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Effectiveness and efficiency between CuO/natural zeolite catalysts and ZnO/natural zeolite in naphthol blue–black waste management by photolysis degradation method

Zilfa[a,*], B. Arifin[b], R. Zein[c], Rahmayeni[d], S. Ummi[a], S. Ramadhan[a]

[a]*Laboratory of Application Analysis, Department of Chemistry, Faculty of Mathematics and Natural sciences, Andalas University, Padang 25163, West Sumatera, Indonesia, Tel. +62751-71671; Fax: +62751-73118; emails: zilfa_58@yahoo.com/zilfa@sci.unand.ac.id (Zilfa), pinkyaumi@yahoo.com (S. Ummi), ramadhansyukri71@gmail.com (S. Ramadhan)*
[b]*Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Mathematics and Natural sciences, Andalas University, Padang 25163, West Sumatera, Indonesia, Tel. +62751-71671; Fax: +62751-73118; email: bustanularifin@sci.unand.ac.id*
[c]*Laboratory of Analytical Environmental Chemistry, Department of Chemistry, Faculty of Mathematics and Natural sciences, Andalas University, Padang 25163, West Sumatera, Indonesia, Tel. +62751-71671; Fax: +62751-73118; email: rzein@sci.unand.ac.id*
[d]*Laboratory of Material Chemistry, Department of Chemistry, Faculty of Mathematics and Natural sciences, Andalas University, Padang 25163, West Sumatera, Indonesia, Tel. +62751-71671; Fax: +62751-73118; email: rahmayenni@sci.unand.ac.id*

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ABSTRACT

This research compares the level of effectiveness and efficiency of photolysis catalysts made from natural Clinoptilolite-Ca type zeolite with CuO or ZnO for naphthol blue–black dyes. Degradation was carried out using 365 nm UV light at 10 W. The degradation products were analyzed by UV-VIS spectrophotometer and Fourier transform infrared (FTIR). FTIR, X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used in catalyst characterization. The results showed that degradation of 20 mL naphthol blue-black 6 mg/L after 45 min irradiation without a catalyst was 5.30%, with 0.6 g ZnO/zeolite this increased to 80.43% while 0.8 g CuO/zeolite resulted in 41.41% degradation. If irradiation time was increased to 90 min, the percent degradation was 88.54% for the ZnO/zeolite catalyst and 57.25% for CuO/zeolite. Degradation without irradiation after 90 min was 37.62% for CuO/zeolite and 43.33% for ZnO/zeolite. When simulated naphthol blue–black industrial waste was used 0.6 g ZnO/zeolite use resulted in 81.55% degradation and 0.8 g CuO/zeolite 37.36%. FTIR result shows a shift in the wavenumber confirming that degradation had indeed occurred. Characterization of both catalysts before and after the degradation reaction using FTIR, XRD, and SEM showed no change in the structure of the catalyst.

Keywords: Degradation; Photolysis; Naphthol blue–black; CuO/zeolite; ZnO/zeolite

1. Introduction

The rapid growth of industry often leads to growth in waste products and the challenge to find methods in dealing with these. Zeolites are commonly found in Indonesia and can form the basis of catalysts that can be used to break down some of these waste products into less harmful chemicals. Zeolites are compounds with a regular structure that consist of alumina and silica and can bond to semiconductor catalyst compounds such as CuO and ZnO where they act as buffers [1,2]. The catalytic ability of CuO and ZnO is increased when supported by zeolites [2].

In Indonesia, the home-weaving industry uses many dyes that do not meet current standards regarding hazardous wastes. One of these is naphthol blue–black [3]. Naphthol blue–black is an organic compound with a ring

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* Corresponding author.

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structure that is difficult to degrade naturally into harmless compounds such as CO_2 and H_2O. One of the degradation methods that can be used is photolysis with UV light. The photon energy of UV light is high enough to decompose water molecules forming OH radicals. These OH radicals then attack functional groups in the compound to form fractions of these compounds [1,3–5].

Photocatalysis such as CuO/zeolite and ZnO/zeolite can be used to enhance the efficiency of this reaction. CuO/zeolite and ZnO zeolite have long been used as catalysts for the removal of hazardous organic compounds and result in both degradation and adsorption, where CuO and ZnO cause degradation and zeolite acts as an adsorbent. CuO/zeolite and ZnO/zeolite are catalysts from the support of CuO and ZnO catalysts with zeolites. Structure of CuO and ZnO catalysts were that of typical semiconductors of which ZnO has the smallest bandgap [5–8]. This indicates that ZnO is likely to be a stronger degrading agent than CuO.

