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Synthesis Beads Photocatalyst TiO$_2$/N-zeolite/chitosan to photodegradation Methylene Blue with Sunlight

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Abstract : The purpose of this study was to synthesize a photocatalyst to form a ball making it easy to reuse activity is still high. Photocatalyst which has been synthesized then performed to characterize and test activities on various parameters include the concentration of methylene blue, while irradiation, the effect of pH methylene blue and reuse photocatalyst. Characterization is done by using FTIR, SEM and UV-Vis spectrometer Diffuse Reflactance. The concentration of methylene blue test is 10-25 ppm, long irradiation with sunlight 1-5 hours. Based on an analysis by FTIR, the N atom in TiO$_2$ is shown in wave numbers from 1520 to 1570 cm^{-1}. The results of the analysis with Diffuse Reflectance Spectroscopy is the energy band gap of TiO$_2$, TiO$_2$-N, TiO$_2$-N/zeolite, and TiO$_2$-N/zeolite-chitosan respectively are 3,28; 3.09; 3.3; 3.25 eV. The specific surface area of zeolite, zeolite activation, TiO$_2$, TiO$_2$-N, TiO$_2$-N/zeolite, and TiO$_2$-N/zeolite-chitosan is determined by the surface area analyzer with successive BET method was 224.233; 251.686; 119.42; 273.997; and 306.275 m^2/g. Based on the research showed that the concentration of MB is the effect on the degradation rate constant. Constant rate of degradation is increasing at a concentration of methylene blue from 10, 15 and 20 mg/L. The highest rate constant was 0.5198 h^{-1}, these constants is generated from MB 20mg/L.

Keywords : photocatalyst; methylene blue; TiO$_2$/N-zeolite; sunlight.

Introduction

The use of photocatalysts are Often known as "advanced oxidation processes" (AOPs) can Facilitate the degradation of organic waste that can accelerate the declining value of the COD of the waste. Vinu, R. and Madars, G. have been using TiO$_2$ as a photocatalyst for the degradation and mineralization of various toxic organic compounds such as chloro phenol, phenolic, dyestuffs, pesticides, and pharmaceuticals[1]. Ibhadon suggested that the TiO$_2$ photocatalyst can degrade organic waste in the water efficiently, because the strong oxidizing ability of TiO$_2$ when irradiated with light corresponding to the band gap of TiO$_2$[2]. This process Organic Pollutants can degrade into harmless inorganic materials items, namely CO$_2$ and H$_2$O[3].

The catalytic activity of a semiconductor can be enhanced through the developing of a porous material, such as zeolite[4,5,6]. Distribution of TiO$_2$ in the inner and outer surface of the zeolite results in specific surface area and total pore volume increases[5]. Research Faghihian and Bahranifard mentions that the developing of TiO$_2$ in the zeolite can improve percent degradation safranin-O by 69% compared with TiO$_2$ without entrusted[4].

TiO$_2$ has an energy band gap in the region of UV light, so the ability to absorb light in the visible region (visible) is still relatively low. UV rays from the sun is only about 5-8%[2]. The use of the sun as an energy source

becomes less efficient at using TiO_2 photocatalytic process, so that the necessary modifications to the other on TiO_2 photocatalyst-zeolite that can absorb light in the visible light region. The addition of non-metal N can cause the photocatalyst TiO_2-zeolite provides absorption at the wavelength of visible light). According Gandhe addition of N in TiO_2 lowers the band gap of the photocatalyst is originally 3.26 to 2.35 eV[7]. This decrease causes the photocatalysts can use sunlight evidenced by decreasing the concentration of the dye to be close to 0 after irradiation for 2 hours.

Based on research Pekakis TiO_2 to degrade reusable textile waste to use all three[8]. Despite the decline in the efficiency of photocatalytic degradation but the user back to the third still shows the percentage of degradation is quite high. Photocatalyst is effective, it can be reused but there are constraints on the separation process. Photocatalyst in powder form is difficult to be separated from the filtrate before reuse. This problem can be solved if the photocatalyst is made in the form of beads to be easily separated from the filtrate but have the same catalytic activity in powder form. Based on these facts, this research photocatalyst is made in the form of a ball. Although UV light provides increased efficiency degradation dye, sunlight as an effective substitute because of the cost and abundant presence in nature. Photodegradation reached 96% after 300 minutes of solar radiation[9].

