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Removal of Methyl Tert-Butyl Ether from Contaminated Water Using ZnO and CuO Nanocatalyst and Investigation of Effect of Nanoparticle Structure in Removal Efficiency

Leila Fereidooni*, Kambiz Tahvildari†, Parisa Maghsoodi** and Mehdi Mehrpooya*****

*Young Researchers and Elites Club, Islamic Azad University, North Tehran Branch, Tehran, Iran

**Department of Applied Chemistry, Faculty of Chemistry, Islamic Azad University, North Tehran Branch,Tehran, Iran

***Renewable Energies and Environment Department, Faculty of New Sciences and Technologies, University of Tehran, Tehran, Iran

†Corresponding author: Kambiz Tahvildari

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ABSTRACT

MTBE (Methyl Tert-Butyl Ether) is an oxygen-containing organic compound that has been used in unleaded gasoline. MTBE is a gasoline additive commercially used as an octane enhancer and combustion promoter. Unfortunately, it is recognized that dumping MTBE in nature, contaminates the groundwater and thus its removal is an important process. This research is an experimental-laboratory study, investigating the removal of MTBE using ZnO and CuO. The effect of important operational parameters on the MTBE removal from the groundwater such as pH, changes of initial MTBE concentration, particle size of zinc and copper oxide nanoparticles, and UV irradiation time was studied as well. The results showed that using copper oxide nanoparticles for MTBE removal yielded higher efficiency compared with using zinc oxide nanoparticles. The increase in nano-oxide particle size led to an enhancement in MTBE removal efficiency. This study has shown that the yield of MTBE removal from contaminated water can be expected to be higher in the presence of UV irradiation, acidic pH, high initial concentration using copper and zinc nanocatalyst.

INTRODUCTION

MTBE is a hydrophilic ether with a molecular formula of $CH_3OC(CH_3)_3$ which is manufactured via the chemical reaction of methanol and isobutylene. MTBE can be a replacement for tetraethyl lead in gasoline for the purpose of ease of production, reduction of exhaust emissions of CO and NO_x, octane number enhancement, relative improvement in air quality, optimized oxidation during combustion, and facilitation of fuel combustion in motor vehicles. Although MTBE usage was first considered due to its environmental benefits, its toxicity to human and environment is well documented (Squillace 1997) and the US Environmental Protection Agency (USEPA) has classified it as a possible human carcinogen.

Underground leaking fuel tanks are the main sources of ground and surface water contamination. The high water solubility and resistance to natural degradation associated with MTBE results in contamination of ground and surface waters and leads to a danger for human health and environment. As a result, leaving methyl tert-butyl ether in the environment will lead to hazardous consequences, and the removal of MTBE should be considered (U.S. Environmental Protection Agency 1997). MTBE removal from water and groundwater can be complicated due to the following characteristics: hydrophilicity, low constant of Henry's law, and low tendency to adsorbents. There are various methods for MTBE removal from the contaminated water and groundwater which can be subdivided into:

- Air stripping which requires more air purification for MTBE removal.
- Membrane methods which are proven to be costly.
- Hydrogen peroxide/ozone advanced oxidation process which is the most effective treatment process. However, it should be noted that a significant disadvantage of this method is the formation of dangerous and non-biodegradable products that should be removed from drinking water.
- Biological treatment which, due to the MTBE resistance, can be relatively slow and difficult and requires more time for parameters that should be considered in designing the biological reactors (Ke 2008).

A few studies have examined the MTBE removal from contaminated water. However, due to the limitations and

dangers of this process, Zn and Cu nanocatalysts were used to remove MTBE from water in the current study. During the oxidation process, an organic compound such as MTBE is converted into carbon dioxide and water. The ZnO and CuO nanocatalysts were first prepared with different particle sizes using sol-gel auto combustion technique (Patil 2002, Safaei-Naeini 2011, Wang 2010, Baythoun 1982). Moreover, the effectiveness of each nanocatalyst and further parameters such as particle size of the ZnO and CuO nanocatalysts, UV irradiation, solution pH, and changes of initial concentration of MTBE were also studied for MTBE removal from water and wastewater.

