

Removal of Remazol Brilliant Blue R (RBBR) by Absorption on Zeolit CuO Catalyst



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ABSTRACT: The pollution caused by dyestuffs has been a serious environmental problem for years. Within the overall category of dyestuffs, Remazol Brilliant Blue R (RBBR) is an anthraquinone dye used in textile industries. This paper concerns the study of the different experimental parameters which affect the decolorization efficiency of the RBBR mixture. Thermal degradation is done by carried out with 4 mL of 10 ppm RBBR solution into the reaction flask. Added a number of H₂O₂ and CuO zeolite catalyst. The reactor was heated in oil bath glycerin and stirred for 90 minutes. The optimum catalyst weight was obtained at 100 mg, which was able to decrease the reaction time 50 minutes compared to the reaction without catalyst. The percentage of dye removal on this catalyst loading was 96.26%. The micro pores of CuO zeolite is about 20 nm, which shows formation of nanoCuO particles in zeolite structure. This structural feature may be important since it increases the total surface area. The diffusion into such pores can explain the absorption capacity.

KEYWORDS: Dyestuffs pollutant, Absorption capacity, Remazol Brilliant Blue R, Zeolite, CuO, Catalyst.

INTRODUCTION

Natural zeolites comprise significant amount of iron cations embedded naturally in cavities. When the natural zeolites are treated by high temperature calcination or steaming, the iron species move into the extra framework of the zeolite as found for iron containing zeolites prepared by hydrothermal methods [1]. Thereafter, the resulting zeolite can be used as a catalytic material in N₂O decomposition and oxidation of hydrocarbons with N₂O such as hydroxylation of benzenin into toluene, oxidative dehydrogenation of propane and epoxidation of propene. An additional feature of practical attractiveness is that the promoting effect of SO₂ was found independent on the zeolite framework, preparation method, and iron content, suggesting that the reaction is not highly sensitive to the iron speciation [2]. However, the use of natural zeolites as catalytic materials is much less studied compared with synthetic materials due to the difficulty in obtaining homogenous material, the reproducibility of samples obtained from natural ores, the thermal and hydrothermal instability. Therefore, to allow them to be used, the characteristics of natural zeolites have to be improved by various methods such as ion exchange with simple inorganic salts and alkali bases, acid leaching (typically HCl or HNO₃), steaming and high temperature calcination[3]. Recently, core/shell composite zeolites have been paid many attentions due to their synergistic performance in catalytic reactions [4]. Due to the optimum performances as solid acid catalysts, more and more consideration has been given to zeolite catalysts to investigate the applicability for the destruction of chlorinated compounds in last years.

Environmental pollution has increased more and more public concern nowadays. Aromatic compounds specially their sulfo, nitro, amidocyanogen or chloro series, are present in industrial wastewater, and are counted an important source of the environmental pollution [5]. Among the many organic compounds found in wastewaters, the pollution caused by dyestuffs has been a serious environmental problem for years[6]. Synthetic dyestuffs are used by several industries such as textile, dyeing and printing industries. Within the overall category of dyestuffs, Remazol Brilliant Blue R (RBBR) is an anthraquinone dye used in textile industries. It is a harmful dye and can damage aquatic life and also vegetative life if the contaminated water is used for irrigation. Recent years have seen a biological approach to this solving problem. Use of microorganisms to degrade it has seen faster and better results than the chemical method. Thus, the treatment of effluents containing such compounds is important for the protection of waters and environment in general [7]. Especially, decontamination of polluted water and air by photocatalysis

Removal of Remazol Brilliant Blue R (RBBR) by Absorption on Zeolite CuO Catalyst

has been attracting a lot of attention for its efficiency and promising economy. Semiconductor photocatalysis, as one of the advanced physicochemical processes, was extensively studied for solving existing environmental problems [8].

