

Photocatalytic removal of Cu (II) in an aquatic solution using TiO₂-Chitosan NanocompositesImelda Fajriati^{1*}, Mudasir², Endang Tri Wahyuni²¹Department of Chemistry, State Islamic University, Sunan Kalijaga, Yogyakarta,²Department of Chemistry, Gadjah Mada University, Yogyakarta*Corresponding author email: imelda.fajriati@uin-suka.ac.id

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ABSTRACT. Photocatalytic removal of Cu(II) in aquatic solutions using TiO₂-chitosan nanocomposite had been studied. The photocatalytic process was carried out using a batch system in a closed reactor equipped with a UV lamp. The results show that the percentage of photocatalytic removal of Cu(II) by TiO₂ – chitosan nanocomposite was higher than that of TiO₂ bulk catalyzing. Under solution containing 20 mg/L of Cu(II), pH 7, three hours of contact time, and employing 20 mg TiO₂-chitosan nanocomposite, the Cu(II) removal was successfully done up to 94.55%. The maximum adsorption capacity was obtained under nanocomposite with the highest amount of chitosan(TiO₂-chit 0.13). The highest kinetic constant was obtained with nanocomposite containing the highest amount of TiO₂ (TiO₂-chit 1.3). The method offers high reusability up to three times, with a percentage of more than 50% of Cu(II) removal.

Keyword: Photocatalytic, Cu(II) removal, TiO₂-chitosan nanocomposite

INTRODUCTION

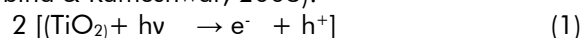
Cu(II) is one of the heavy metal widely used in textile, metallurgy, and electroplating industry. Its persistence in the aquatic solution can cause environmental problems and lead to a serious problem for humans and animals (Mohsen & Nazila, 2016). Accumulation of Cu(II) in the water system is due to its ability to mix with organic waste, and it could lead to biochemical effects (Joseph et al., 2010). Therefore, its accumulation in an aqueous solution could be very toxic and dangerous for humans, plants, and other living systems (Wolowiec, Komorowska, Alina, Grzegorz, & Tomasz, 2019).

Many wastewater treatments have been proposed for removals of Cu(II), such as coagulation and flocculation, biosorption, photo-decomposition and ultrafiltration (Patterson, 2011; Raouf & Raheim, 2017). However, those methods have been reported to be unable to detoxify the hazardous ion efficiently and effectively. They only moved the hazardous ion from the solution into solid surfaces of the adsorbent. After being covered with hazardous ions, the methods produced solid waste and finally caused further environmental problems. Therefore, it is vital to use other methods to detoxify Cu(II) in the water system.

The photocatalytic method is effectively able to detoxify Cu(II) in an aquatic solution. Photocatalytic removal of Cu(II) is a reduction process by capturing electrons induced by photon or UV light and sensitized by a TiO₂ photocatalyst. Photoreduction process over TiO₂ has some advantages compared to the other reduction reactions, for simplicity, cost-effectiveness,

efficiency, less chemical usage, and green chemistry principles (Wahyuni, Aprilita, Hatimah, Wulandari, & Mudasir, 2015).

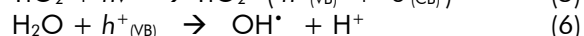
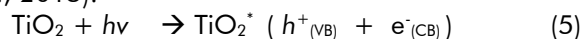
Cu(II) can be reduced into dissolved Cu(I) and/or undissolved Cu(0). The photoreduction of Cu (II) that catalyzed TiO₂ may occur due to the reduction potential of electrons in the conduction band of TiO₂ is smaller than the standard reduction potential of Cu(II) ($E^{\circ}\text{Cu}^{2+}/\text{Cu} = +0.34$ volt; $E^{\circ}\text{Cu}^{2+}/\text{Cu}^{+} = +0.153$ volt) (Chowdhury, Pankaj, Elkamel & Sanjay, 2014). The Photoreduction equation of Cu(II) catalyzed TiO₂ occurs as the reaction below (Kabra, Rubina & Rameshwar, 2008):



TiO₂-chitosan nanocomposite is one of the photocatalyst materials which has a semiconductor structure. It was characterized by the separation of the electron-filled valence band and the empty conduction band with a bandgap energy of 3.07 - 3.19 eV. TiO₂-chitosan nanocomposite demonstrates an absorption edge ranging from 300 to 450 nm, which corresponds to absorption edge of semiconductor material (Fajriati, Mudasir, & Wahyuni, 2017).

Photocatalytic processes were initiated by the excitation of an electron in the valence band of TiO₂-chitosan nanocomposite to the conduction band. The excitation of an electron generated a positively charged hole, which turned into forms of OH radicals. The following process represents the photogeneration

of electrons and holes and the formation of OH radicals as reactions (5), (6), (7) and (8) (Wahyuni et al., 2015):



Furthermore, the electron ($e^-_{(\text{CB})}$) reacts with dissolved oxygen (O_2) to form OH^\bullet , O_2^\bullet , HO_2^\bullet radicals (8). These radicals act as strong oxidizing agents to oxidize pollutant compounds (Nawi & Sheilatina, 2012). On the other hand, photoreduction reactions occur when the electrons ($e^-_{(\text{CB})}$) react with metal ions in solution.

