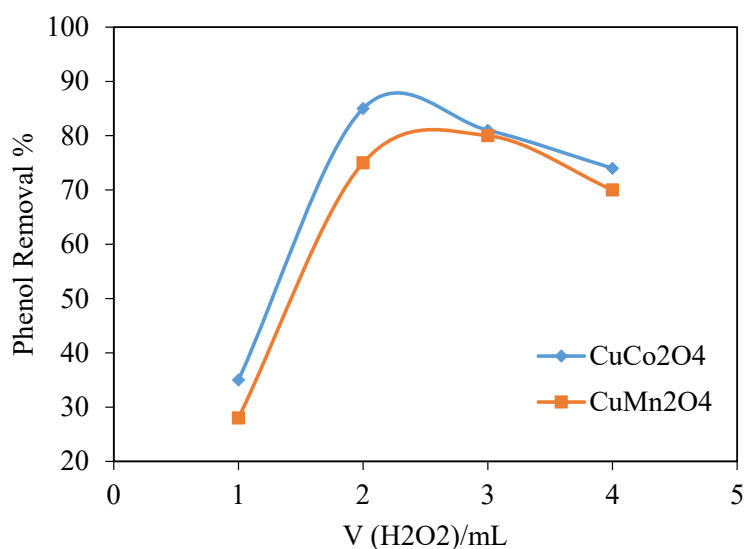


Fig. 3. The effect of different peroxide dosage on phenol removal percent.

accomplished with different loadings of H₂O₂ and the results are presented in Fig.3. There is an optimum value for peroxide volume in that the 2.3 mL and 3 mL for the reaction over Cu-Co and Cu-Mn catalysts, respectively, where the removal of phenol reached 86 and 80 %.

The effect of reaction time on phenol removal was also studied and the results are shown in

Fig.4. It is observed that the maximum removal of phenol (82%) onto Cu-Co mixed oxide occurs at 40 min. So it was considered an optimum time. In the case of phenol oxidation onto Cu-Mn oxide, the optimum time was 50 min in that 78% of phenol was removed. It has resulted that the Cu-Co catalyst is more reactive than Cu-Mn oxide. The maximum COD removal achieved at a reaction

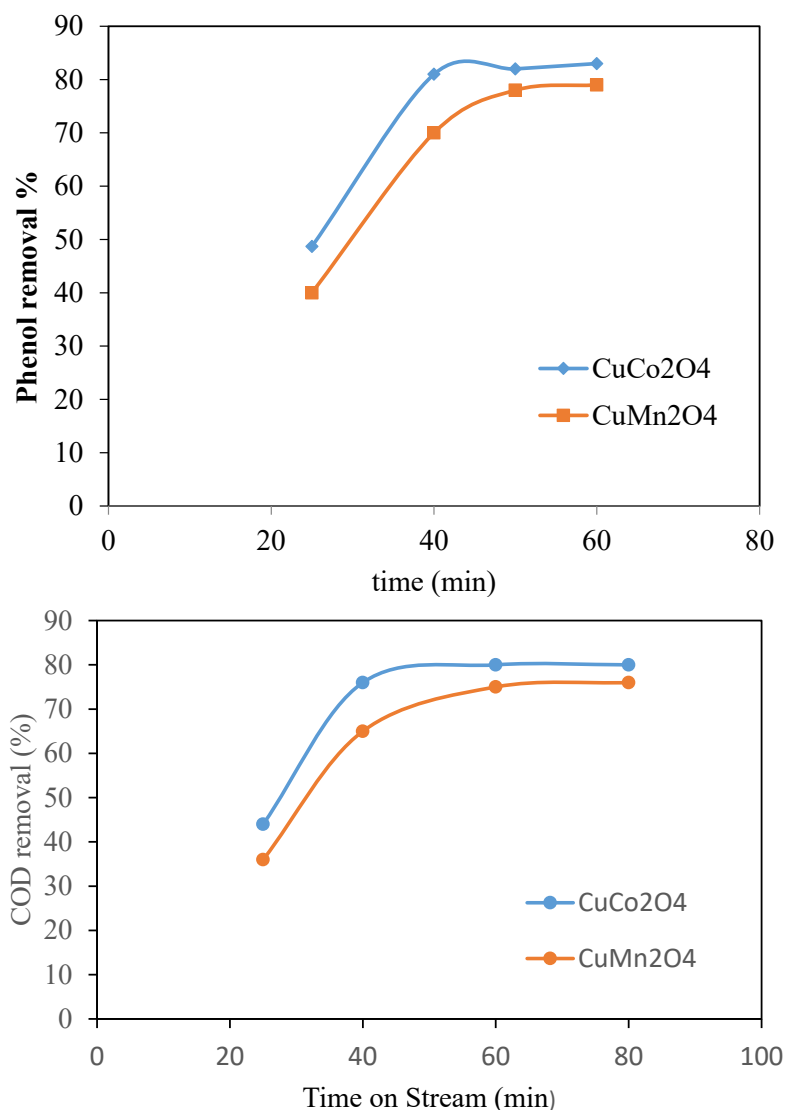


Fig. 4. Phenol Removal and COD removal percent at different times on stream in the Catalytic wet peroxide oxidation process.