Different methods such as: flocculation, the chemical oxidation including Fenton's reagent, O₃ etc., air floatation processes, adsorption processes, anaerobic-aerobic two stage biochemical process, advanced oxidation process (AOP) and other methods have been used to remove different pollutants from water and especially wastewaters [9]. Heterogeneous photocatalysis has already been investigated and successfully applied to the degradation of different organic pollutants [10]. Adsorption is a process that occurs when a fluid (liquid or gas) is bound to a solid and finally forms a film (thin layer) on the surface of the solid. In contrast to absorption, where the fluid is absorbed by other fluids to form a solution. Photocatalysis is a combination reaction between photochemical and catalyst. Process Photochemical reactions involving a light (photo). Photocatalysis itself is a process that is assisted by the presence of light and catalyst material. Catalyst is a substance that affects the reaction rate process without changing it chemically. The catalyst can accelerate photoreaction by interacting with the substrate in either the ground or excited state or with the main photoproduct, depending on the photoreaction mechanism. Copper oxide (CuO) as an important p-type semiconductor with low cost, toxicity, and narrow band-gap (1.2–1.7 eV) absorbs visible light to generate electron-hole pairs (e⁻–h⁺) with enough life-time to let chemical reactions occur. There are some reports in the literature on the synthesis and applications of the CuO as a catalyst in the photo degradation processes of different organic pollutants [11][12][13]. Ameta et al. reported comparative studies on the photocatalytic activity of the copper(II) and nickel(II) oxides in the removal of rose Bengal [14]. On the basis of the rate of the reaction, photocatalytic activity of the CuO semiconductor was higher than NiO. Among the various methods, a great deal of attention has paid to the AOP for the treatment of air and water streams [15]. AOP can generate free radicals, such as hydroxyl radicals (OH^{*}) which are strong and nonselective oxidant species that react with the majority of organic pollutants. Free radicals such as HO₂^{*} and O₂^{*} may also be involved in the degradation process, but these radicals are less effective than the hydroxyl radicals [12][16].

Metal-loaded zeolites are efficient catalysts for direct N₂O decomposition into N₂ and O₂. A number of metals (i.e., Fe, Co, Ni, Cu, Mn, Ce, Ru, Rh, Pd, Pt) deposited in various zeolite structures (especially ZSM-5, but also ZSM-11, beta, mordenite, USY, ferrierite, zeolites A, and X) has been reported as active components for this reaction [17]. Noble metal supported zeolites catalysts show an enhanced catalytic performance for the deep oxidation of Chlorinated Volatile Organic Compounds, CVOCs (benzene, toluene, methyl chloride, etc.) with respect to the pure protonic zeolites, but the major drawback for the application of these catalysts is the halide poisoning of volatile metal oxychlorides as well as the formation of polychlorinated compounds, which are more toxic and recalcitrant than the starting material. It has been reported in previous literature that transition metal (Cr, Mn, Co, Cu, etc.) modified zeolite catalysts exhibit good catalytic activity for the destruction of CVOCs in spite of relatively less active than noble metal modified catalyst [18]. In the past two decades, photocatalytic degradation organic pollutant by semiconductor oxide such as TiO₂, ZnO, NiO, SnO₂, Cu₂O, and In₂O₃ has attracted public concern due to their high photocatalytic efficiency, low cost and low toxicity, high physical and chemical stability, especially, strong ability of fully decomposing organic pollutant into harmless species (e.g. CO₂, H₂O, etc.) [19].

This paper concerns the study of the different experimental parameters which affect the decolorization efficiency of the RBBR mixture. We are choosing dyes mixture because of good solubility in water, as well as its similarity to a real wastewater sample. According to the obtained results, the mixture containing RBBR was chosen as our object and investigated in more details.

EXPERIMENTAL SECTION

Materials

The materials used in this experiment are natural zeolite (CV Transindo Citra Utama), Remazol Brilliant Blue R, RBBR (PT Dyestar Indonesia), H₂O₂ 30% (Merck), HCl (Merck), NaOH (Merck), Cu(NO₃)₂·3H₂O (Merck), aquadest (PT IkapharmindoPutramas) and 87% glycerin (Merck).