TiO_2 -chit nanocomposites had been reported to be effective in photodegradation of cationic and anionic dyes (Fajriati, Mudasir, & Wahyuni, 2019). This research provides an extension of the TiO_2 -chit nanocomposites application in the Cu(II) photoreduction. The use of TiO_2 -chit nanocomposite photocatalysts to remove heavy metals from aquatic solutions is the novelty of this research.

The nanocomposite was synthesized with various concentrations of titanium tetra isopropoxide (TTIP) as a TiO_2 precursor via the sol-gel process. The formation of TiO_2 nanoparticles was carried out at room temperature to form the crystalline phase. This synthesis used chitosan as a host material where it inhibited the growth of TiO_2 and generated the production of TiO_2 nanoparticles. Ti-chitosan bonds were reportedly formed in the nanocomposites through basic sites (NH_2) available on the polymer chains and Lewis acidic sites from titanium (Fajriati, Mudasir & Wahyuni, 2013).

EXPERIMENTAL SECTION

Materials and Method

Titanium tetra isopropoxide (TTIP) was purchased from Sigma-Aldrich. Acetic acid 99.8% and Cuprum nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; MW 259.6 g/mol) were purchased from Merck. Chitosan (with 87% degrees of deacetylation) was purchased from Biotech Surindo

Cirebon, Indonesia. Bidistilled water and deionized water were supplied by Jakarta Pharmaceutical Laboratories. All chemicals were of reagent grade and were used without any further treatment. TiO_2 bulk photocatalyst and TiO_2 -chitosan nanocomposite photocatalyst had been prepared as described in previous research (Fajriati et al., 2013). The characterization of the nanocomposite's crystal phase was using the X-Ray spectrophotometer (Shimadzu x-ray Diffractometer 6000), Transmission Electron Microscope (JEOL JEM-1400). Photocatalytic Removal of Cu(II) was carried out using a closed photoreactor equipped with a 40 watt UV lamp (290 - 390 nm) with a magnetic stirring plate. Determination of Cu(II) concentration using atomic absorption spectroscopy.

Photocatalytic removal of Cu(II) was studied using a mixture solution containing 20 mL of Cu(II) 20 ppm and 0.02 g of TiO_2 -chitosan nanocomposite (TiO_2 -Chit 0.13, TiO_2 -Chit 0.33, TiO_2 -Chit 0.65 and TiO_2 -Chit 1.3) in an Erlenmeyer flask. It was also placed in the photoreactor and was allowed to react to a different contact time (1; 2; 3; 4; 5 and 6 h). Afterward, the mixture was centrifuged at 3000 rpm (Boeco C-28 Centrifuge) for 5 minutes. The filtrate was taken out and measured by Atomic Absorption Spectrometry (Perkin Elmer). This experiment was then repeated for different concentrations of Cu(II) (6; 8; 10; 12 and 14 mg / L) and pH (4; 5; 6; 7; 8). As a reference, TiO_2 powder (bulk) was also used for the photocatalytic process using the same conditions.

RESULTS AND DISCUSSION

Characteristics of TiO_2 -Chitosan nanocomposite

Characterization of TiO_2 -Chitosan nanocomposite was carried out using X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). X-Ray Diffraction (XRD) study was investigated to identify the presence of TiO_2 polymorphs and crystal phases in the TiO_2 -chitosan nanocomposite. X-ray diffraction pattern of the TiO_2 -chitosan nanocomposite types are shown in **Figure 1**.

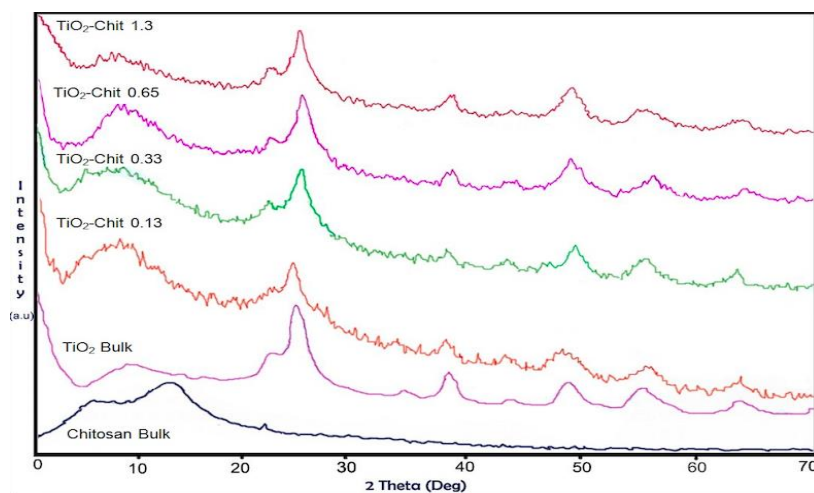


Figure 1. XRD Patterns of chitosan bulk, TiO_2 bulk, and TiO_2 -chitosan nanocomposite (TiO_2 -chit 0.13, TiO_2 -chit 0.33, TiO_2 -chit 0.65, and TiO_2 -chit 1.3)