time of 40 min in the presence of Cu-Co₂ mixed oxides was 76% and it reached 75% at the presence of Cu-Mn₂ oxide after 60 min. It means that the type of catalysts also affects on the COD reduction in wastewater. Cu-Co₂ oxide has more effect to reduce the COD at lower times.

Besides, the effect of solution pH on the efficiency of phenol removal by CWPO process over the catalysts, and the results are presented in Fig.5. The results indicated that the optimum pH is 7 for the CWPO of phenol over both catalysts. Britto et al. reported that the optimum pH for the removal of phenol is 6.5 in the industrial scale [18]. The maximum COD removal occurred at

pH around 7 and indicated that the pH of 7 is the optimum pH for COD removal in the presence of both catalysts.

The activity of the catalysts was calculated based on the rate of phenol removal on the catalysts and compared with that of reported in the literature. The results are presented in Table1. The concentration of the catalysts at the wastewater of the ref.17 is 1g.L⁻¹, whereas in our studies the catalyst concentration was 0.5 g.L⁻¹. It is observed that the rates of phenol oxidation on the CuCo₂ and CuMn₂ oxides are much more than those reported in ref [17], indicating the superior activity of our catalysts in CWPO process.

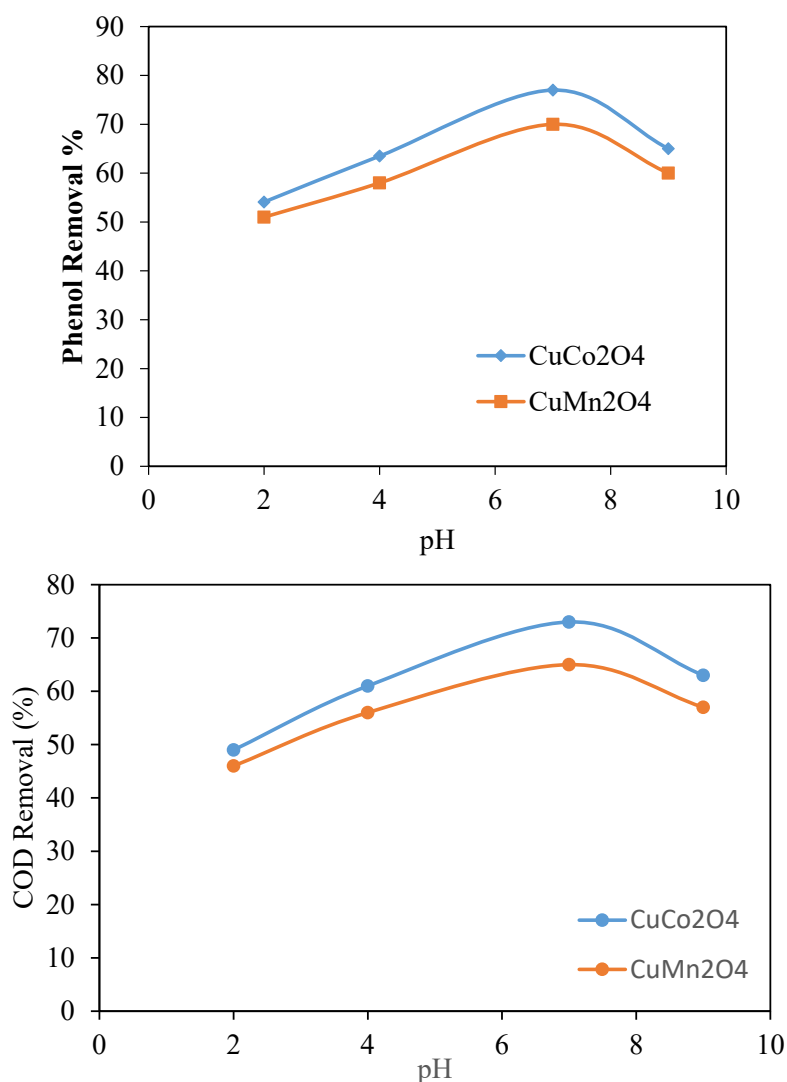


Fig. 5. Phenol Removal percent and COD removal at different pH.