MATERIALS AND METHODS

Materials: The following materials were employed in this study: Zinc nitrate, copper (II) nitrate, potassium dichromate, MTBE, and twice distilled water that was made by Merck-Schuchardt Hohenbrunn.

Equipment: Programmable furnace (heats to 1200°C), X-ray diffraction instrument (XRD) (STOE Stadi P model, made by Germany), scanning electron microscope (SEM) (XL30 model, made in Holland), centrifuge KUKUSAN (H-11n model, made in Japan), UV-Visible spectrophotometer (Cary 100 Bio model, made in Australia), magnetic stirrer (RCT basic IKAMAG model made in Germany), UV lamp (30W, made by Philips (UV-C) company)), Kern & Sohn GmbH balance (KERN KB-200-3N model, made in Germany).

ZnO and CuO (II) nanocatalysts: ZnO and CuO (II) nanocatalysts were synthesized with different particle sizes using auto-combustion sol-gel method.

This process was performed in four separate experiments. Zinc oxide nanocatalysts were produced using two different experiments. In one experiment, zinc nitrate [$Zn(NO_3)_2.4H_2O$] and in another, urea [$CO(NH_2)_2$] was used with glycine [NH_2CH_2COOH] as a fuel, respectively.

For the aim of producing CuO (II) nanocatalysts with different particle sizes, two experiments were performed. In one experiment, copper nitrate [$Cu(NO_3)_2.3H_2O$] was combined with urea and in another it was mixed with glycine, respectively. These mixtures were then dissolved in twice distilled water (as a solvent) with a molar ratio of fuel: metal nitrate of 3:1. Drops of ammonia were added gradually over time, in order to maintain the neutral pH of the solution (Sol) (~7). Evaporation of volatile compounds was also carried out using a water bath with a temperature range of 60-70°C. Water evaporation causes the solution to become viscose and concentrated. The resulting viscose gel was heated in a crucible and the combustion reaction occurred under heating conditions. Viscose gel started to boil and rise rapidly through the crucible wall and an exothermic reaction occurred. Removal of hot gasses from solution leads to producing light and porous nanoparticles. In the next stage, the final particles were prepared by grinding the porous powder and finally for the purpose of removing the remaining organic compounds, they were calcined for 2 hours at the temperature of 600°C.

Identification of ZnO and CuO (II) nanaocatalysts: Identification of particle size and morphology was done by X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Braun 1987, Christian 1986, Ewing 1985). The presence of CuO and ZnO was also confirmed by XRD spectra and SEM images. Average particle sizes of nanocatalysts with urea and glycine fuel were calculated using XRD spectra and Scherrer equation. The average particle size of ZnO nanocatalyst was 57, 60 nm and it was 48, 59 nm for CuO (II) nanocatalyst, respectively. The results are shown in the Figs. 1-3.

Application of the synthesized nanocatalysts for MTBE removal: An investigation was conducted in batch laboratory scales. The influential factors in MTBE removal from water were expected to be the following parameters: effect of copper and zinc nano-oxides particle size (with the average particle size of 48, 57, 59, and 60 nm), UV irradiation, changes of the initial concentrations of MTBE, and pH solution, which was examined through separate experiments. In the current examination, some distilled water containing MTBE was used for the preparation of simulated contaminated water.

The effect of zinc and copper oxide nanoparticles in MTBE removal from water: Four 0.1g doses of zinc and copper oxide nanoparticles with the average particle sizes of 48, 57, 59 and 60 nm were added to a 500 mg/L solution of MTBE during four separate experiments. Also, sampling process was performed at selected interval times of 30, 60, 90 and 120 minutes. MTBE concentration was studied and analysed by a UV-Visible spectrophotometer. The absorption was measured by an inverse analysis in which potassium dichromate ($K_2Cr_2O_7$) was added to each sample during the process, and the absorption of each sample was also determined in the presence of potassium dichromate as reagent (Fig. 4).