It can be seen that the only observed peaks are at 2θ of 25.4° , 38.0° and 48.0° corresponding to the standard JCPDS No. 21 2272, which characteristically corresponds to the anatase crystal phase. There is no single peak observed for brookite in all of the nanocomposite types (TiO_2 -chit 0.13, TiO_2 -chit 0.33, TiO_2 -chit 0.65, and TiO_2 -chit 1.3). These results are confirmed by the TEM-SAED in **Figure 2**, showing that the TiO_2 nanoparticles have a spherical shape which appears uniformly dispersed. It can be seen in the ringspot on the same diffraction field from the selected area of electron diffraction (SAED).

Effects of Contact Time

Effects of contact time at various concentrations of the nanocomposites (TiO_2 -chit 1.3; TiO_2 -chit 0.63; TiO_2 -chit 0.33; TiO_2 -chit 0.13) was studied. Experiments were carried out in UV reactors with and without light, with contact time intervals of 1-6 hours. It has been found that the percentage of Cu(II) removal increased with the increase of contact time up to 3 hours. After 3 hours, the photocatalytic decolorization did not show any significant increase. It is due to the number of pollutants contacted to the photocatalyst surface to be less. Therefore, the additional percentage of Cu(II) removal was slow, as shown in **Figure 3**.

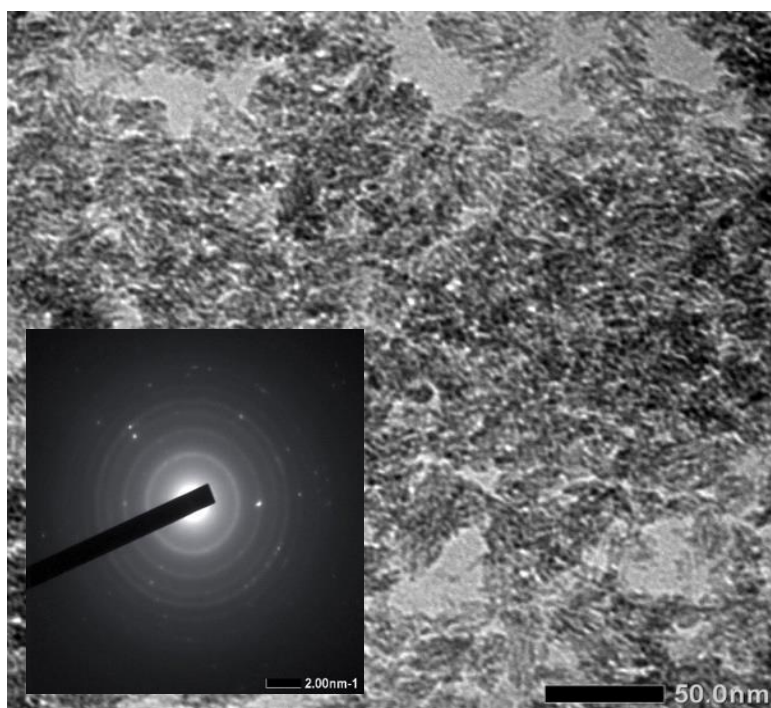


Figure 2. TEM-SAED images of TiO_2 -chitosan nanocomposite at magnification scale of 50 nm