In this study, the authors have tested the degradation effectiveness and efficiency of a CuO/zeolite catalyst and ZnO/zeolite on naphthol blue–black dyes. The degradation results were analyzed by UV-VIS spectrophotometer and Fourier transform infrared (FTIR). Catalyst characterization was conducted using FTIR, X-ray diffraction (XRD), and scanning electron microscopy (SEM) [1].

2. Experimental

2.1. Tools

The tools used include UV lamps with a power of 10 W and wavelength 365 nm, UV-VIS spectrophotometer, glassware, hot plates, furnaces, FTIR, XRD, and SEM

2.2. Materials

Blue–black naphthol compounds (amido black (10BC.1.20470)), HCl pa, NaOH, $AgNO_3$ NaCl, clinoptilolite-Ca, CuO, ZnO, and distilled water.

2.3. Method

2.3.1. Activation of clipnoptilolite-Ca zeolite

Clinoptilolite-Ca zeolite was activated using HCl by stirring for 45 min to increase activity photocatalytic and after that, filtered and rinsed with distilled water. The residue was dried for 60 min at 100°C. After being heated by the oven, the zeolite was homogenized with 0.1 M NaCl, then filtered, and the residue tested with $AgNO_3$ to find out the loss of Cl in zeolites [1].

2.3.2. Preparation of CuO/zeolite and ZnO/zeolite catalysts

Activated zeolite was measured around 200 g into distilled water in a beaker while slowly adding 8 g of ZnO and CuO. The mixture was stirred for 6 h, separated then dried at 100°C. After drying, it was sifted using a 125 mesh sieve and then heated in a furnace for 24 h at 350°C to form a ZnO/zeolite catalyst and CuO/zeolite catalyst [1].

2.3.3. Determination of several parameters of optimum degradation conditions

2.3.3.1. Determination of the effect of degradation time without catalyst

Naphthol blue–black 6 mg/L as much 20 mL entered to six petridishes. Then, each plate was photolyzed for 30, 45, 60, 75, 90, or 105 min. After photolysists, we have taken the filtrate, after that the filtrate was measured with a UV-VIS spectrophotometer.

2.3.3.2. Determination of the effect of addition of catalysts on degradation

- Blue–black naphthol was placed in five petridishes with a concentration of 6 mg/L as 20 mL. Then to each petridish, CuO/zeolite was added as much as 0.2, 0.4, 0.6, 0.8, and 1.0 g. All petridish irradiated with UV light for 45 min. After that centrifuge for 15 min, the filtrate was measured with a UV-VIS spectrophotometer.
- Blue–black naphthol was placed in five petridishes with a concentration of 6 mg/L as 20 mL. Then to each petridish added ZnO/zeolite as much as 0.2, 0.4, 0.6, 0.8, and 1.0 g. All petridish irradiated with UV light for 45 min. After that centrifuge for 15 min, the filtrate was measured with a UV-VIS spectrophotometer.

2.3.3.3. Determination of time effect on degradation after addition of CuO/zeolite and ZnO/zeolite

- CuO/zeolite was placed into six petridishes as 0.8 g and then added to each of 20 mL of naphthol blue-black 6 mg/L. Then, each of them was photolysis with time variations of 30, 45, 60, 75, 90, and 105 min. After that, centrifuged for 15 min and the filtrate were measured with a UV-VIS spectrophotometer.
- ZnO/zeolite was placed into six petridishes as 0.8 g and then added to each of 20 mL of naphthol blue-black 6 mg/L. Then, each of them was photolysis with time variations of 30, 45, 60, 75, 90, and 105 min. After that, centrifuged for 15 min and the filtrate was measured with a UV-VIS spectrophotometer.

2.3.3.4. Determination of the effect of degradation time with UV and without UV exposure with the addition of CuO/zeolite catalysts

- Naphthol blue–black was placed into seven petridishes as much as 20 mL with a concentration of 6 mg/L then added 0.8 g CuO/zeolite. Then irradiated for time variations of 30, 45, 60, 75, 90, and 105. Then centrifuged for 15 min and the filtrate were measured with a UV-VIS spectrophotometer.
- Naphthol blue–black was placed into seven petridishes as much as 20 mL with a concentration of 6 mg/L then added 0.8 g CuO/zeolite. Then leave it in a dark room or without irradiation with time variations of 30, 45, 60, 75, 90, and 105. Then centrifuged for 15 min and the filtrate were measured with a UV-VIS spectrophotometer.

2.3.3.5. Determination of the effect of degradation time with UV and without UV exposure with the addition of a ZnO/zeolite catalyst

- Naphthol blue–black was placed into seven petri dishes as much as 20 mL with a concentration of 6 mg/L then added 0.6 g ZnO/zeolite. Then irradiated for time variations of 30, 45, 60, 75, 90, and 105. Then centrifuged for 15 min and the filtrate was measured with a UV-VIS spectrophotometer.
- Naphthol blue–black was placed into seven petri dishes as much as 20 mL with a concentration of 6 mg/L then added 0.6 g ZnO/zeolite. Then leave it in a dark room or without irradiation with time variations of 30, 45, 60, 75, 90, and 105. Then centrifuged for 15 min, and the filtrate was measured with a UV-VIS spectrophotometer.