Materials and Methods

1. Materials

The materials used in this study include natural zeolites Turen, TiO_2 (pharmacy grade), demineralised water (aqua DM), distilled water, urea pa (CH_4N_2O), CH_3COOH technical (98%, bj = 1.049), chitosan (food grade), absolute ethanol (96%, bj = 1.36), HCl (32% bj = 1.16 g/mL), NaOH and methylene blue dye (Uni Chem).

2. Synthesis beads photocatalyst

- zeolite powder is washed with water and activated with acid and then washed until acid free.
- TiO_2 coupled with urea is stirred for 60 minutes then filtered and the precipitate is heated. The precipitate was subsequently calcined at temperatures of $300^{\circ}C$ obtained $N-TiO_2$. Photocatalysts were characterized using XRD, surface area analyzer
- 1% acetic acid was added to the chitosan stirred until dissolved. This solution was added TiO_2/N-zeolite and then stirred further dripped into a solution of NaOH 0.4 m. Beads were formed was washed with distilled water until neutral and dried in an oven. Beads photocatalyst obtained is used for photodegradation of methylene blue.

3. Photodegradation Methylene Blue

- The degradation of methylene blue carried in a variety of conditions, namely the concentration of methylene blue, long irradiation, the ratio of the photocatalyst to a methylene blue. the concentration of methylene blue used is 5-25 ppm, long exposure 1-5 hours.
- 25 ml of methylene blue solution 5 mg/L was poured into a glass beaker and added 0.1 g beads TiO_2N-chitosan-zeolite. Photodegradation done under the sun. Each glass is irradiated for 1, 2, 3, 4, and 5 hours. The same thing is done for the concentration of MB 10, 15, 20, and 25 mg / L. Methylene blue solution had an absorbance is measured using the UV-Vis spectrophotometer at a wavelength 664,50nm.

4. Photocatalyst Characterization

The surface structure and morphology of the pothocatalyst were capture by using Scaning Electron Microscopy (SEM-EDX) Hitachi TM 3000, Brunaurer-Emmet-Teller (BET) Analysis was carried out using NOVA 1000 to determine the spesifik surface area of the pothocatalyst where liquid N_2 was used as adsorbate.

Results and Discussion

1. Characterization

Zeolite and photocatalyst characterized using FTIR, XRD, spectroscopy and diffuse Reflactance. The results of characterization by FTIR presented in Figure 1 and 2. The results of the characterization by diffuse UV

Spectroscopy Reflactance presented in Figure 3. Levels of N contained in the photocatalyst was conducted by Kjeldhal. Results of analysis of the N content contained in Table 1.

FTIR spectra for the activation of zeolite contained in Figure 1, the measurements are made at wave number 4000-500 cm^{-1}. Peak at 3620.14 and 3419.56 cm^{-1} is an OH group on the hydrated zeolite, 1026.06 cm^{-1} is an asymmetric range of O-Si-O or O-Al-O, 765.59 cm^{-1} is a bond peak the main structure of the zeolite unit symmetrical[10].

At the height of 466.74 cm^{-1} and 430.10 cm^{-1} indicate the presence of vibration and bending vibration T-O bond[11], there are peaks OH buckling wave number 1514.02 cm^{-1}. Type of change and movement intratetrahedral symmetric Si-O-Al indicated by the peak at 646.11 cm^{-1}, a peak at 578.60 and 528.4 cm^{-1} is the vibration of Si-O / Al-O buckling[12,13].

