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## Utilization Natural Zeolyte From West Sumatera For $TiO_2$ Support in Degradation of Congo Red and A Waste Simulation by Photolysis

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### ABSTRACT

Zeolite Clinoptilolite-Ca was successfully supported  $TiO_2$  in synthesis  $TiO_2$ /Zeolyte as photo catalyst in degradation of Congo Red 20 mg/L and a waste simulation of Congo Red under UV light irradiation 365 nm.  $TiO_2$ /zeolite were characterized by Fourier Transform InfraRed (FTIR) and X-Ray Diffraction (XRD). The result of FTIR showed the structure fungsional of  $TiO_2$ /zeolite not change before and after degradation. The XRD patterns showed  $TiO_2$ /Zeolyte photo catalyst were successfully formed, it proved with the highest peaks at  $2\theta = 24.950^\circ$ , which were corresponded to anatase peaks and  $26.594^\circ$  to  $SiO_2$  peaks. The percentage degradation showed 20 g  $TiO_2$ /Zeolyte degraded Congo Red 20 mg/L under UV light irradiation 365 nm with 60 minute reached 94,23 % and a waste simulation of Congo Red reached 85,14 %.

**Key Words:**  $TiO_2$ /zeolite, Photo catalyst, Congo Red, A Waste simulation of Congo Red

### INTRODUCTION

In modern industrial society, dyes are widely used in textiles, printing, dyeing, and food [1,2,7]. Azo dyes constitute more than fifty percent of the dyes produced annually and are the most important group of synthetic colorants [1-3]. They are recalcitrant and pose toxicity to various aquatic organisms and animals. Azo dyes are the largest and most versatile class of dye with one or more azo (N=N) bridges linking substituted aromatic structure viz. aromatic, hydrocarbons, derivatives of benzene, toluene, naphthalene, phenol, and aniline like as Congo red [2,4].

Photocatalytic is emerging as an innovative approach for treatment of organic pollutants such as TiO<sub>2</sub>[1]. It has been reported UV is suitable for most waste water treatment [5,8]. Photocatalytic degradation rate is strongly dependent of the efficiency of adsorption of pollutants on the catalyst, thus, good photo catalyst design is essential for effective adsorption and subsequent degradation of pollutants [5].

Titanium dioxide (TiO<sub>2</sub>) is one of the most effective photo catalysis because it is biologically and chemically inert. With near-UV band gap energy, it has no toxicity low price, high activity, large stability in aqueous media and safe to handle [6-7]. Structure modification of the TiO<sub>2</sub> includes improvement in surface area by incorporating high surface area matrices such as silica (SiO<sub>2</sub>) and zeolite [8-10,11].

Zeolite offer a promising support for TiO<sub>2</sub> photo catalyst because of its regular pores and channel sizes and good adsorption ability. Zeolite have a rigid, three-dimensional crystalline structure similar to a honeycomb which consist of network of interconnected tunnels and cages [1,3,8-10]. In the other word, TiO<sub>2</sub> supported on zeolite have large surface area and its light transparent nature offers improves in adsorption and uniform diffusion of pollutants toward TiO<sub>2</sub> for efficient degradation [12].

## MATERIALS AND METHODS

### *Materials*

Materials were Congo Red Dye, Titanium Dioxide (TiO<sub>2</sub>) Anatase (*Merck*), Zeolite *clinoptilolite*-Ca, aquades, aquabides (*Pirogen*), Chloride Acid (HCl) 0,2 M (*Merck*), Sodium Chloride (NaCl) 0,01 M (*Merck*), Silver Nitrate (AgNO<sub>3</sub>) 0,05 M.

### *Experimental*

#### **Preparation Zeolite Clinoptilolite-Ca**

Zeolites clinoptilolite - Ca 250 µm activated by 0.2 M HCl and allowed to stand for 30 minutes. Then after 30 minutes the pH was measured and the mixture of zeolite + HCl rinsed with distilled water to pH neutral. After pH, neutral zeolite was filtered and put into oven for 1 hour at 100 ° C. After that saturated zeolite by addition 0,01 M NaCl and stirred until 1 hours. The zeolite was separated from the filtrate by filtration, the filtrate from the zeolite was tested with AgNO<sub>3</sub> if they formed a white precipitate the zeolite was washed with distilled water until no further white precipitate formed.