Instrumentation

To determine the crystal phase composition of the CuO zeolite catalyst powders, X-ray powder diffraction (XRD) analysis was carried out at room temperature using a Rigaku D/max-2550PC diffractometer (Rigaku Industrial Corporation, Japan) with Cu K α radiation ($\lambda = 0.15406$ nm), over the 2 θ collection range of 5–80°. The accelerating voltage of 40 kV, emission current of 300 mA and the scanning speed of 4°/min were used. The particle size of the CuO zeolite catalyst powders was measured using Scanning Electron Microscope (SEM). The FTIR spectra of WS and MWS were obtained with a Bruker IFS 66/S IR Spectrophotometer. The scanning range was 450–4000 cm⁻¹. The absorption study was conducted at different concentrations of RBBR aqueous solutions ranged from 2 to 10 ppm. The absorption behaviors were employed by UV-Vis spectrophotometer.

Removal of Remazol Brilliant Blue R (RBBR) by Absorbion on Zeolit Cuo Catalyst

Procedure

First zeolites are physically and chemically activated. Physically zeolite activation is done by washing zeolite with aquadest, then stirring for 1 hour at 70° C. Colloid formed then precipitated and dried at 105° C. Chemical activation is done by adding HCl 0.05 M and 0.05 NaOH M into the zeolite and heated at 70° C and stirred for 1 hour. The precipitate formed was dried at 105o C. The dried zeolite was then uniformed with 1M NaCl and then heated at 70° C and stirred for 6 hours. To prepare the copper exchanged zeolite, Na zeolite added 1E-3 Cu(NO₃)₂ then stirred and heated at 80° C for 4 hours. The obtained solid zeolite@Cu²⁺ was filtered, washed with water, and finally dried at 60° C for 30 min in an air oven. Zeolite@Cu²⁺ was formed and then mixed with 1E-4 M NaOH solution so that it was pH 8 and heated at 80° C. The obtained Cu(II)-exchanged zeolite was calcined at 350° C for 2 hours. Thermal degradation is done by carried out with 4 mL of 10 ppm RBBR solution into the reaction flask. Added a number of H₂O₂ and CuO zeolite catalyst. The reactor was heated in oil bath glycerin and stirred for 90 minutes.

RESULTS AND DISCUSSION

Characterizations

XRD was used to investigate the phase structures of the CuO zeolite catalyst powders. Fig.1 shows the XRD patterns of the CuO zeolite catalyst powders. The diffraction peaks of the sample can be indexed with the CuO phase. From the characterization results with XRD there is a peak with weak intensity at angles 31, 35.75 and 38.93 indicating CuO according to JCPDS 45-0937 that has good agreement with the literature [8]. The peaks between 2θ =35 and 39 show formation of copper oxide. The intensity of peaks at 2θ values of 25.5° and 36.5° in the XRD pattern of CuO zeolite sample, indicate the incorporation of Cu²⁺ in the zeolite structure. In addition, some differences such as: broadening of peaks, changing the intensity of some peaks and also the slightly shifts in positions of peaks can be observed in the spectra. In fact, changing in the intensities of peaks in the host–guest composite materials with respect to the Na zeolite can be related to presence or incorporation of CuO as a semiconductor inside the zeolite structure [12][20].

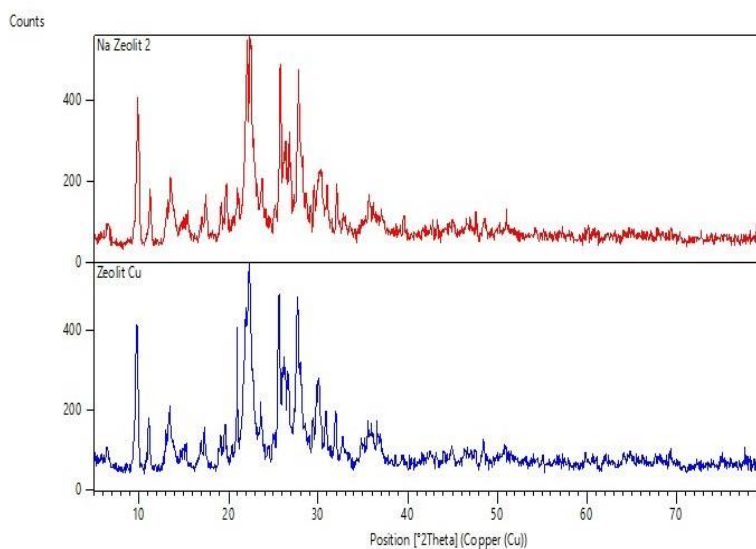


Figure 1. The XRD patterns of the Na zeolite and CuO zeolite catalyst powders.