FTIR characterization results for TiO_2, TiO_2N, TiO_2N-zeolite, zeolite-chitosan-TiO_2N contained in Figure 2. The typical zeolite absorption shown by the vibrations of Si, O, and Al. Zeolite at wave number 1026.06 cm^{-1} is an asymmetric range of O-Si-O/O-Al-O, 765.59 cm^{-1} is a unit structure of zeolite asymmetric[14]. Movement of Si-O-Al intratetrahedral contained in 646.11 cm^{-1} [12], 578.60 and 528.46 cm^{-1} is Si-O/Al-O buckling [13] while at 466.74 cm^{-1} and 430.10 cm^{-1}, which is symmetrical movement of Si-O-Al [15]. Uptake typical TiO_2 contained in 676.97; 669.25; 684.86 cm^{-1}, the N on the surface of TiO_2 detected at wave number 1525.59 cm^{-1} (TiO_2N), 1523.66 cm^{-1} (TiO_2N-zeolite), 1645.17 and 1569.95 cm^{-1} TiO_2N-zeolite-chitosan[11]. The presence of chitosan on zeolites characterized by absorption at 3411.84 cm^{-1} numbers which are hydrated OH groups of chitosan[14]. FTIR spectra of TiO_2-N/zeolite-chitosan (Figure 2 D) there NH stretching vibration absorption at wave number 3743.57 cm^{-1}, the wave number 3411.84 and 1645.17 cm^{-1} are OH stretching and bending OH deformation of H_2O. N-TiO_2 bond shown in absorption wave number 1514.02 cm^{-1}. Wavenumber 1033.77 cm^{-1} and 765.69 to 655.75 cm^{-1} is a strain uptake asymmetry and symmetry of the O-Si-O and O-Al-O. Characteristics of TiO_2 is shown on the uptake from 516.89 to 430.10 cm^{-1} which is a Ti-O stretching vibration on TiO_2. Their uptake of N-H stretching vibration which is an active group of chitosan indicating that chitosan has been tied into the pores of the photocatalyst TiO_2-N/zeolite[15].

Measurements to determine the characteristics of the specific surface area of solids photocatalysts can show photocatalyst contact with the reactants. The solids from the photocatalyst is assumed as a solid monolayer will adsorb N_2 gas at very low pressure. The pressure before and after the N_2 gas adsorption is determined[16]. The method used to determine the surface area, pore diameter and pore volume are the Branauer-Emmet-Teller (BET) method. On the results of the analysis of data obtained with this method the specific surface area, mean pore and total pore volume of the photocatalyst are shown in Table 1.

Natural zeolite has a specific surface area and total pore volume smaller than the zeolite activation, due to the pore surface of zeolite is still contained impurities which cover while the zeolite compound impurity activation is lost on the activation process. TiO_2-N/ zeolite has a specific surface area and total pore volume greater than pure TiO_2 as the catalyst TiO_2-N/zeolite are zeolites that can increase the surface area and total pore volume. In catalyst TiO_2-N/zeolites made possible aggregation and cause the formation of cavities characterized by an increased average pore. catalyst TiO_2-N/zeolite-chitosan has a specific surface area greater than the catalyst TiO_2-N/zeolite, it indicates that the addition of chitosan on the catalyst TiO_2-N/zeolite may increase the specific surface area of the catalyst. TiO_2-N/zeolite particles associated with chitosan as a binder so that TiO_2-N/zeolite-chitosan have cavities larger. This is consistent with the SEM results indicate the presence of fibers binder particles TiO_2-N/zeolite.

In Figure 3 a on the leading TiO_2 adsorption isotherms classification of type III which shows the increasing pressure the more the quantity adsororbat. In this type of interaction is smaller than the adsorbent adsorbate-adsorbate interactions. Figure 3 b, c, and d is the type IV adsorption isotherm profile which has a characteristic similar to the type II and shows the size of the mesoporous (2-50 nm)[17]. Increasing the relative pressure accompanied with increasing adsorbate that goes into the pore material[18]. Desorption isotherms are formed leads to Type C, which in this type produced by the type of taper-shaped pores and is open at both ends.

The structure and morphology of photocatalysts can be known through characterization by Electrone Scanning Microscope (SEM). Morphology and structure of zeolite activation, TiO_2, TiO_2-N, N-TiO_2/zeolite and TiO_2-N/zeolite-chitosan is known that the morphology is different from one another. The morphology of the N