#### **Synthesis TiO<sub>2</sub>/Zeolite Clinoptilolite-Ca**

Zeolite active were dissolved using aqua bidets and stirred for 5 hours, then added TiO<sub>2</sub> ratio (1:25) gradually. After 5 hours' mixture was filtered and put into oven 1 hours with 100°C. After that calcination, the mixture for 10 hours with 350°C and finished calcination TiO<sub>2</sub>/Zeolite was sieved to 125 µm.

### *Effect of Optimum Condition*

#### **Determination of Optimum Wavelength Absorption**

Created concentration Congo Red 10, 20, 30, 40 and 50 mg / L in a 100-mL volumetric flask and then measured each solution by using spectrophotometer UV-Vis.

**Determination of Optimum Concentration Congo Red**

Created concentration Congo Red 10, 20, 30, 40 and 50 mg/L and then irradiated under UV light wavelength of 365 nm for 15 minutes. Then the results of irradiation were measured by using UV-Vis Spectrophotometer at a wavelength of absorption.

**Determination of The Effect Degradation Time Without Addition of Catalyst**

20 ml of Congo Red 20 mg/L (at point 2.2.3.2) was inserted into tube, and then a solution of 5 pieces on each tube was photolysis with variation time 5, 15, 30, 45, 60, and 75 minutes under the UV lamp with wave length 365 nm, and then measured the absorbance of degradation with Spectrophotometer UV-Vis at a wavelength.

**Determination of The Effect Addition Amount Catalyst TiO<sub>2</sub>/zeolyte Clinoptilolite-Ca for Degradation**

20 ml of Congo Red 20 mg/L (at point 2.2.3.2) was inserted into 5 pieces of tubes and each tube was added catalyst TiO<sub>2</sub>/zeolite as much as 0.04; 0.08; 0.12; 0.16; 0.2; and 0.24 mg and each of tube was photolysis under UV light, then the solution was centrifuged 15 minutes, and then filtrate was measured absorbance by spectrophotometer UV-Vis at wavelength.

**Determination of The Effect Time After Addition Catalyst TiO<sub>2</sub>/zeolyte Clinoptilolite-Ca**

20 ml of Congo Red 20 mg/L (at point 2.2.3.2) was inserted into 5 pieces of tubes and each tube was added catalyst TiO<sub>2</sub> / zeolyte with optimum mass (in point 2.2.3.4) and photolysis with time variation 5, 15, 30, 45, 60 minutes under the UV lamp. Then centrifuged for 15 minutes. Then the filtrate was measured absorbance with Spectrophotometer UV-Vis at a wavelength.

***Application of TiO<sub>2</sub>/zeolite Clinoptilolite-Ca*****On Waste Congo Red with Optimum Condition**

Congo Red 200 mL of 50 mg/L was heated to 100 °C. Then dipped in white cotton cloth that had been washed with a size of 20x20 cm. Then allowed to stand to infuse for 1 hour. After 1 hour of fabric removed from the solution and rinsed clean. Remaining water immersion taken 20 mL then degraded with 0.2 g TiO<sub>2</sub>/Zeolyte under UV light wavelength of 365 nm for 1 hour. Degradation products were analyzed using a spectrophotometer UV - Vis instrument.

**Characterization**

The results were characterized using FTIR which aims functional groups contained in TiO<sub>2</sub>/Zeolyte as well as on samples of Congo Red degraded ago to determine structure and size of the crystal particle TiO<sub>2</sub>/Zeolyte used XRD

RESULT AND DISCUSSION

Measurement Absorption Spectra of Congo Red

Figure 1 shows maximum absorption peaks at 496 nm. Based on R<sup>2</sup>value, it can be seen that absorbing and concentration have linier relation [13]. The regrestion formula for *Congo Red* is:

$$y = 0,0311x - 0,007, R^2 = 0,9998.$$

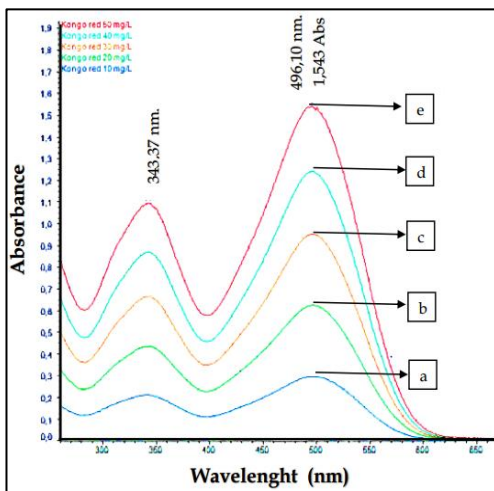


Figure-1: Absorption spectra of *Congo Red* with concentration (a) 10 mg/L, (b) 20 mg/L, (c) 30 mg/L, (d) 40 mg/L, (e) 50 mg/L

Determination of optimum concentration of in degradation process

Figure 2 shows the concentration influences the amount of *Congo Red* which is degraded. The increased of *Congo Red* concentration is followed by the increased of amount of *Congo Red* which is degraded. In a point, high concentration decreased degradation percentage due to the uncomplete energy. It can be seen optimum concentration of *Congo Red* was 20 mg/L irradiated under UV lamp for 15 minutes.