2.3.3.6. Naphthol blue–black waste degradation simulation results

A 30 cm × 30 cm white cloth was stirred into 500 mL of 50 mg/L of naphthol blue–black dye for 45 min. Then the dyed cloth was rinsed and dried. The residue from the rinsing was combined with the waste dye and its absorbance measured with a UV-VIS spectrophotometer. 20 mL of this waste dye was added to a Petri dish containing 0.8 g of CuO/zeolite and degraded for 90 min under a UV lamp. The degraded waste dye catalyst mixture was centrifuged for 15 min, and for the absorbance of the filtrate measured using UV-VIS spectrophotometer.

Dipped into a cup containing 0.6 g of ZnO/zeolite as much 20 mL. After that, it was degraded using a UV lamp for 90 min. The degradation results were centrifuged for 15 min, and the filtrate was absorbed using a UV-VIS spectrophotometer.

2.3.4. Analysis of naphthol blue–black before and after degradation using FTIR

Blue–black naphthol was degraded with optimum parameter conditions and then analyzed by FTIR. Naphthol Blue back solution before and after degradation was analyzed using FTIR.

2.3.5. Characterization of catalysts before and after degradation with FTIR, XRD, and SEM

FTIR, XRD, and SEM characterized CuO/zeolite and ZnO/zeolite catalysts before and after degradation

3. Result and discussion

3.1. Determination of the effects of degradation time without a catalyst

The photolysis of naphthol blue–black is affected by some of the time variations shown in Fig. 1.

Fig. 1 shows that the longer the irradiation time, the higher the percentage degradation up to 45 min when the degradation percentage was 5.30%. Longer degradation times did not increase the degradation significantly. Likely, after 45 min the optimum number of OH radicals had already been formed so that further irradiation did not increase the degradation and the ability to decompose the groups present in naphthol blue–black dyes does not occur again [1,6,8].

3.2. Determination of the effect of addition of CuO/zeolite and ZnO/zeolite catalysts on degradation

Without a catalyst degradation of naphthol blue–black is low even after a long reaction time. The impact of the amount of catalyst CuO/zeolite, ZnO/zeolite on improving the degradation can be seen in Fig. 2.

The catalyst used is CuO/zeolite and ZnO/zeolite, which were expected to help and increase the percentage of degradation. Determination of the effect of adding the amount of catalyst CuO/zeolite and ZnO/zeolite to the percent of degradation of naphthol blue black can be done by inserting several catalysts which shows the results of different amounts of catalysis on the dye solution after 45 min of 365 nm UV light irradiation [7–10].

It can be seen that larger amounts of catalyst results in higher degradation percentages of naphthol blue–black. CuO/zeolite and ZnO/zeolite are catalysts of both CuO and ZnO, supported by zeolite act to degrade and adsorb the dye with CuO and ZnO acting as photolysis catalysts, and the zeolites as adsorbents. Also, zeolite will fill the pores and expand the surface of CuO and ZnO, to enhance their

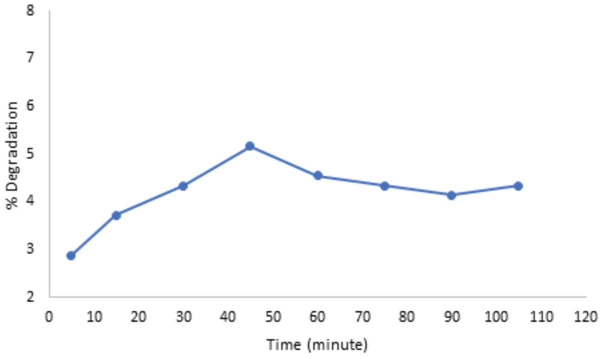

Fig. 1. Effect of photolysis time on degradation percentage of 20 mL, 6 mg/L naphthol blue–black without catalyst.