atom is known that already in the TiO_2, TiO_2N already bound in the zeolite, and the chitosan causes TiO_2N/zeolite can be spread out evenly. Morphology of the results of characterization using Electrone Scanning Microscope (SEM) is shown in Figure 4. Activation of zeolite morphology Figure 4.a shows that zeolite activation has many pores and forming clots. Morphology of TiO_2 in Figure 3.b with 5.000x magnification showed that the TiO_2 in the form of balls that belong together and have pores that quite a lot. TiO_2-N in Figure 4.c with a magnification of 5.000x morphology in the form of a set of balls possible of TiO_2 and there is a section which dominates with a diameter greater than the morphology of TiO_2. In morphology TiO_2-N has a surface which is denser than TiO_2 because the pores that exist in TiO_2 has been filled with N. Morphology of TiO_2-N is not much different from the TiO_2, TiO_2 is more dominating, This is due to the basic material is TiO_2 and TiO_2 have a ratio of more than N. TiO2 and urea has been calcined at a temperature of 300° C, the morphology of TiO_2-N shows the aggregate particles[19]. In Figure 4.d morphology of TiO_2-N/zeolite through magnification 4.000x there are several forms including some lumps which come from TiO_2-N and shapes with diameters wide, rectangular shape is derived from the zeolite. Morphology of TiO_2-N/zeolite-chitosan in Figure 4.e with 5.000x magnification can be seen that each TiO_2, N, zeolite and chitosan have been distributed evenly on the surface of the photocatalyst. Long form that resembles a needle is chitosan contained in the photocatalyst

The energy band gap of a material can be measured using the DRS (Diffuse Reflactance Spectroscopy), which is the distance between the valence band and the conduction band. Data obtained from the characterization is then processed by making the curve relationship between wavelength and K/S to determine the equation of a straight line with R^2 close to 1[20].

Characterization of DRS is able to provide great information value of the band gap of the photocatalyst. Data absorbance, % R, and the wavelength can be processed using Kubelka-Munk equation and made the curve relationship between the wavelength and the value of K/S with R^2 close to 1, the point of intersection on the wavelength axis (x axis) is the wavelength edge. Wavelength edge obtained is converted into energy band gap (eV). Based on the calculation, the energy band gap of the photocatalyst is as follows TiO_2 3.28 eV, 3.09 eV TiO_2-N, TiO_2-N/zeolite of 3.3 eV, TiO_2-N/zeolite-chitosan 3.25 eV. The addition of N dopant capable of lowering the energy band gap of TiO_2. The addition of chitosan, a large energy bandgap decreased, Chitosan itself has an energy band gap in the range of 1.6 to 2.3 eV [21].

TiO_2 band gap 3.28 eV according to the literature, namely 3.2 eV (387 nm)[22,23]. The presence of dopant N in TiO_2 causes a shift to larger wavelengths called Red Shift shift the band gap value is down. It is due to the formation of mid gap between the valence band and the conduction band of the TiO_2 semiconductor. The formation of mid gap is the result of a 2p orbital hybridization N and O 2p[24]. TiO_2N lower band gap of TiO_2 may be caused by a deficiency of stoichiometric TiO_2 by N or due to the formation of defects energy levels[25]. Decreased energy band gap in the presence of N dopants according to research Permatasari[9].

2. Photodegradation MB

TiO_2-N/zeolite-chitosan beads photocatalyst tested for their ability to degrade MB at various concentrations and various long irradiation. The constant rate of degradation is presented in Figure 5 and Table 2. Based on Figure 5 and Table 2 that the initial concentration of MB affect the degradation rate constant. Based on research from Hasan (2016) showed that the initial concentration of the dye will affect the speed of degradation of congo red, the rate of degradation is decreased with increasing the initial concentration of congo red[26]. While in this study for methylene blue at a concentration range of 10-25 ppm, a concentration of 20 ppm gives a constant degradation of the greatest. Degradation rate constant at MB was increased to concentrations of 10-20 ppm MB whereas when the concentration increased further degradation rate constant is decreased.

Research Wardhani[27] stated that constant rate degradation is decreased with increasing concentrations of 10-40 ppm MB using powder photocatalyst TiO_2/zeolite and UV rays. Increased degradation rate constant at higher concentrations caused more chances OH radicals and MB to interact. In the MB concentration increased, the more MB adsorbed on the photocatalyst so MB which exist on the surface of the catalyst is more likely to interact with OH radicals, which are produced by the photocatalyst. Degradation rate constant is decreased at MB concentrations were higher due to the increased intensity of the color of the MB. The intensity of this color affects the intensity of light that interacts with photocatalysts. So this will affect the OH radicals are generated so that the number of MB degraded decline.