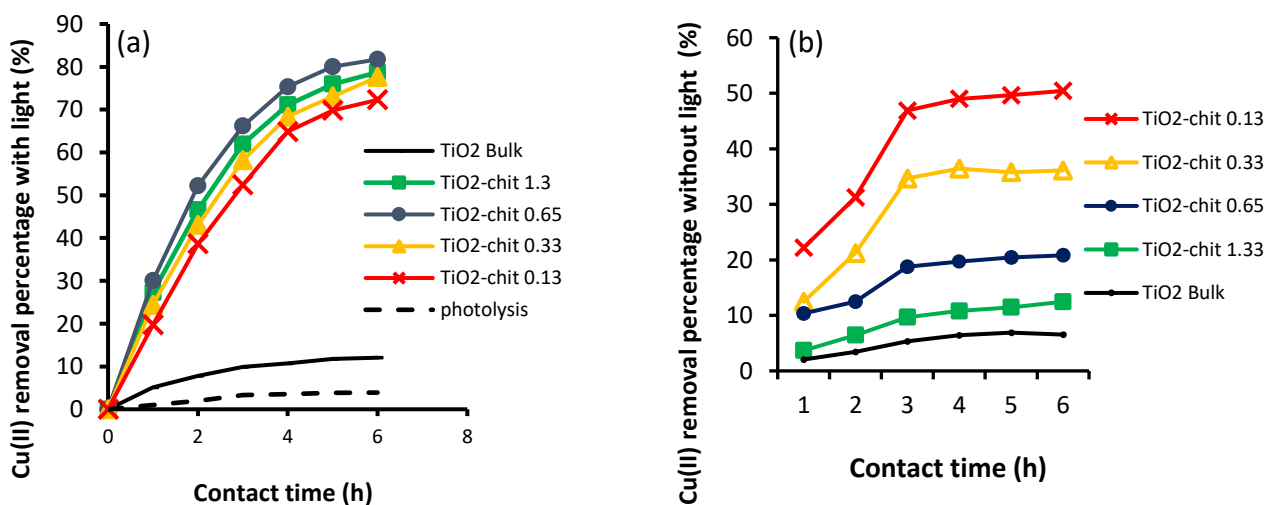


Figure 3. Effect of contact time on photocatalytic removal of Cu(II) with light (a) and without light (b)

Figure 3 shows that the photocatalytic removal of Cu(II) using TiO₂-chitosan nanocomposite provides a better result than TiO₂ *bulk*. It might be due to the higher E_g of TiO₂-chitosan nanocomposite (E_g = 3.07-3.25 eV) than that of TiO₂ *bulk* (E_g = 2.82 eV) (Fajriati, Mudasir, & Wahyuni, 2014). The E_g value is obtained from the edge absorption wavelength obtained from the UV-vis absorption extrapolation of TiO₂-chitosan nanocomposites, as follows: (Hagfeldt & Graetzel, 1995).

$$E_g \cong \frac{1236}{\lambda} \quad (9)$$

E_g is bandgap energy, and λ is the edge absorption wavelength. The high value of E_g generates optimal photocatalytic activity of TiO₂-chitosan nanocomposites. It is due to the high value of E_g that indicates the broader distance between the HOMO and LUMO levels. This condition makes the possibility of holes recombination in the valence band and electrons in the conduction band are getting smaller. These abundant electrons induce a Cu(II) reduction reaction, so Cu(II) removal is optimal.

The removal of Cu(II) without light condition indicates that adsorption of Cu(II) occurred on the chitosan surface because chitosan used as a host material was a suitable adsorbent. The maximum adsorption capacity of Cu(II) on TiO₂-chitosan nanocomposite can be determined using the Langmuir isotherm model. The equation for Langmuir isotherm is as follows (Nghah, Teonga, & Hanafiha, 2011; Ahmad, Ahmed, Swami, & Ikram, 2015):

$$\frac{C_e}{q_m} = \frac{C_e}{q_e} + \frac{1}{K_L q_e} \quad (10)$$

C_e is the concentration of Cu(II) solution (mg/L), q_e is the quantity of Cu(II) absorbed per 1 g of catalyst (mg/g), q_m is the maximum adsorption capacity (mg/g), and K_L is the Langmuir adsorption constants that related to the adsorption energy (L/mg). The adsorption isotherm graph obtained was employed in various contact times to describe the adsorption equilibrium constant or the adsorption capacity (**Figure 4**). Based on the adsorption isotherm graph (**Figure 4**), the maximum adsorption capacity (q_m) value and the Langmuir adsorption constant (K_L) of the nanocomposite to Cu(II) molecules could be calculated from the equation of the line curve C_e/q_m versus C_e (**Table 1**). The adsorption of Cu(II) on nanocomposite followed the Langmuir isotherm model proposed that the adsorption capacity of Cu(II) is induced on the composition of TiO₂ and chitosan host in TiO₂ – chitosan nanocomposite. It might be due to Cu(II) formed chelate complexes [Cu(NH)₂(OH)₂] chitosan required 2 amine groups and 2 hydroxyl groups. Therefore, it needed more active groups of chitosan for each Cu(II) ions (Schmuhl, 2001). Chitosan could also adsorb Cu(II) through the formation of chelates with active groups -NH₂ (Inger, Volda, Eric, & Olav, 2003; Guibal, 2005). The type 0.13 of TiO₂-chit nanocomposite provided the highest adsorption capacity (q_e = 3.22 × 10² mg/g) because of the highest chitosan availability (Fajriati et al., 2017).