The morphology of bulk Na zeolite and CuO loaded on zeolite samples are presented in Fig. 2. The image of the loaded indicates the zeolite crystallites are affected by the Cu²⁺ and CuO loading. The average particle sizes of Na zeolite samples is about 25 μm and decrease to 5 μm at bulk CuO loaded. The average particle size of CuO zeolite is about 20 nm, which shows formation of nanoCuO particles in zeolite structure. A SEM micrograph of unloaded zeolite is shown in Fig. 2(a), and indicates the ball shape structure of the Na zeolite. The particle has irregular pores with a diameter of about 3 μm, which indicates that the parent zeolite has a porous structure. This structural feature may be important since it increases the total surface area. Fig. 2(b) shows an SEM micrograph of the Na zeolite loaded with CuO. The structure upon cation exchange had a tendency to form agglomerates of small crystals and also an observed decrease in particles and pore sizes[21].

Removal of Remazol Brilliant Blue R (RBBR) by Absorption on Zeolite CuO Catalyst

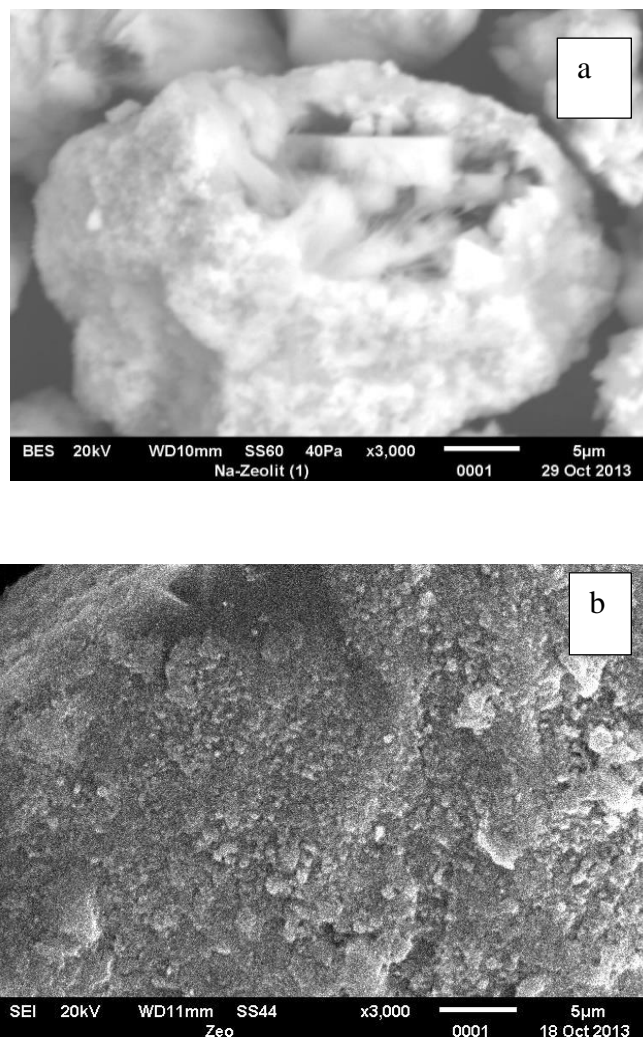


Figure 2. The SEM photographs of Na zeolite (a) and CuO zeolite (b).