Conclusion

Beads photocatalyst TiO_2-N/zeolite-chitosan have can be made of TiO_2, urea, zeolite and chitosan. Beads photocatalyst characterized by FTIR and showed absorption at wave number range of 1520 cm^{-1} which showed absorption bond of N-TiO_2. The specific surface area of TiO_2 will increase when TiO_2 is added bearers of zeolite and increase even more when added to chitosan. The specific surface area, average pore radius and total pore volume of TiO_2-N / zeolite chitosan are respectively 306.275 (m^2/g), 29.13 (Å) 4,462x10^{-1} (cm^3/g). The energy band gap of TiO_2 decreased when TiO_2 is implied by N. Energy band gap of TiO_2, TiO_2-N, N-TiO_2/zeolite, TiO_2-N/zeolite-chitosan are respectively 3.28; 3.09; 3.3 and 3.25 eV. MB degradation rate constant is affected by the concentration of MB.

Table 1 specific surface area, mean pore and total pore volume by the BET method.

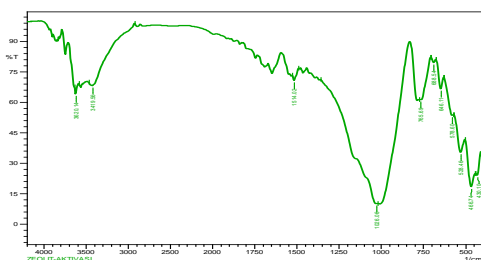| The catalyst	specific surface area (m^2/g)	Average pore (Å)	Total pore volume (cm^3/g)
natural zeolite	224,233	30,03	3,668x10^{-1}
zeolite activation	251,686	30,23	3,804x10^{-1}
TiO_2	119,42	23,40	1,395
TiO_2-N/zeolite	273,997	38,37	5,257x10^{-1}
TiO_2-N/zeolite-chitosan	306,275	29,13	4,462x10^{-1}

Figure 1. FTIR spectra of Zeolite Activation
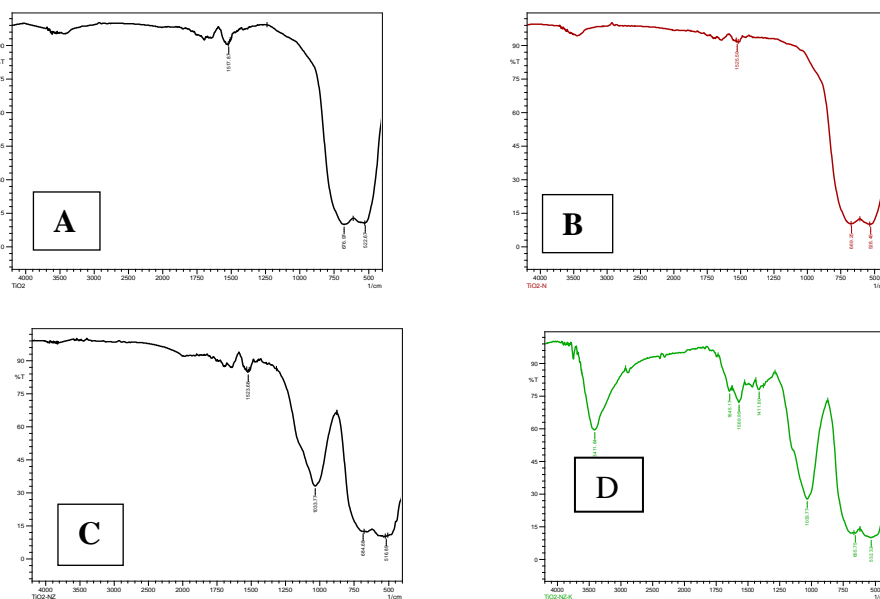
Figure 2. FTIR Spectra of (A) TiO$_2$, (B) TiO$_2$N, (C)TiO$_2$N-Zeolite, (D) TiO$_2$N-Zeolite-Chitosan

Relative Pressure, P/POPressure, P/Po

(a)

Relative Pressure, P/POPressure, P/Po

(b)

Relative Pressure, P/POPressure, P/Po

(c)