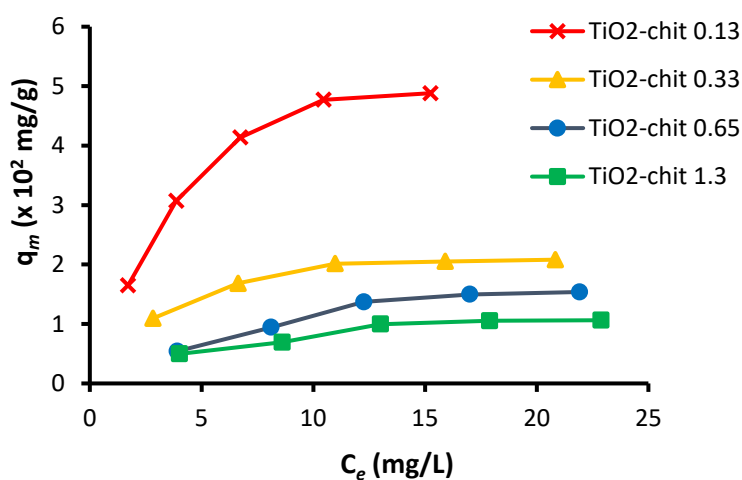


Figure 4. Adsorption isotherm of TiO₂-chitosan nanocomposite for Cu(II)

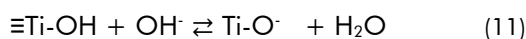
Table 1. The adsorption isotherm constants of TiO₂-chitosan nanocomposite for Cu (II)

Types of Nanocomposite	q _e × 10 ² (mg / g)	K _L × 10 ⁻¹ (L / mg)	R ²
TiO ₂ -chit 0.13	3.22	2.29	9.92
TiO ₂ -chit 0.33	2.22	1.89	9.98
TiO ₂ -chit 0.65	1.31	1.65	9.41
TiO ₂ -chit 1.33	0.74	1.22	9.66

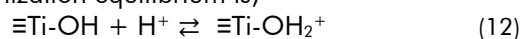
Effect of Solution pH

The removal of Cu(II) in aquatic solutions using photocatalyst was affected by pH conditions. The solution's pH could change the charge of the photocatalyst surface and Cu(II) speciation (Wahyuni et al., 2015). The effect of pH on photocatalytic removal of Cu(II) (Figure 5) shows that the optimum photocatalytic removal of Cu(II) using TiO₂-chitosan nanocomposites was achieved at pH 7. It was proven that after pH 7, Cu(II) began to precipitate, and Cu(II) in the form of the solution was unstable. It was indicated by the removal percentage that started to decrease. Figure 5 shows that the pH solution could affect the speciation of the Cu(II) solution. It could be attributed to the states of the surface of the TiO₂ as photocatalyst and Cu (II) speciation.

In a neutral solution (pH_{pzc}), the surface of TiO₂ can be denoted as >TiOH (titanol group). In alkaline condition (pH>7), the surface of the photocatalyst became negatively charged by following ionization equilibrium (Shapovalov, 2010).



On the contrary, in pH condition below 4, the ionization equilibrium is,



The dominant species of Cu(II) was available in the solution in the range pH of 4–6, as seen in Figure 6 of the Copper Pourbaix diagram for copper species (Jonathan, Susan & Andrea, 2006). It had the same charge as the TiOH(II) on the photocatalyst surface. The same charge of Cu(II) and TiOH(II) caused the electrostatic repulsion effect between the photocatalyst surface and Cu(II). In the pH range of 6-7, the dominant species of Cu was in the form of [Cu(OH)]⁺ and the surface can be denoted as >TiOH and >TiOH₂⁺. The different charges between Cu state and photocatalyst surface reinforced electrostatic attraction. Its condition enhanced the removal of Cu(II) from the aqueous solution (Kabra et al., 2008). The Cu(II) species began to precipitate in the form of Cu(OH)₂ at a pH of more than 8. Besides, the surface of TiO₂ can be denoted as >TiO⁻ which is not easy to release electrons. Therefore the removal of Cu(II) at high pH could occur due to the precipitation (Wahyuni et al., 2015).

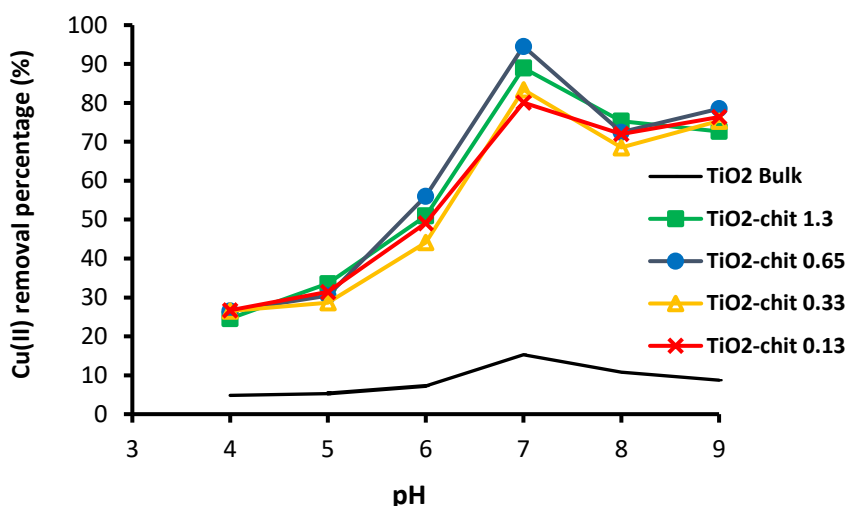


Figure 5. Effect of pH solution on photocatalytic removal of Cu(II)