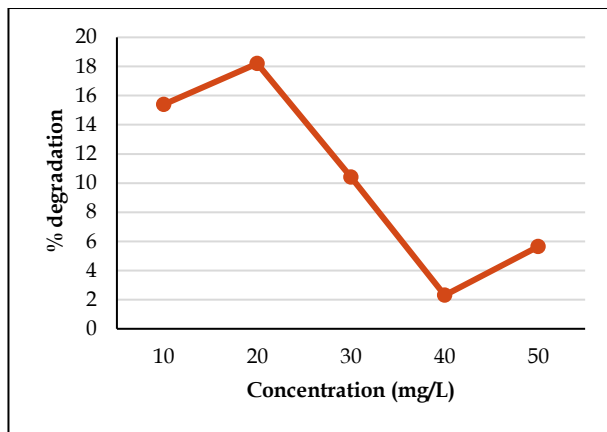


Figure-2: The comparison between concentration and *Congo Red* dye in degradation process.

**Determination of TiO<sub>2</sub>/zeolyte catalyst effect to Congo Red degradation percentage**

TiO<sub>2</sub>/zeolyte catalyst was made by supported zeolyte into TiO<sub>2</sub> (1 TiO<sub>2</sub> :25 zeolyte). Fig. 3 presents, the increased of catalyst mass increased the Congo Red degradation percentage. The highest degradation percentage was 94,23 % within adding 0.2g TiO<sub>2</sub>/zeolyte catalyst irradiated under UV lamp (365 nm) for 60 minutes.

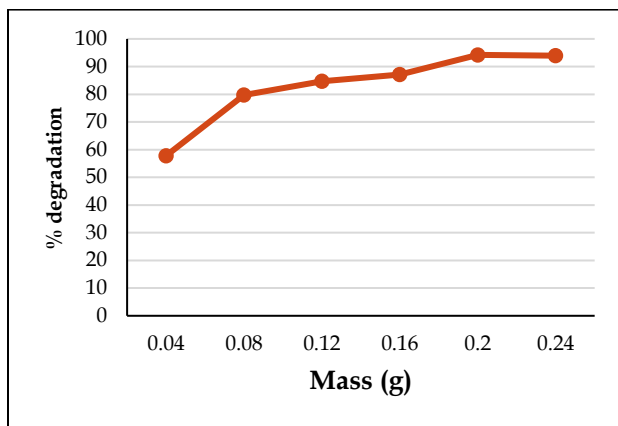


Figure-3: the comparison between Congo Red degradation percentage and mass of TiO<sub>2</sub>/zeolyte catalyst

**Determination Congo Red degradation percentage with and without TiO<sub>2</sub>/zeolyte catalyst**

Figure 4 illustrates degradation time increased with the increased of OH•, it was formed by photon which absorbed to catalyst surface (degraded dye) [14]. The degradation percentage for 60 minutes without catalyst, with Zeolyte, TiO<sub>2</sub>, and TiO<sub>2</sub>/zeolyte catalyst were 10,73 %, 28,68%, 56,09 % and 94,23% respectively. It can be seen that Zeolyte was successfully used as support for TiO<sub>2</sub> in degradation 20 mg/L Congo Red.