Relative Pressure, P/POPressure, P/Po

(d)
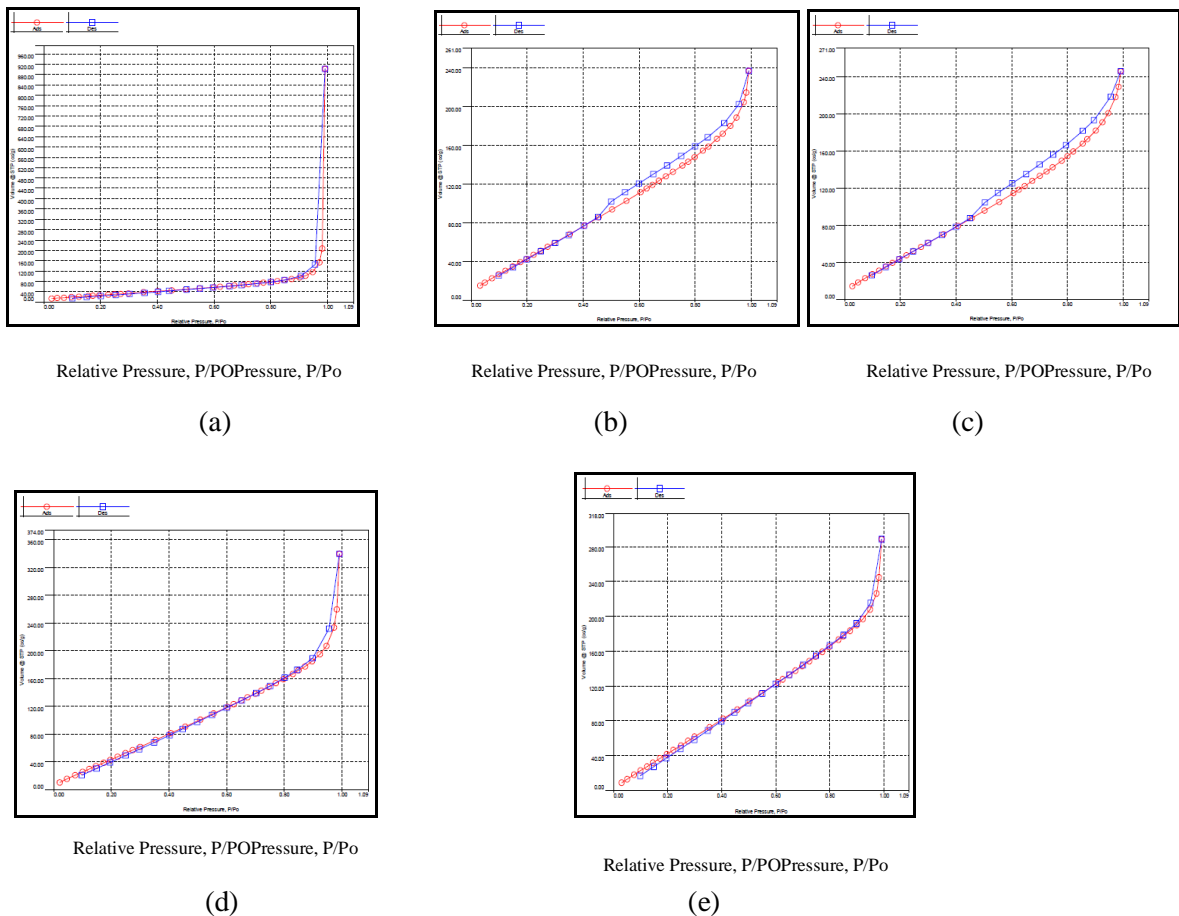
Relative Pressure, P/POPressure, P/Po

(e)