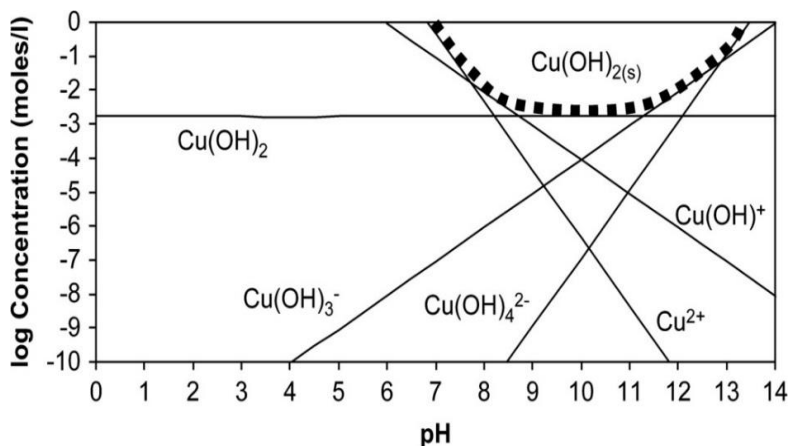


Figure 6. The species of Cu(II) the solution with various pH

Effect of initial concentration of Cu(II)

The initial concentration of Cu(II) in the solution affected the photocatalytic removal as it involved the amount of reacted compound. The effect of the initial concentration of Cu(II) on the photocatalytic removal by TiO₂-chitosan nanocomposites were evaluated using different initial Cu(II) concentration of 5.0, 10.0, 15.0, 20.0 and 25.0 mg/L (Figure 7). The removal percentage for all of the types of nanocomposites decreases markedly with the increase in the initial dye concentration. It can be attributed to the capacity of TiO₂-chitosan nanocomposite in adsorbing Cu(II) has saturated. In this condition, the equilibrium of adsorption-desorption was reached. Therefore, the photocatalytic removal could be reduced because the abundant Cu(II) solution could block the penetration of light into photocatalyst (Engates & Shipley, 2011).

The Kinetics of Cu(II) removal

The kinetics of the photocatalytic removal of Cu(II) followed the Langmuir-Hinshelwood equation (LH

equation). The kinetics of the heterogeneous catalytic processes can be easily explained by LH equation (Kumar, Porkodi, & Rocha, 2008).

The kinetics of Cu(II) removal relates to the ratio of the concentration of Cu (II) and time. The study was done in a solution with 10 mg/L of Cu(II). The effect of the ratio of initial concentration (C₀) and concentration after t (min) (C_e) during photocatalytic removal of Cu(II) was shown in Figure 8.

Figure 8 showed that the concentration of the Cu(II) follows a first-order exponential decay and it is always a decreasing function from the initial value C₀. The indication proved that the photocatalytic removal of Cu(II) is a first-order reaction. The kinetic constant (k) is determined by the Langmuir-Hinshelwood (LH) equation, as follows (Hoffman, Martin, Choi, & Bahnemann, 1995; Kumar et al., 2008):

$$r = -\frac{dC}{dt} = \frac{kK_L C_e}{1+K_L C_e} \tag{13}$$

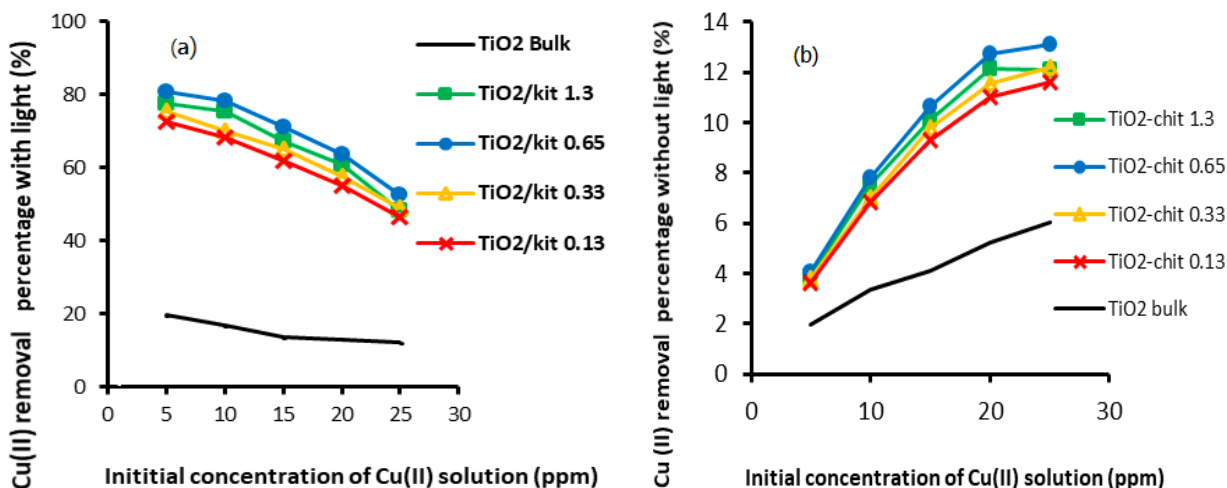


Figure 7. Effect of the initial concentration of Cu(II) on photoreduction of Cu(II) catalyzed by TiO₂ bulk and nanocomposite TiO₂-chitosan with light (a) and without light (b)

