CUPROUS OXIDE AS A SEMICONDUCTOR PHOTOCATA-LYST USED FOR ORGANIC POLLUTANTS DEGRADATION

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Abstract: This paper contains discussion about photocatalytic water treatment. Contaminated water is purified by semiconductor photocatalytic material cuprous oxide exposed to light. Cuprous oxide is inexpensive and easy to synthesize and does not need any additional energy for its production. Cuprous oxide is synthesized purely chemically and the reaction requires commonly used chemicals as sodium hydroxide, cupric sulphate and ascorbic acid. The photocatalytic activity of cuprous oxide was examined on degradation of methyl orange dye that is used as a substitute for organic pollutants. The best achieved level of methyl orange degradation was 61.88 %. At the end of this paper the system for photocatalytic degradation was designed.

Keywords: cuprous oxide, Cu₂O, photocatalysis, water treatment, methyl orange

1 INTRODUCTION

In modern world the demand for innovation of reusable and renewable technologies is ascending more rapidly than ever. The use of fossil fuel as the main source of energy is not ecological; from this process a lot of toxic substances are generated. Photocatalytic materials have huge field of use in various environmental saving applications. These applications are CO₂ reduction, water splitting, self-cleaning surfaces or water purification.

Principle of CO₂ reduction methods is that the photocatalytic material can react with this green-house gas and produce harmless products from this reaction. Water splitting photocatalytic methods can produce hydrogen and oxygen from pure water. Hydrogen than can be used in fuel cells and oxygen produced by this method have huge window of use. The self-cleaning surfaces are mostly used in civil engineering. Facades of building in towns are being painted by photocatalytic material to stay clean as they were new. Last but not least the water purification is very important technology and is used all over the world.

All of these applications have one important thing in common: the use of photocatalytic material allows reduction of energy requirements. The only energy used in these applications is solar energy. With use of solar energy as the only source, these methods became environmentally safe, accessible and relatively cheap.

2 THEORY OF PHOTOCATALYSIS

The basic principle of photocatalysis is that when photon falls on surface of photocatalyst the photocatalytic material generates electron-hole pair. Basically, it is the same principle as in any other semiconductor and is commonly used in photovoltaic cells. The generated particles than travel through the volume of this material and when they end on the surface (separately) they can take part in two different reactions. Electrons cause oxidation of substance that is in contact with photocatalytic material and the holes cause reduction of this substance. The important parameter of these

materials is band gap. This parameter says how much energy the photon must have to generate electron hole pair.

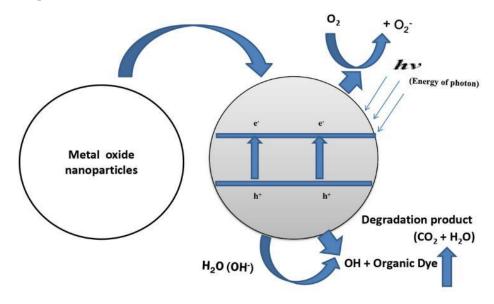


Figure 1: Principle of photocatalytic water treatment [1]

3 CUPROUS OXIDE

Cuprous oxide is monovalent and most stable oxide of copper metal. Band gap of cuprous oxide is 2.2 eV which corresponds with wavelength 563 nm. That means the wavelength of photon must be 563 nm and lower to generate electron-hole pair. In solar spectrum it is in part with highest fraction of solar energy and goes down to UV part of spectrum with higher energy irradiation. Cuprous oxide has some very useful properties such as environmental acceptability, very low toxicity, is inexpensive and simple to synthesize.

4 PREPARATION

Cuprous oxide nanoparticles were prepared by reducing $CuSO_4$ using ascorbic acid at room temperature. All used reagents were of analytical grade and were used without any further purification. In this procedure, 40 mL (0.5 mol/L) aqueous solution of NaOH was added into 20 mL aqueous solution of $CuSO_4$ (1.5 mol/L) with stirring. Then, 50 mL (0.1 mol/L) ascorbic acid aqueous solution was added dropwise into the above solution with vigorous stirring at room temperature. After 30 min reddish precipitate was observed. The particles were separated from the solution by filtration on a sinter glass filter. The product was washed by distilled water and absolute ethanol. The final product was dried in vacuum at $60 \,^{\circ}\text{C}$ (more than $6 \,\text{h}$) [2].