Figure 3: Graph adsorption-desorption isotherms of N_2 (a) TiO_2, (b) the natural zeolite, (c) zeolite activation, (d) TiO_2-N/zeolite, and (e) TiO_2-N/zeolite-chitosan
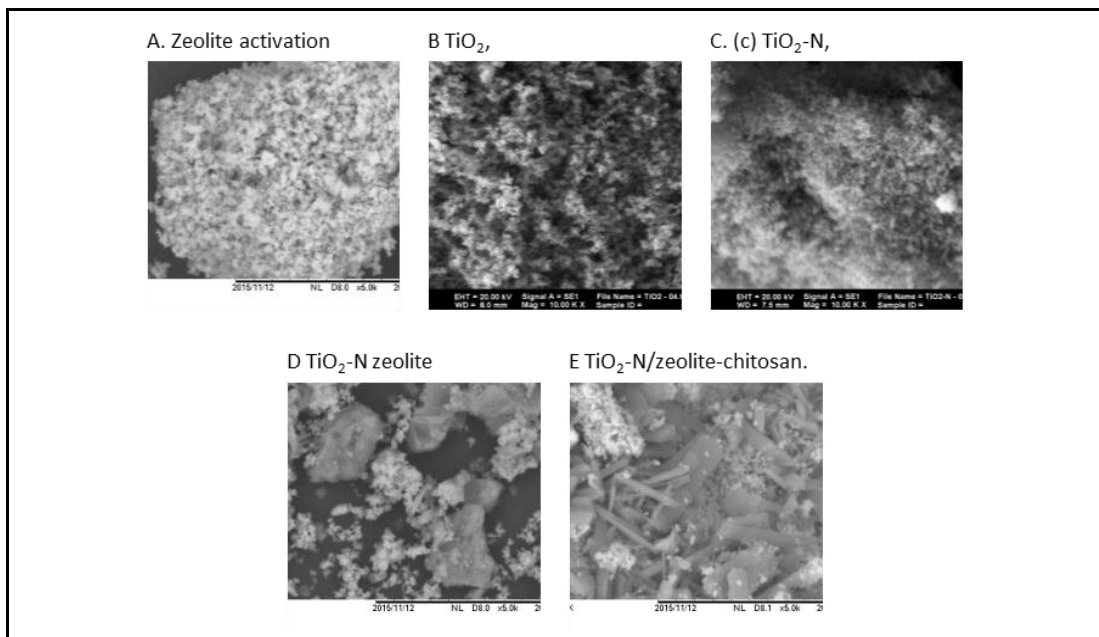

Figure 4: Morphology SEM results. (A) Zeolite activation, (b) TiO_2, (c) TiO_2-N, (d) TiO_2-N zeolite, (e) TiO_2-N/zeolite-chitosan.
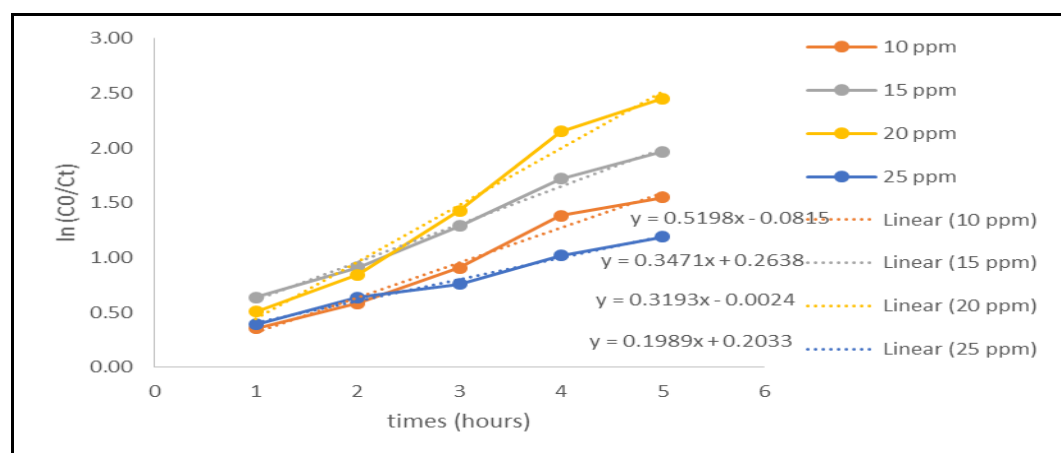
Figure 5 Correlation of irradiation time and ln (C$_0$/ C$_t$) at various initial concentration of MB

Table 2 Degradation rate constant at various concentrations MB

MB ppm	Rate constant (h^{-1})
10	0.3193
15	0.3471
20	0.5198
25	0.1989

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