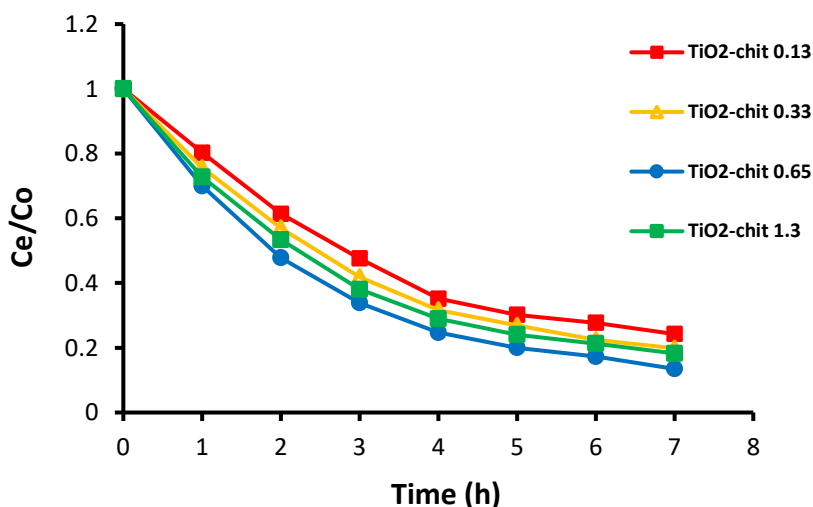


Figure 8. Effect of time on the ratio of CU(II) concentration after t (min) (C_e) and initial concentration (C₀)

r is the reaction rate, C_0 is the initial concentration, C_e is the concentration after t, with t represent the reaction time (min), k is the kinetic constant and K_L is the Langmuir adsorption constant, which was determined independently from dark adsorption isotherms, as in **Figure 4** and **Table 1**. The constants k and K_L can be derived from the corresponding integrated expression, as follows:

$$\ln\left(\frac{C_0}{C_e}\right) + K_L(C_0 - C_e) = kK_L t \quad (14)$$

This equation can be integrated between the limits: $C_e = C_0$ at $t = 0$ and $C_e = C_e$ at $t = t$.

If the term $K_L C_e \ll 1$; the Eq. (13) is reduced to:

$$r = kK_L C_e \quad (15)$$

Integrating Eq. 14 with respect the limits, LH equation can be simplified into the first order reaction and is given by:

$$-\ln\frac{C_e}{C_0} = K_{obs}t \quad (16)$$

where $K_{obs} = kK_L$.

K_{obs} is observed kinetic constant (min^{-1}) which was determined by fitting the curve of $-\ln C_e/C_0$ vs t, and the observed kinetic constant was calculated based on the slope value of the graph regression equation. The

graph describing the observed kinetic constant (K_{obs}) in the photocatalytic removal of Cu(II) was given in **Figure 9**.

The reaction rate of photocatalytic removal of Cu(II) depends linearly on the concentration which means it followed a (pseudo) first-order reaction (**Figure 9**). The linearity of fitting the curve are in accordance with the correlation coefficient (R^2). The parameters of the observed kinetic constant rate (K_{obs}) did not considering the adsorption during heterogeneous photocatalytic reactions. Therefore, when adsorption was one of the kinetics determinant variables, the kinetics constant (k) corrected by the adsorption process was determined based on the $K_{obs} = k.K_L$ equation. The K_{obs} values are given in **Table 2**,

Table 2 shows that the observed kinetic (K_{obs}) of TiO_2 -Chit 0.65 was the highest because it had the maximum value of Eg and crystallinity. On the other hand, the corrected kinetic (k) of the TiO_2 -Chit 1.3 nanocomposite was the highest because it had the minimum value of Langmuir adsorption constant (K_L); hence the time needed by Cu(II) to achieve the adsorption equilibrium on the TiO_2 -Chit 1.3 nanocomposite was shorter.