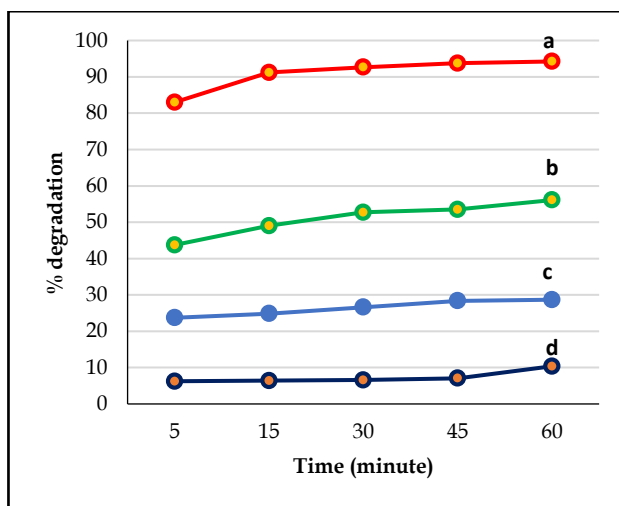
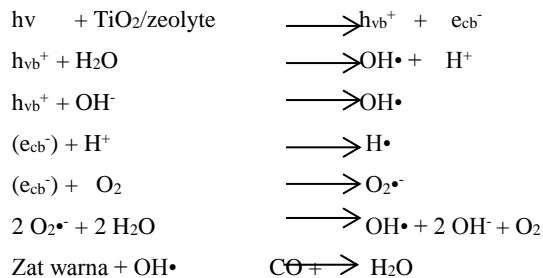


Figure-4: the comparison between degradation percentage of Congo Red with catalyst (a) TiO<sub>2</sub>/zeolyte, (b) TiO<sub>2</sub>, (c) Zeolyte, and (d) without catalyst

The reaction cans occur for a process degradation [11,12]:



**Determination degradation percentage of Congo Red waste water simulation with TiO<sub>2</sub>/zeolyte catalyst**

Fig. 5 shows the steeply decreased of absorb and value from 50 mg/L Congo Red solution, it was followed by waste water which was formed from submerged. It proves the decreased of concentration due to absorption of material up to 83,86 %. From the absorption of material, it can be said that material could not absorb dye until 100% while there was 16,14 % dye left became wastewater. The wastewater treatment in this research used photocatalytic method by using TiO<sub>2</sub>/zeolyte catalyst with irradiation under UV lamp (365 nm) for 60 minutes. The highest degradation percentage was 85,14 % [15].

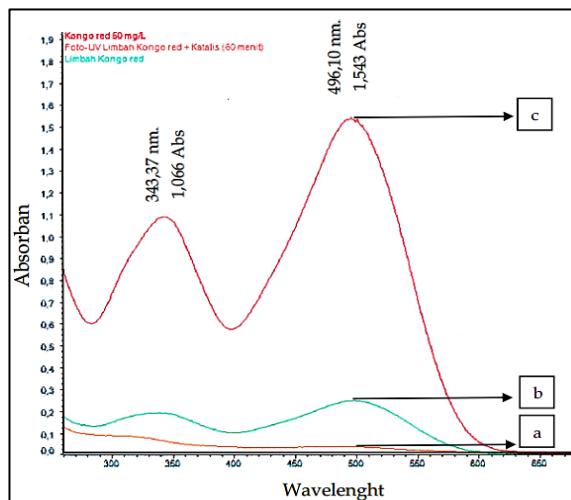


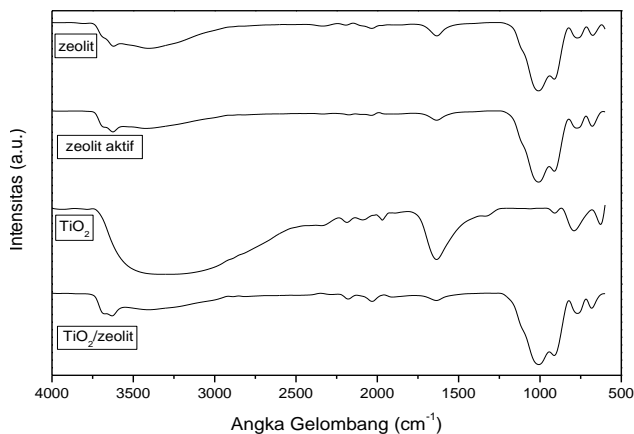
Figure-5: Absorbance spectra of Congo Red wastewater simulation (a) Congo Red 50 mg/L (b) before degradation (c) after degradation.