5 PRACTICAL CONSIDERATIONS AND EXPERIMENTS

For the measurement of photocatalytic effectivity of cuprous oxide used for organic pollutant degradation the methyl orange dye was used. In practice, the spectrophotometer Helios Delta by ThermoFisher Scientific measures visible absorption spectrum of methyl orange solution with photocatalyst cuprous oxide powder added. As a result the degradation ratio was calculated by equation (1).

$$D = \frac{A_0 - A_T}{A_0} \cdot 100\% \tag{1}$$

D ... degradation ratio [%]

 A_0 ... absorption of solution in time T = 0 min [-]

A_T ... absorption of solution after time T [-]

To see how much photocatalytic material is needed for methyl orange reduction, the different concentrations of cuprous oxide were measured. In Figure 2 the four different absorption spectra are shown. The first absorption spectrum shows methyl orange dye solution degradation without use of any cuprous oxide. The other three graphs show the absorption spectrum of the concentrations 0.5 g/L, 1.5 g/L and 2.0 g/L respectively. The shade of curves goes from lightest to darkest as the individual absorption spectra were measured. The measurement of each spectra was performed every 20 minutes.

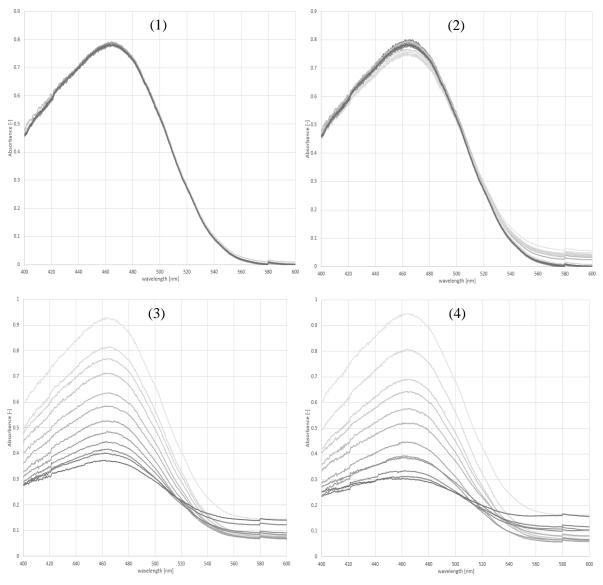


Figure 2: Absorption spectra of methyl orange without photocatalyst (1), with cuprous oxide photocatalyst at concentrations of 0.5 g/L (2), 1.5 g/L (3) and 2.0 g/L (4)

Figure 3 shows time dependence of degradation ratio of measured solutions. From this it is obvious that the amount of used photocatalyst is important factor in methyl orange or organic pollutant degradation.

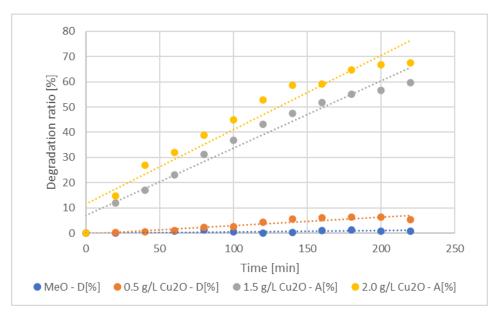


Figure 3: Degradation ratios of measured solutions

6 FUTURE APPLICATIONS

Cuprous oxide as photocatalyst for organic pollutant degradation has a big potential in future applications of water treatment. For this application a photocatalytic system was designed. In Figure 4 this system is illustrated. Basically, the photocatalytic material will be deposited on glass substrate and put into as called photocatalytic chamber. This chamber will be 3D printed with transparent cover so that the solar irradiation can go through and the photocatalytic substrate will be illuminated. The polluted solution of water goes through the system via water pump.

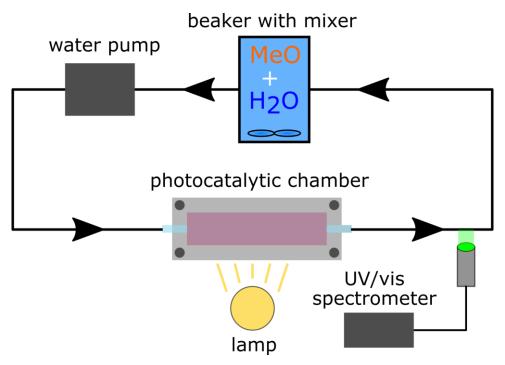


Figure 4: Photocatalytic methyl orange degradation system

7 CONCLUSION

This work contains basic information about photocatalysis and its use for organic pollutant degradation in water treatment applications. In practical and experimental part of this work the measurement of photocatalytic degradation of methyl orange dye was achieved. Results are that the highest ratio of 61.88 % was measured. The degradation ratio depends on concentration of photocatalytic material cuprous oxide. With this it is possible that higher degradation ratio of methyl orange can be observed. At the end of this work the future application is discussed. The photocatalytic methyl orange degradation system has high potential in increasing the effectivity of cuprous oxide as a photocatalyst.

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