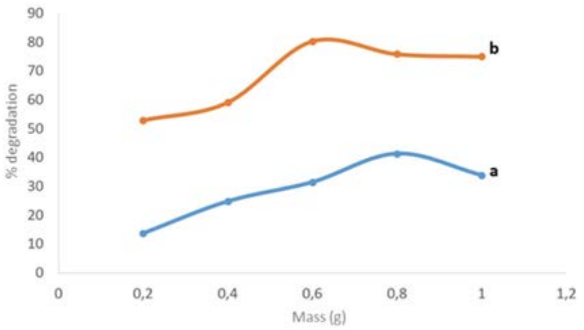

Fig. 2. Effect of catalyst addition of: (a) CuO/zeolite and (b) ZnO/zeolite against the degradation percentage of 20 mL, 6 mg/L naphthol blue–black with UV light for 45 min.

effectiveness as catalysts [1,8]. Along with the addition of the amount of CuO/zeolite and ZnO/zeolite catalysts, there was an increase in the degradation of naphthol blue–black. With more catalysts the interaction between UV light and CuO and ZnO, and the OH radical formation is faster increasing the percent degradation. The highest degradation percentage achieved 80.43% came with the addition of 0.6 g ZnO/zeolite. Only 41.41% degradation could be achieved with CuO/zeolite and that was when 0.8 g was used. Larger amounts of either catalyst failed to increase degradation percentages presumably because the solution had become saturated with the catalyst and so its ability as an absorbent decreased [6,8,9,11].

3.3. Determination of time effect on degradation after addition of CuO/zeolite and ZnO/zeolite

The level of degradation of naphthol blue–black in the presence of either catalyst was strongly time-dependent as can be seen in Fig. 3.

Initial, longer irradiation times led to the formation of a greater number of OH radicals. After an optimum time, the degradation percent will decrease again due to OH radicals that are formed constantly while the concentration of naphthol blue–black in high conditions, this is caused by the nature of scattering. After 90 min of irradiation time with 0.8 g CuO/zeolite the highest percent degradation achieved was 57.25%, and for 0.6 g ZnO/zeolite it was 88.54%. It appears that with the addition of CuO/zeolite or ZnO/zeolite, electrons are excited from the valence band into the conduction band resulting in holes being formed which come into contact with OH ions converting them to OH radicals. These OH radicals break down the functional groups in the blue–black naphthol compound so that the dye is broken down [10,12].

ZnO/zeolite is a more effective catalyst than CuO/zeolite in degrading naphthol blue–black. Less ZnO/zeolite is required and the optimum time is shorter at 90 min for ZnO/zeolite and 105 min for CuO/zeolite. This is because ZnO has a smaller bandgap so electron excitation requires less energy resulting in the quicker formation of holes and a larger number of OH radicals. This results in a faster and larger OH radical attack on the dye structures.

3.4. Determination of the effect of degradation time with and without UV exposure by addition of CuO/zeolite and ZnO/zeolite catalysts

The effect of UV irradiation on the degradation time of naphthol blue–black dyes can be seen from the comparison of the percentage of degradation between being subjected to UV rays and without UV rays in Fig. 4.

Figs. 4a and b show that without UV irradiation, little degradation of naphthol blue–black occurred. Adsorption with a small percentage of degradation resulted in a 37.62% decrease with CuO/zeolite and 43.33% with ZnO/zeolite. This happens because CuO/zeolite and ZnO/zeolite are less effective where there is no light as their photocatalytic properties depend on irradiation.

The longer the UV exposure time, the higher the percent of degradation. After 90 min of UV exposure, a significant percentage of degradation (57.25%) had occurred. The presence of UV light causes can help the performance of CuO/zeolite and ZnO/zeolite catalysts in degrading the naphthol blue–black dyes and causing the formation of holes and OH radicals more so that it can oxidize the naphthol blue–black dyes [11,13].

Fig. 4 shows that the results of degradation using CuO/zeolite and ZnO/zeolite catalysts either irradiated or not irradiated by degradation results using ZnO/zeolite was a more effective catalyst than CuO/zeolites but neither was as effective without irradiation. In terms of Figs. 4a and b are degraded without irradiation using CuO/zeolite and ZnO/zeolite. At the same time, Figs. 4c and d are degraded by irradiation using CuO/zeolite and ZnO/zeolite. Between degradation without radiation with irradiation without irradiation, the adsorption process only occurs and a slight degradation, whereas with irradiation, the adsorption process occurs simultaneously with degradation or irradiation.

3.5. Naphthol blue–black waste degradation simulation results

The effect of the addition of CuO/zeolite and ZnO/zeolite catalysts on simulated Naphthol blue–black waste degradation is shown in Fig. 5. The use of a CuO/zeolite catalyst resulted in 37.36% degradation and ZnO/zeolite 81.55% degradation of the simulated waste It is because CuO and ZnO have valence bands containing electrons, and conduction bands were empty so when the CuO/zeolite or ZnO/

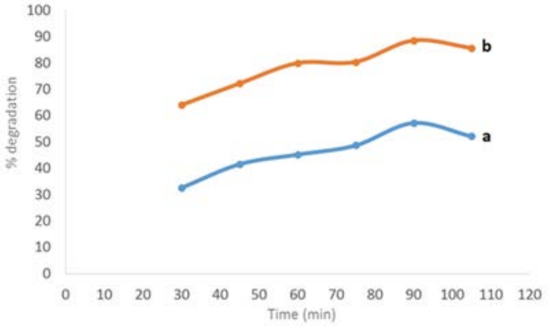

Fig. 3. Degradation of 20 mL naphthol blue–black 6 mg/L with the addition of 0.8 g of CuO/zeolite catalyst and 0.6 g of ZnO/zeolite with various variations of irradiation time.