FT-IR spectra of the parent zeolite Na and CuO zeolite are shown in Fig. 3. Ion exchanged zeolite (CuX zeolite) shows a band about 1388cm^{-1} after ion-exchange process, which is attributed to the C-H bending vibration (1380cm^{-1}) [3]. This confirms that the compound $\text{Cu}(\text{NO}_3)_2$ is converted to CuO after heat treatment. Because of the copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ undergoes decomposition at elevated temperature and copper oxide is generated. Furthermore, a broad band is observed in the range of $3200\text{--}3700\text{cm}^{-1}$, corresponding to per-turbid OH groups. The presence of a specific band at 3625cm^{-1} which is attributed to $-\text{OH}$ stretching vibrations suggests the existence of CuO in the zeolite structure. In addition, the shift of bands from 986 to 995, 761 to 767, 680 to 684, 571 to 567, and 496 to 463cm^{-1} , which can be seen in the Fig. 3, suggests the existence of structural defects in the zeolite structure. Such structural defects can be interpreted by distortions caused by the presence of occlusions, likely Cu precipitates, in the zeolite structure and generation of new bonds such as Cu-O-Si and Cu-O-Al with surface O of zeolite [8]. The peak at 950cm^{-1} corresponds to silanol nests [22].

Removal of Remazol Brilliant Blue R (RBBR) by Absorption on Zeolite CuO Catalyst

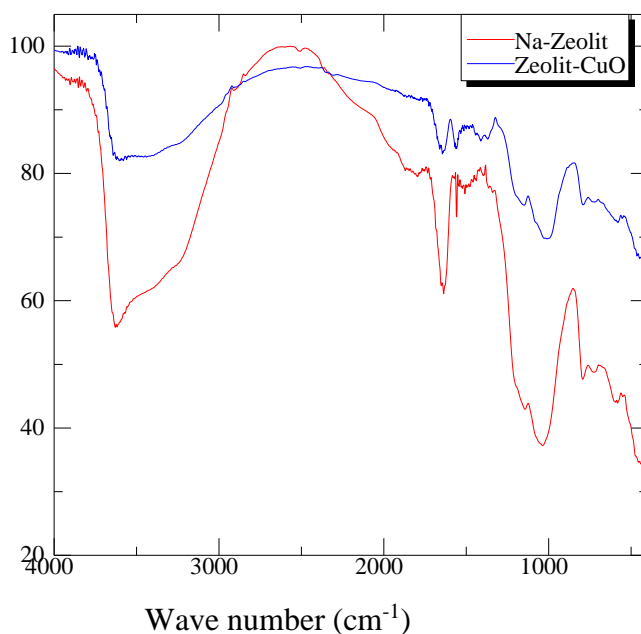


Figure 3. FT-IR spectra of the parent zeolite Na and CuO zeolite.

The results of powder XRD and framework IR clearly indicate that the modification by ion-exchange technique does not change in framework composition (Si/Al ratio), phase purity and crystallinity of parent NaX and its exchanged forms.

Catalyst loading

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst i.e. 20, 50, 100 and 150 mg. The absorption spectra of thermal degradation due to the catalyst loading and the dye removal are depicted in Fig. 4 and 5. The graph show trends and they are maximized at the same catalyst loading of about 100 mg. The optimum catalyst weight was obtained at 100 mg, which was able to decrease the reaction time 50 minutes compared to the reaction without catalyst. The percentage of dye removal on this catalyst loading was 96.26%. The percentage of dye removal to the catalyst loading is shown in Fig. 5 or Table 1. This extreme point results from the conflicting effects of this parameter on the photocatalytic process; at lower loading levels, such as 50 mg, photonic adsorption azo dye is approximately 58 minutes at the end of which a noticeable increase in dye removal rate occurs; various naphthalene and benzene derivatives intermediates, generated during initial steps, are further degraded progressively to di-carboxylic acid derivatives (saturated or unsaturated), simple carboxylic acids such as acetic acid, formic acid, and finally to H_2CO_3 (liq) or CO_2 (gas) [10].