**Characterization**

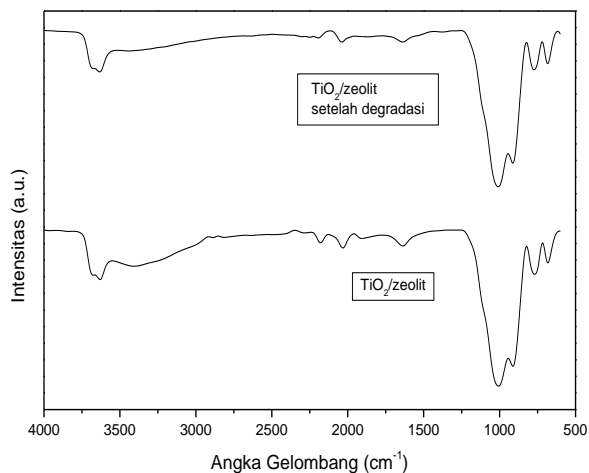
**FTIR (Fourier Transform Infra-Red)**

Pure zeolyte, activated zeolyte, TiO<sub>2</sub>, and TiO<sub>2</sub>/zeolyte catalyst were characterized by FTIR with range of wavelength numbers 500-4000 cm<sup>-1</sup>. On the Figure 6 can be seen the specific peaks of absorption was appeared on wavelength number 675,71-1008,24 cm<sup>-1</sup> which is a strain absorption of asymmetric and external asymmetric O-T-O (T=Al or Si) after then also appear some peaks on wavelength number 1634 cm<sup>-1</sup>, 2335,73 cm<sup>-1</sup>, 3406,43 cm<sup>-1</sup> and 3630,02 cm<sup>-1</sup> where each of peak is absorption of O-H buckling, C-H (carbon distracted group), O-H and C-C stretching [16] [17]. Figure 7 can be seen the peaks of figure not change after and before degradation. Where is explain the structural functional of TiO<sub>2</sub>/zeolyte was not changed after and before degradation [16]. And Figure 8 show the significant peaks of absorption Congo red on 643,18 cm<sup>-1</sup> which is a range absorption of asymmetric S=O, 1635,45 cm<sup>-1</sup> is Amine primer vibration bonding, 2104-2231 cm<sup>-1</sup> for C-H (organic compound), and 3325 cm<sup>-1</sup>

for O-H. On the spectrum can be seen as changes of absorption peaks O-H and S=O asymmetric on Congo red from before and after degradation process by 0,2 g TiO<sub>2</sub>/zeolite [18] [19].



**Figure-6: FTIR Spectra of zeolite, activated zeolite, TiO<sub>2</sub>, and TiO<sub>2</sub>/zeolite catalyst**



**Figure-7: FTIR spectra of TiO<sub>2</sub>/zeolite and TiO<sub>2</sub>/zeolite after degradation**

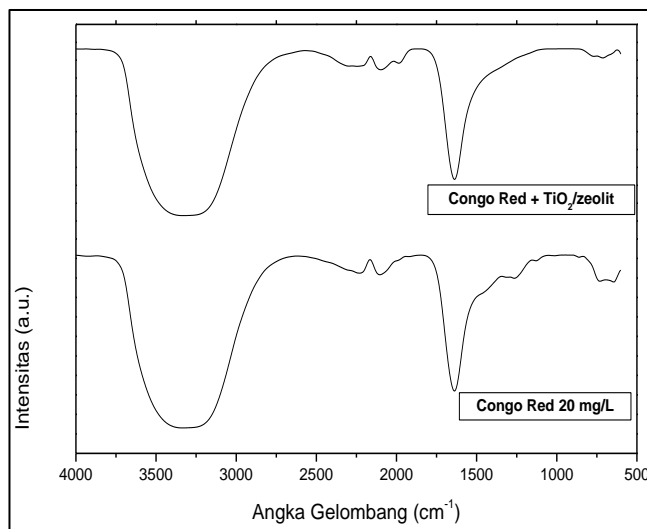


Figure-8: FTIR spectra *Congo Red* 20mg/L and *Congo Red* after degradation using  $TiO_2/zeolite$

**XRD (X-Ray Diffraction)**

On the figure can be seen the synthesis of  $TiO_2/zeolite$  was successfully formed evidenced by the formation of some pattern on  $2\theta$  that are  $24.950^\circ$  (101),  $38.017^\circ$  (004),  $47.176^\circ$  (200) which indicates of pattern corresponding to anatase pattern by ICDD 01-075-2551 and formed also pattern on  $2\theta$  that are  $20.827^\circ$  (100),  $26.594^\circ$  (101),  $50.047^\circ$  (112),  $59.854^\circ$  (211) which indicates of pattern corresponding to Quartz ( $SiO_2$ ) pattern by ICDD 01-083-0539. On the figure 10 it can be observed the XRD pattern of  $TiO_2/zeolite$  after and before degradation was not significant changes. From these result, it can be said no changes in crystal form of  $TiO_2/zeolite$  so that it can be said the catalyst was reusable.