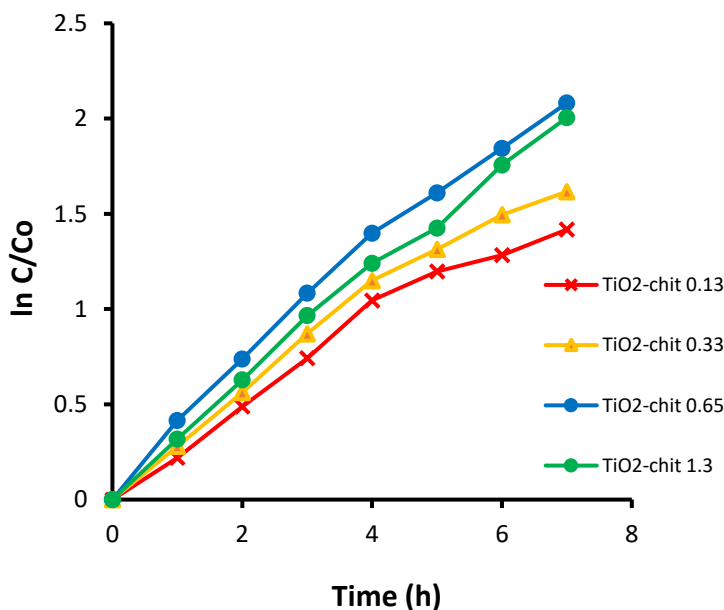


Figure 9. Observed kinetic constant (K_{obs}) of Cu(II) removal follows the first order reaction

Table 2. The photocatalytic removal rate parameters of Cu(II) using TiO_2 -chitosan nanocomposite

Types of Nanocomposite	K_{obs} (min^{-1})	K_L ($\times 10^{-1}$, L/mg)	k ($\times 10^2$, $\text{mg.L}^{-1}.\text{min}^{-1}$)	R^2
TiO_2 -chit 0.13	6.024	0.229	2.883	0.941
TiO_2 -chit 0.33	80.424	0.189	4.255	0.966
TiO_2 -chit 0.65	117.82	0.165	7.141	0.992
TiO_2 -chit 1.3	109.36	0.122	8.964	0.998

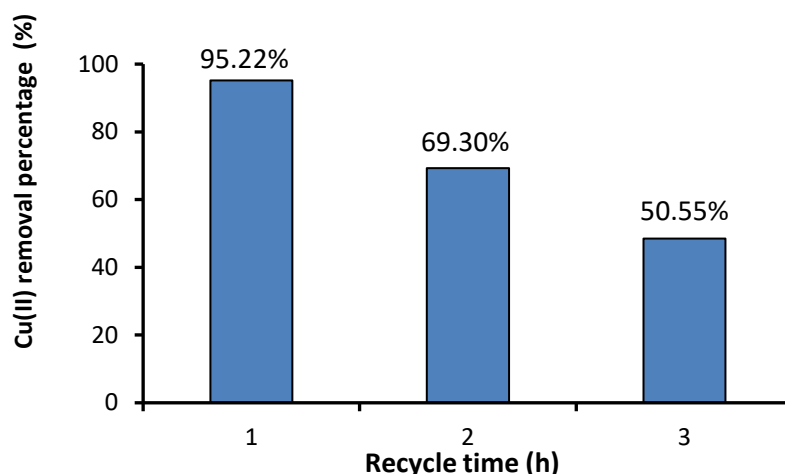


Figure 10. Reusability of TiO₂-chit 0.65 for photocatalytic removal of Cu(II) (Cu(II) concentration: 20 mg / L; TiO₂.chitosan nanocomposite dosage: 0.02 g, pH 4; contact time: 5 h).

Reusability of TiO₂-Chitosan Nanocomposite

The reusability of TiO₂-chitosan nanocomposite is an important parameter to evaluate the performance of photocatalyst. The experiment was carried out by regenerating TiO₂-chitosan nanocomposite (TiO₂-chit 0.65). It had been done by washing the reuse nanocomposite using distilled. Hereafter, the nanocomposite was dried and re-tested in the same experimental condition (10 mg/L of Cu(II), 20 mg of photocatalyst). The time for each run was 3 hours, as in **Figure 10**.

Figure 10 shows that Cu(II) removal percentage slightly decreased after the second running/cycle. The results indicate that the performance of TiO₂-chitosan nanocomposite gradually decreased at third using. It may be due to the closure of active sites by Cu(I) and Cu(O) on the photocatalyst's surface, which can block UV radiation and inactivate the generate holes and e⁻ pair on the photocatalyst. Therefore photoreduction was down (Chun, Ya, & Xi, 2002; Jaeyeon et al., 2017).

CONCLUSIONS

The TiO₂-chitosan nanocomposites were successfully studied for photocatalytic removal of Cu(II) in aqueous solution. In the selected experiment conditions, the Cu(II) removal percentage reached 94.55% (20 mg/L Cu (II), pH 7, 3 hours of contact time, using 20 mg TiO₂-chitosan nanocomposite). The photocatalytic removal of Cu(II) allowed the synergy process of Cu(II) adsorption to occur in chitosan in photocatalysts. The type 0.13 TiO₂-chit nanocomposite offered the highest adsorption capacity ($q_e = 3.22 \times 10^2$ mg / g) because of the highest chitosan availability. The type 1.3 of TiO₂-chit nanocomposite provided the highest reaction rate constant ($k = 8,964 \times 10^2$ / min) because of the highest TiO₂ availability. The reusability of TiO₂-chitosan nanocomposite was up to 3 times, with more than 50% of Cu(II) removal.

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