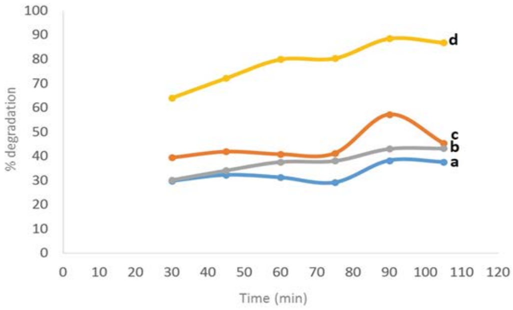

Fig. 4. CuO/zeolite of: (a) without irradiated and (c) with UV light. ZnO/zeolite of (b) without irradiation and (d) with UV light.

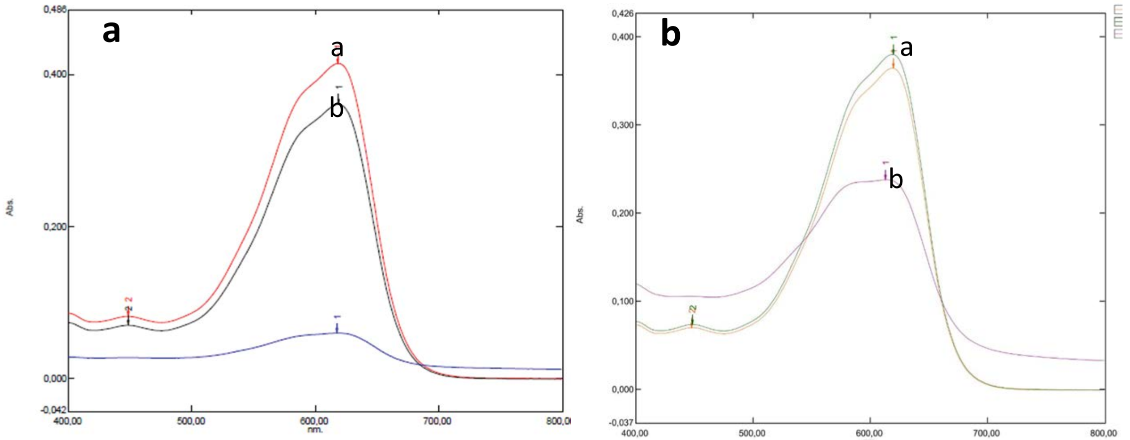

Fig. 5. Degradation spectrum of simulated naphthol blue–black waste with the addition of: (a) CuO/zeolite and (b) ZnO/zeolite.

zeolite catalysts are exposed to UV light, the electrons were excitation from the valence band to the conduction band (producing ecb–). That caused the existence of vacancies or holes (hcb+), which can act like positive charges. Then the hole (hcb+) will react with a metal hydroxide, namely CuO and ZnO hydroxide, in the solution to form a metal hydroxide radical which is a strong oxidizing agent to oxidize naphthol blue-black. Electrons (ecb–) that are on the surface of the semiconductor are trapped in metal hydroxides, then react with electron capture in a solution such as H_2O or O_2 to form hydroxyl radicals ($^{\bullet}OH$) or superoxide (O_2^-) which will oxidize naphthol blue–black in solution [12–15].

It can be seen that 0.6 g ZnO/zeolite is more than twice as effective at degrading the simulated naphthol blue–black waste than using 0.8 g of CuO/zeolite with degradation percentages of 81.55% and 37.36%, respectively.

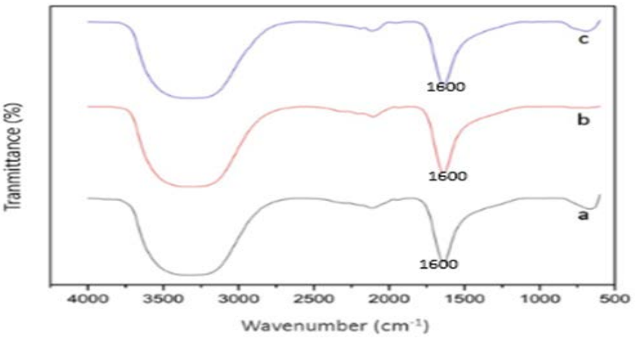

Fig. 6. FTIR results of naphthol blue–black of (a) before and (b) after degradation with CuO/zeolite, (c) after degradation with ZnO/zeolite.