***The effect of UV irradiation in the presence of zinc and copper oxide nanoparticles in MTBE removal from solution*:** Four 0.1g doses of zinc and copper oxide nanoparticles with the average particle sizes of 48, 57, 59 and 60 nm were added to a 500 mg/L solution of MTBE during four separate experiments. During UV irradiation, the solution was magnetically stirred. Additionally, sampling process was performed at selected interval times of 30, 60, 90 and 120 minutes. Finally, by adding potassium dichromate ($K_2Cr_2O_7$)

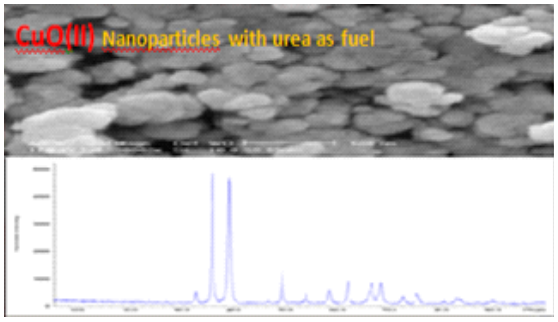

Fig. 1: SEM images and XRD pattern of CuO (II) nanoparticles with urea as fuel.

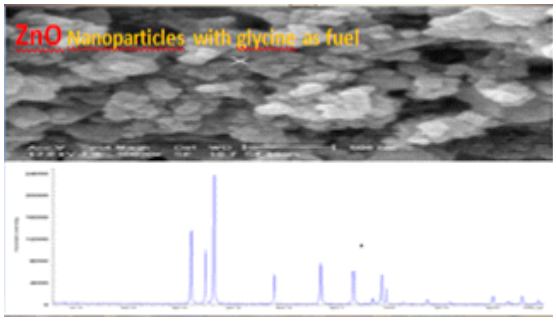

Fig. 2: SEM images and XRD patternof ZnO nanoparticles with glycine as fuel.

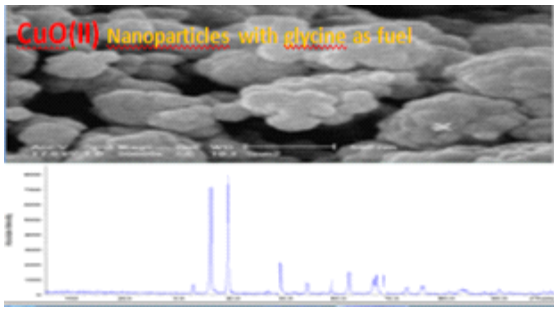

Fig. 3: SEM images and XRD pattern of CuO (II) nanoparticles with glycine as fuel.

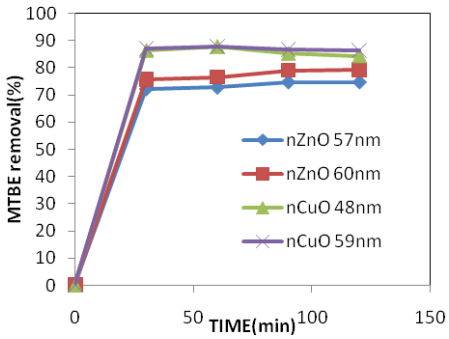

Fig. 4: MTBE removal percentage by zinc and copper oxide nanoparticles with different particle sizes.

to each sample, the absorption was measured using a UV spectrophotometer (Fig. 5). .

The effect of pH in MTBE removal from water: The effect of pH for MTBE removal in the presence of metallic nano-oxides was determined under acidic, basic and neutral conditions in the pH ranges of 5.5, 7 and 9, respectively. Also, 0.1 N ammonium was used to change the pH (Figs. 6 to 9).

The effect of changes in MTBE initial concentration: In order to examine the effect of changes in MTBE initial concentration, the initial concentration was decreased from 500 mg/L to 100 mg/L (Figs. 9 & 10).