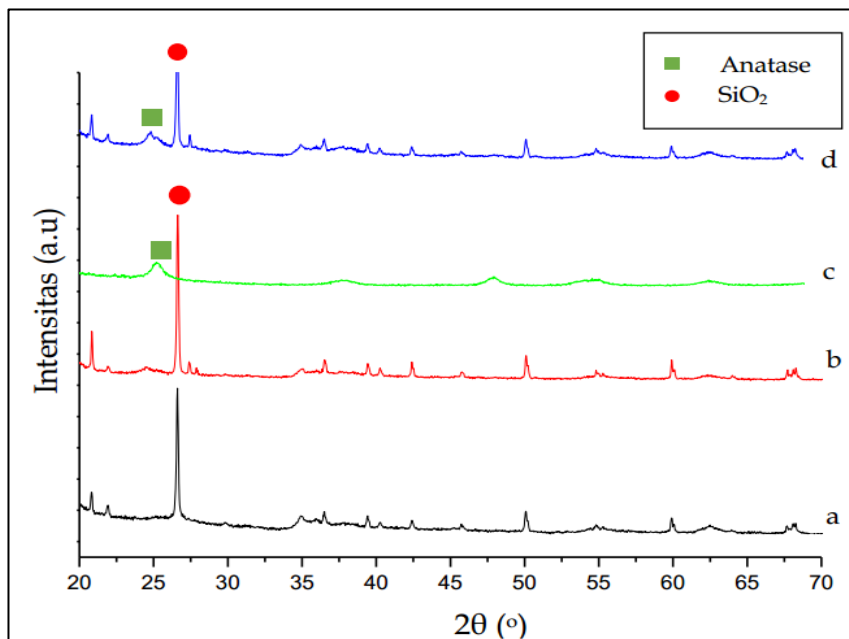


Figure-9: XRD pattern (a) zeolite, (b) zeolite active, (c)  $TiO_2$  and (d)  $TiO_2/zeolite$



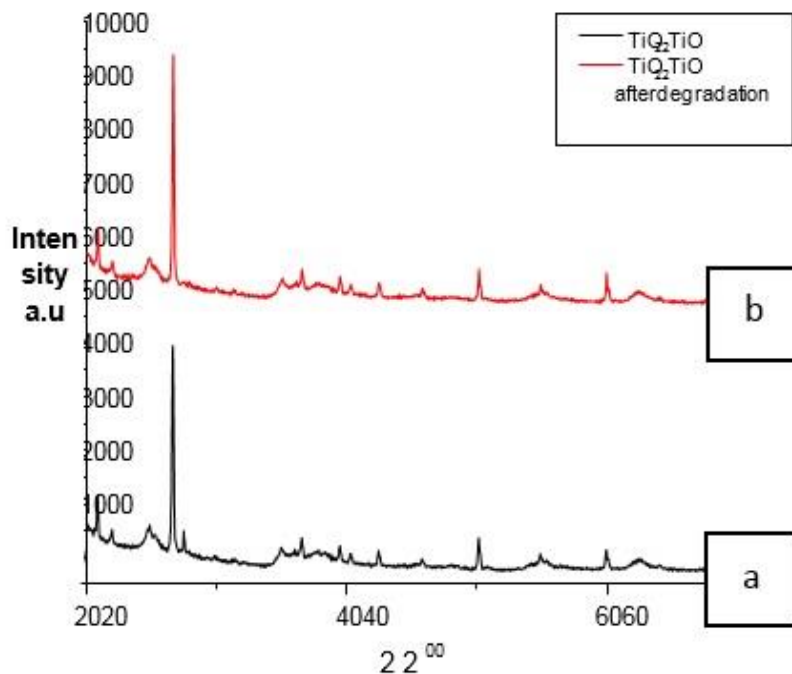


Figure-10: XRD pattern (a) TiO<sub>2</sub>/zeolite before degradation and (b) TiO<sub>2</sub>/zeolite after degradation

## CONCLUSION

TiO<sub>2</sub>/zeolite has been synthesized with support zeolite clinoptilolite-Ca into TiO<sub>2</sub> with ratio (25: 1). 0.2 g TiO<sub>2</sub>/zeolite can degrade of Congo Red 20 mg/L and simulation waste of Congo Red 20 mL under UV light wavelength of 365 nm for 60 minutes until it reaches the percentage of degradation of Congo Red 94.23% and the percentage of degradation waste simulation Congo Red 83.86%. The results of XRD and FTIR characterization of TiO<sub>2</sub>/zeolite after use and prior use did not show any significant change in the crystal and the functional groups.

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