3.6. Analysis of naphthol blue–black before and after degradation using FTIR

Fig. 6 shows FTIR spectra of (a) sample of naphthol blue–black dye, (b) the product of degradation of naphthol blue–black with CuO/zeolite, and (c) the product of degradation of naphthol blue–black with ZnO/zeolite. There is no significant difference in the pattern of peaks between each of these dye samples. However, the peak at 3,338.69 cm^{-1} has shifted to 338.34 cm^{-1} indicating the absorption of –OH vibrations from H_2O molecules. It shows that there is a shift in wavenumbers [1,14,16].

Fig. 6 is the FTIR pattern of the simulated naphthol blue–black waste solution before degradation and after degradation. Based on this pattern, the shifts in the wavenumbers can be seen. Comparing the pattern above, it can be seen that the peak shift before degradation and after degradation shows a difference that is not far or significant. Changes in the band occur at the wave number 600–1,000 cm^{-1} which indicates that the aromatic C–H bond is broken in naphthol blue–black and at the wave number 1,500–2,500 cm^{-1} there is a slight shift in the wavenumber. These results indicate that the compound was successfully degraded. At the wavenumber between 3,000 and 3,500 cm^{-1}, a sharp sloping absorption band appears which indicates that the OH strain vibrations originate from the H_2O molecule which is used as a solvent and there is also a peak that appears at the wave number 1,637.74 cm^{-1} with absorption that is strong and tapered which indicates the presence of aliphatic C–C strain vibrations.

Fig. 7 shows that the FTIR pattern of the ZnO/zeolite catalyst before degradation and after degradation there is a change in intensity at the 1,500–2,500 cm^{-1} wave number due to leaching from the use of the catalyst in the degradation process. In general, the IR spectrum of the zeolite structure is in the range 1,600–3,700 cm^{-1}. Based on the picture above there are peaks at wave numbers 782.34 and 1,019.32 cm^{-1}. The wavenumbers are close to the values of 790.34 and 1,079.16 cm^{-1}, which indicates that there is a T–O–T bond, where T is Si or Al. The absorption band that appears at wavenumber 1,674.39 cm^{-1} is the absorption from the OH bond originating from the H_2O molecule, while at wavenumber 3,632.33 cm^{-1} the value ranges from 3,500 to 3,700 cm^{-1} indicating the strain vibration from OH originating of the Al–O–Si bond. The bond between Si–O (Si) and Si–O (Al) is in the range 400–1,200 cm^{-1}. According to Breck, when the transition metal cations enter the zeolite structure, the ion exchange structure of the zeolite remains unchanged and only a few small shifts occur in the absorption band which is to the right of the Si–(Al)–O bond. In general, a weak absorption band

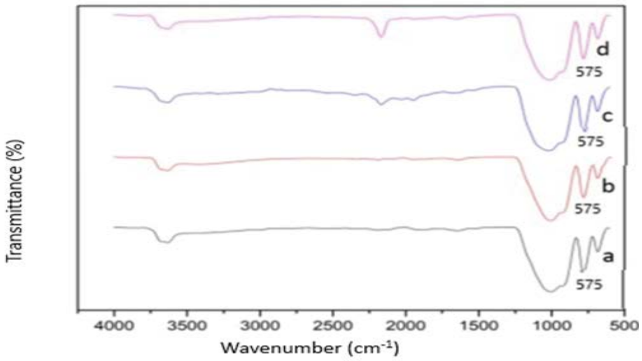

Fig. 7. Results of catalyst characterization with FTIR of CuO/zeolite (a) before and (b) after degradation, ZnO/zeolite (c) before and (d) after degradation.

between 400–600 cm^{-1} and 463–1,700 cm^{-1} indicates the strain of ZnO that has been observed for ZnO in various composites. In this study, the presence of ZnO was shown by the absorption band at wave number 685.52 cm^{-1}. Based on the results of FTIR studies during the calcination process, some ZnO reacted with OH on the zeolite surface which created new bonds such as Zn–O–Si and Zn–O–Al.

3.7. Characterization of catalysts with FTIR, before and after degradation

Fig. 7 shows the FTIR of the zeolite/metal oxides catalysts before and after the degradation reaction. FTIR spectrum before and after degradation with ZnO/zeolite and CuO/zeolite there is no shift in the wavenumber, this indicates that there is no change in the structure of the catalyst so that the catalyst can be used in degradation. The spectra of the lower wavenumbers around 475–1,090 cm^{-1} are typical of clinoptilolite zeolite, for CuO and ZnO in the range of wave numbers 480–580 cm^{-1}. The peak at wavenumber 1,004.66 cm^{-1} has shifted to 1,005.06 cm^{-1}, indicating that there is a Si–O–Si vibration absorption. In the FTIR of the naphthol blue–black sample indicating successful degradation. No such change is observed for CuO/zeolite and ZnO/zeolite indicating the structure remained intact so that it can be used as a catalyst for degradation [12,14,15].