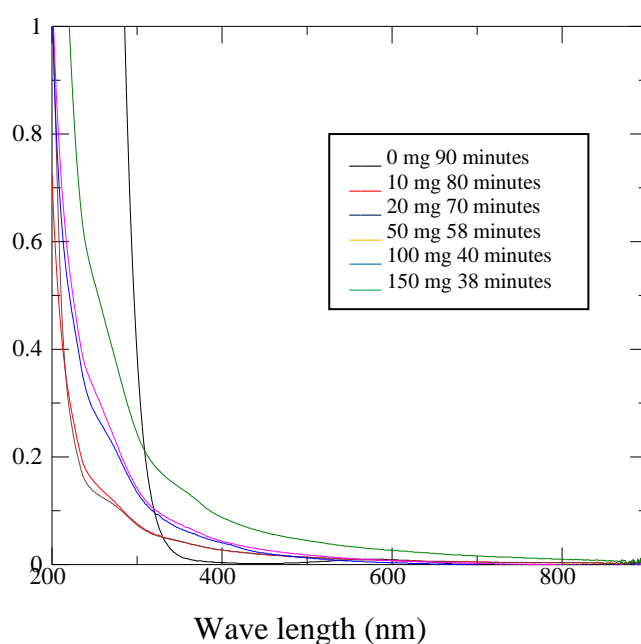


Figure 4. UV-vis absorption spectra of CuO zeolite suspensions.

Removal of Remazol Brilliant Blue R (RBBR) by Absorbion on Zeolit CuO Catalyst

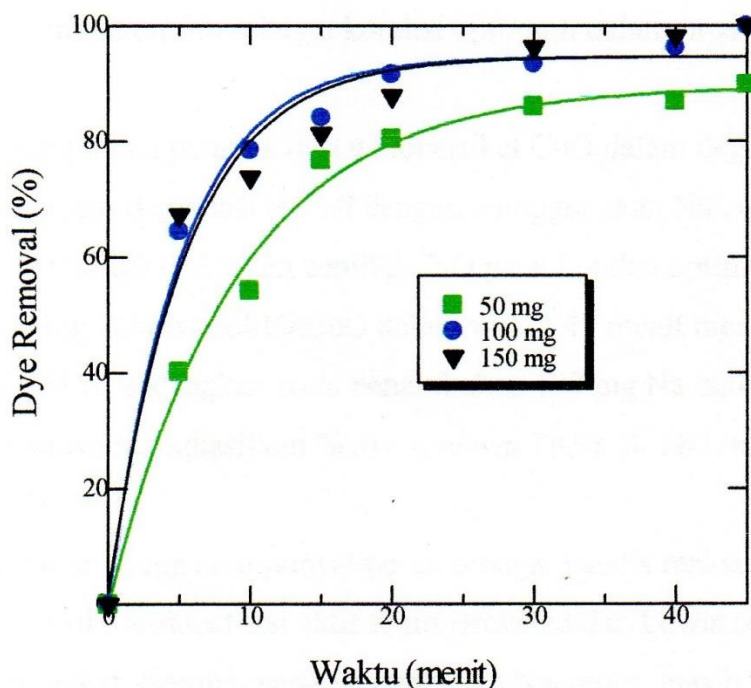


Figure 5. Effect of reaction time to dye removal in various catalysts loading.

CONCLUSION

This work shows that Cu zeolite catalysts could be considered as potential low cost absorbents for dye removal from aqueous solutions. The Cu zeolite has the optimum absorption capacity for Remazol Brilliant Blue R. The optimum catalyst weight was obtained at 100 mg, which was able to decrease the reaction time 50 minutes compared to the reaction without catalyst. The percentage of dye removal on this catalyst loading was 96.26%. The structure upon cation exchange had a tendency to form agglomerates of small crystals and also an observed decrease in particles and pore sizes. The micro pores of CuO zeolite is about 20 nm, which shows formation of nanoCuO particles in zeolite structure. This structural feature may be important since it increases the total surface area. The diffusion into such pores can explain the absorption capacity.

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CONFLICT OF INTEREST

I state that the authors have no conflict of interest.

AUTHOR CONTRIBUTIONS

Kandhi Puspa Melati conducted the experiment, Deswita conducted the SEM measurement, Indra Gunawan and Yoki Yulizar wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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Removal of Remazol Brilliant Blue R (RBBR) by Absorption on Zeolite CuO Catalyst

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