Table 1. The rate of phenol oxidation by CWPO over different catalysts

Catalyst	Phenol conc. (mM)	Time (min)	Conversion (%)	Rate (mM. min ⁻¹)	Rate (mM.g _{cat} .min ⁻¹)	Ref
Cu-Co ₂ oxide	1.065	40	81	2.15×10 ⁻²	4.3×10 ⁻²	This work
Cu-Mn ₂ oxide	1.065	40	70	1.8×10 ⁻²	3.6×10 ⁻²	This work
CuNiAlCO ₃	2.66	90	100	2.95×10 ⁻²	2.95×10 ⁻²	[17]
NaCl/ CuNiAlCO ₃	2.66	60	100	4.42×10 ⁻²	4.42×10 ⁻²	[17]
KCl/ CuNiAlCO ₃	2.66	60	94.4	4.18×10 ⁻²	4.18×10 ⁻²	[17]
NaNO ₃ / CuNiAlCO ₃	2.66	120	41.3	9.14×10 ⁻²	9.14×10 ⁻²	[17]

So, it concluded that among the catalysts, the Cu-Co₂ catalyst is more active and selected as the best catalyst. The high activity of Cu-Co₂ catalyst is due to synergistic behavior between Cu_xCo_{3-x}O₄

spinel and CuO [19, 20]. The optimum conditions for phenol removal over CuCo₂ catalyst resulted in pH, reaction time, and hydrogen peroxide dosage of 7, 40 min, and 2.3 mL, respectively.

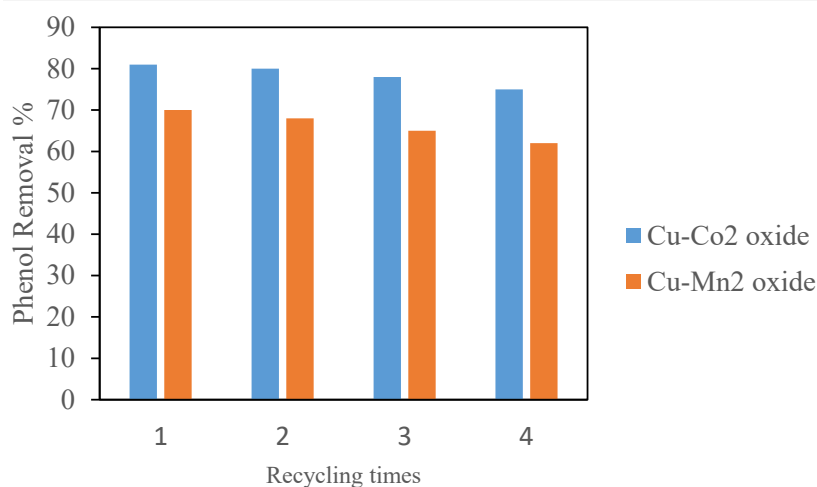


Fig. 6. The reusability of the catalysts in phenol oxidation by CWPO process

Finally, the reusability of the catalysts was evaluated for four cycles (Fig. 6). In the case of Cu-Co₂ oxide, the phenol removal only 7% decreased after four cycles, indicating the acceptable stability and reusability of the catalysts. In the case of Cu-Mn₂ oxide, promising reusability and stability were also observed. The results of the reusability approved that both catalysts are promising to be used in CWPO process.

CONCLUSION

The removal of phenol from wastewater by catalytic wet peroxide oxidation was successfully investigated using Cu-Co₂ and Cu-Mn₂ spinel oxides. The Cu-Co₂ nano mixed oxide was exhibited a considerable activity for phenol remediation. There was no obvious difference between the morphologies of the catalyst. The superior activity of the Cu-Co₂ catalyst at phenol removal and COD reduction of the wastewater is attributed to the higher synergetic behavior between spinel and copper oxide in the structure of the catalyst. The study revealed that the COD reduction of the wastewater is also affected by pH, time on stream, and type of catalysts used at CWPO process. The catalysts exhibited promising reusability for CWPO process. Generally, the process of wet catalytic oxidation with hydrogen peroxide, due to the lack of need for difficult laboratory conditions and the absence of toxic and high toxicity production, can be a good alternative to the various physical and chemical methods of phenol removal.

ACKNOWLEDGMENTS

The authors wish to acknowledge financial and spiritual support from Urmia University.

CONFLICT OF INTEREST

Author declares no conflict of interest.

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