3.8. Characterization of catalysts with XRD before and after degradation

XRD was used to analyze the crystal structure of the catalyst. In this study, the natural zeolite could be identified as Clinoptilolite according to JCPDS No. 25–1349 and exhibited the typical XRD peaks of the natural zeolite before degradation with angles 2θ of 12.28°, 19.77°, 20.80°, 24.82°, 26.59°, and 28.92°. The peaks after degradation were almost unchanged at an angles 2θ of 12.27°, 19.76°, 20.81°, 23.01°, 24.82°, and 26.59°. This is further evidence that the photodegradation reaction did not change the structure of clinoptilolite-Ca [1,14,17].

Fig. 8 shows that CuO/zeolite and ZnO/zeolite exhibit the typical peaks of CuO and ZnO, respectively, at angles 2θ of 38.65°, 48.75°, 59.94°, 65.89°, 68.19°, and 75.63°, after peak degradation typically at an angle of 2θ = 48.76°, 59.93°, 67.66°, 68.25°, and 75.66° (these numbers do not seem to be the same as on your graph). Also, you have four lines on the graph and it is not clear which ones you are describing. I wonder also why the lines for ZnO were the same as for CuO even though Zn was a slightly larger atom than Cu. I would expect the peaks for Zn to be at slightly lower angles) also found peaks for CuO and ZnO at 2θ = 35.306°, 38.502°, 61.475°, and 65.538°. In the XRD spectrum, there is no change in the structure of the catalyst before and after degradation so that the catalyst can be used for degradation (these are standard results and can be regarded as common knowledge – they do not need a citation – the important finding you have made is that adding zeolite does not change the XRD pattern so the crystalline structure of the oxides is unchanged by supporting them on the zeolite).

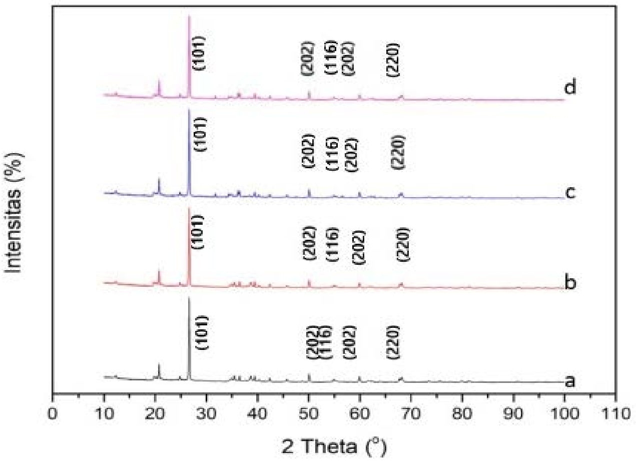

Fig. 8. XRD diffraction of CuO/zeolite (a) before and (b) after degradation, ZnO/zeolite (c) before and (d) after degradation.

The size of natural zeolite crystals before and after degradation based on the Scherrer equation was 28.08 and 17.39 nm.

In Fig. 8, you can see the formation of a ZnO/zeolite catalyst that has been supported by ZnO. Based on the figure, a peak appears at the value of 2θ, namely at 12.3°, 19.8°, 20.8°, 24.8°, 26.6°, and 31.7° which shows the specific peak of clinoptilolite zeolite where the value is in accordance as shown by JCPDS data no. 39–138361 and the 2 value also has the same value as 2θ in a study conducted by M. Bahrami and Nezamzadeh [13]. The peaks that appear at a value of 2θ = 36.4°, 39.4°, 42.4°, 47.7°, 50.1°, 57°, 59.9°, and 68° indicates that there is a crystal phase from ZnO, where the data has several points of similarity to the 2θ value for ZnO in the value range 2θ = 30° and 40° according to the JCPDS data from ZnO (JCPDS 36–1451) 58 and ZnO usually also appears at a value of 2θ = 47°, 57°, 63°, and 68°. This shows that the zeolite support into ZnO during the calcination process was successful. Fig. 8 shows that the XRD pattern of the ZnO/zeolite catalyst before degradation and after degradation shows the same pattern, this proves that there is no structural change to the ZnO/zeolite catalyst in the degradation process so it can be concluded that the ZnO/zeolite catalyst