RESULTS

The effect of Zn and Cu nano-oxide particle sizes in MTBE removal from water solutions indicates the fact that MTBE removal efficiency from water was higher when Cu nano-oxides were used compared to the experiment using zinc oxide nanoparticles, while the energy gap of CuO is lower than ZnO; the energy gap of zinc oxide nanoparticle was 3.3 eV, and for copper oxide nanoparticles it was in the range of 1.21-1.51 eV. Also, it was illustrated that an increase in particle size of nanoparticles led to MTBE removal enhancement (GUEDES 2009, Jia 2009).

During the experiment with copper oxide nanoparticles, it was observed that the MTBE removal performance of such nano-oxides decreased over time. These results are due to the decrease in active surfaces of copper oxide nanoparticles and also the increase in reactivity along with the decrease in selectivity in removing the pollutant from water. Lower selectivity can lead to the reaction of copper oxide nanoparticle with interference ions and results in low MTBE removal efficiency (Al-Momani 2002).

UV irradiation in the presence of zinc and copper oxide nanoparticle increases MTBE removal efficiency. However, using UV irradiation leads to a slight increase in removal percentage and treatment cost. In fact, such nano-oxides have photocatalytic characteristics under UV irradiation and lead to MTBE removal by photocatalystic degradation. The generation of highly reactive hydroxyl radicals ($OH^{\bullet}$) that react indiscriminately with MTBE results in MTBE degradation and removal from wastewater (Ledakowicz 2001, Zahraa 2006, Asadi 2006).

MTBE removal efficiency in the acidic media is higher than in basic and neutral media. During MTBE degradation, the media should be acidic, particularly during the intermediate degradation. Moreover, the basic media reduces the rate of intermediate degradation (Daneshvar 2002, Daneshvar 2003, Leone 2002).

Higher initial concentrations of MTBE lead to higher

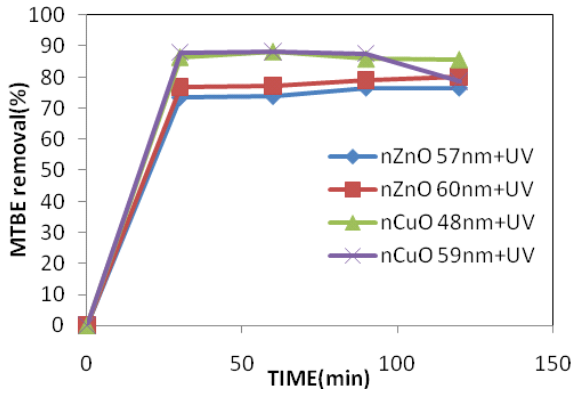

Fig. 5: MTBE removal percentage by using UV irradiation in the presence of zinc and copper oxide nanoparticles with different average particle sizes

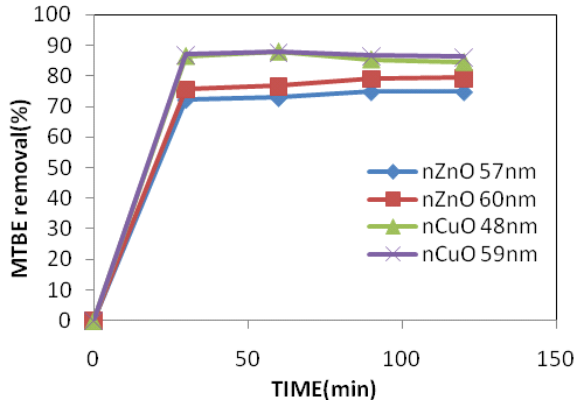

Fig. 6: Comparison of MTBE removal percentage by using zinc and copper oxide nanoparticles with different average particle size, pH=5.5.

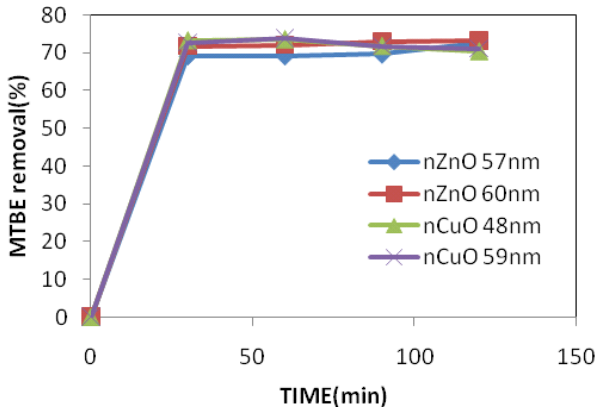

Fig. 7: Comparison of MTBE removal percentages by using zinc and copper oxide nanoparticles with different average particle size, pH=7.

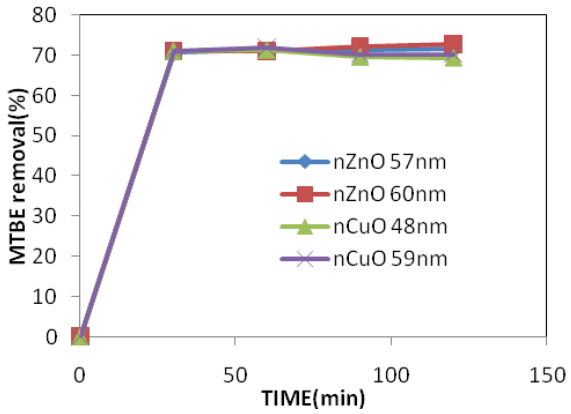

Fig. 8: comparison of MTBE removal percentage using zinc and copper oxide nanoparticles with different average particle size, pH= 9.

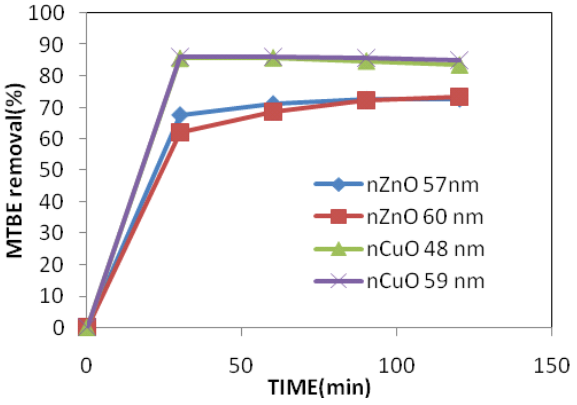

Fig. 9: MTBE removal percentage (100 ppm) using zinc and copper oxide nanoparticles with different average particle size.

MTBE removal efficiency. Based upon our studies, concentrations of 500 mg/L and 100 mg/L have the highest and lowest removal efficiency, respectively.

DISCUSSION

The world is facing big challenges in meeting the rising demands of clean water as the available supplies of freshwater are decreasing with increasing population. The wastewater treatment is the only recycling process which can overcome this problem. Recently, technology advancement has led us to the nanotechnology which accounts for a tremendous scope of wastewater treatment. The physical and chemical properties of nanomaterials can differ significantly from those of their bulk counterpart because of their small size. Nanomaterials are having a much larger surface areas than bulk particles. They also have high capacity/selectivity for toxic substances in aqueous solutions.

Fig. 10: Scheme of MTBE removal by using UV irradiation in the presence of zinc and copper oxide nanoparticles.

CONCLUSION

ZnO nanostructures are of intense interest since they can be grown by a variety of methods with different morphologies. Among the different growth methods, the sol-gel method is a low-temperature, simple, inexpensive and environment-friendly one. On the other hand, natural abundance of copper(II) oxide as well as its low production cost, good electrochemical and catalytic properties make copper oxide one of the best water-purification catalysts. CuO nanoparticle showed a homogeneous morphology and could be considered one of the most important environmental catalysts. The present study showed that using zinc and copper oxide nanoparticles as adsorbent is a potential method for MTBE removal from aqueous matrix. Nanomaterials will become an essential component of industrial and public wastewater treatment systems as more progress is made in nanotechnology in terms of economically efficient and ecofriendly technology developments.

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