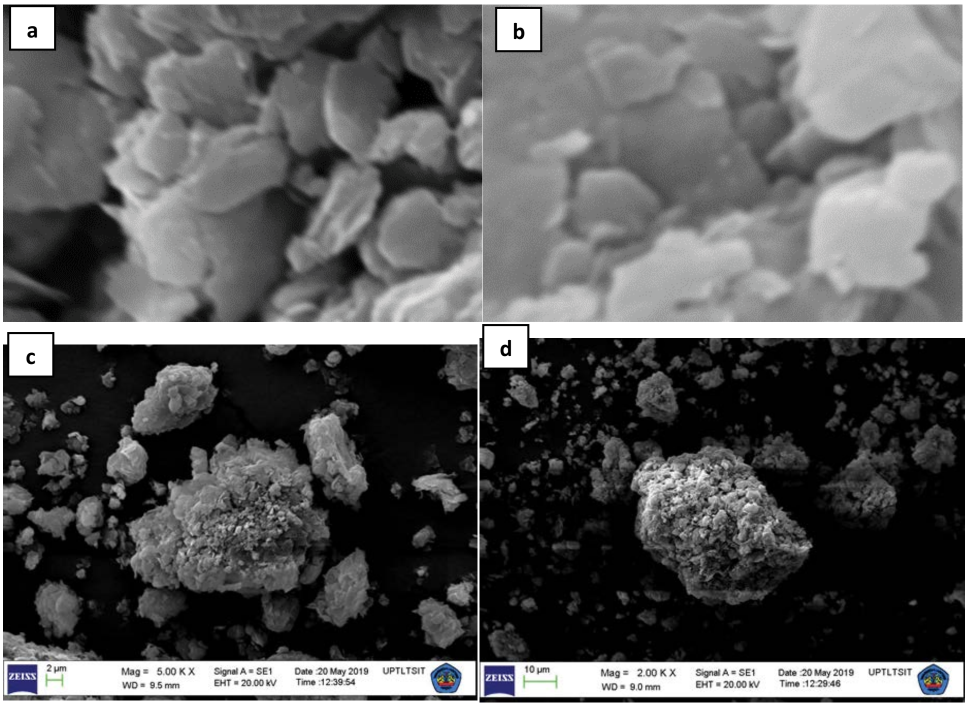

Fig. 9. SEM results of CuO/zeolite catalyst of: (a) before and (b) after degradation; ZnO/zeolite (c) before and (d) after degradation.

can be used as a catalyst in degradation (naphthol blue–black compound).

3.9. Characterization of catalysts with SEM before and after degradation

The SEM characterization shows the morphology of CuO/zeolite (Figs. 9a and b) and ZnO/zeolite catalysts before and after degradation (Figs. 9c and d).

Both catalysts were crystalline and roughly spherical in shape containing apparent cavities before reacting with the dye [1,15,18].

After degradation, the surface area of CuO/zeolite and ZnO/zeolite catalysts was larger and cavities were no longer evident presumably because they have been filled with absorbed naphthol blue-black. This also increases the particle size. The overall shape of the catalyst particles remained spherical, like irregular crystals. This confirms that adsorption does occur alongside the degradation process resulting in an expansion of the surface of the CuO/zeolite, ZnO/zeolite catalyst particles. The overall structure does not change, but the surface catalyst getting wide due to the dissolution [18,19].

Characterization of ZnO/zeolite catalyst before use for degradation and after degradation was carried out by SEM to determine the morphology of the catalyst as shown in Fig. 4.

Fig. 9 SEM photos of ZnO/zeolite catalyst (a) before degradation, (b) after degradation.

Fig. 9 shows the morphology of the ZnO/zeolite catalyst before and after degradation, wherein the Fig. 9, there were small lumps and material on the surface of the lumps. The clot was thought to indicate zeolite material, while the material on the surface of the lump was thought to be ZnO. Based on the SEM photo, it can be seen that there were no change in the morphology of the ZnO/zeolite catalyst before and after degradation, so it can be said that the ZnO/zeolite catalyst can be used to degrade the naphthol blue–black compound.

4. Conclusions

From the results of the study, it can be concluded that the dye Naphthol blue Black can be degraded 57.25% using CuO/zeolite 0.8 g and 85.50% using ZnO/zeolite 0.6 g for 90 min irradiation time. For the simulation degradation of naphthol blue–black waste reached 37.36% using ZnO/zeolite and 81.55% using ZnO/zeolite for 90 min irradiation time.

From the research results, the percentage of degradation of naphthol blue–black was greater by using a ZnO/zeolite catalyst compared to CuO/zeolite. Analysis of naphthol blue–black after degradation using FTIR, there was a shift in the wavenumber in certain bands which indicated that there was a break in the bonds of the naphthol blue–black compound, which means that degradation had occurred.

Catalyst characterization used FTIR, XRD, and SEM. Analysis with FTIR did not change the wavenumber, as well as the results of the XRD spectrum, there was no change in the angle of 2θ, meaning that there was no change in structure or crystals and the results of SEM photos showed that the catalyst morphology did not change.

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