PREPARATION OF HYDROXYAPATITE-CEMENTED TITANIUM DIOXIDE COMPOSITE AND ITS APPLICATION

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Abstract

Using the wet precipitation method, hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, was synthesized from waste crab shells in this study. The prepared hydroxyapatite and titanium dioxide with cement have been fabricated by blending to form a hydroxyapatite-cemented titanium dioxide composite at room temperature. The photodegradation capacities of composites in solar light and in the dark were studied for the degradation of dye (methylene blue) solutions with varying parameters of initial concentration of dye solution and contact time at optimal conditions**.** The results show that the kinetic study of the photodegradation reaction follows the Langmuir-Hinshelwood model equation. SEM technique was applied to characterize the prepared hydroxyapatite-cemented titanium dioxide composite. According to the SEM analysis, it was found that the pores of the composite were filled after the degradation of the dye. The photodegradation of contaminants in water collected from a fish pond near Shwedagon Pagoda was studied using composites. Composite was also found to be the most efficient and effective adsorbent for the degradation of organic pollutants from wastewater. As a result, the prepared hydroxyapatite-cemented titanium dioxide composite can be applied to the reduction of organic pollutants discharged from wastewater into aquatic environments. It would help reduce the public health risk caused by organic pollutants.

Keywords: Hydroxyapatite, Langmuir-Hinshelwood model equation, organic pollutants, photodegradation

Introduction

Hydroxyapatite (HA) is one of the inorganic materials and most methods to synthesize HA are either based on the wet precipitation method of natural sources like seashells, egg shells, fish bones and crab shells, etc. Hydroxyapatite cannot be used at load bearing-sites because of its poor mechanical strength and brittleness. Therefore, various composite materials of HA were fabricated to improve their mechanical strength, by blending with titanium dioxide (TiO_2) because titanium dioxide is an important photocatalyst due to its strong oxidation power, non-toxicity and long term photostability. Moreover, the TiO_2 catalyst can transform organic pollutants into biodegradable compounds of low molecular weight (Rajesh *et al*., 2007).

The hydroxyapatite-titanium dioxide composites were prepared by homogeneous mixing of the hydroxyapatite and titanium dioxide powders using a ball mill, followed by green compaction and then pressure-less sintering at a relatively higher temperature and soaking time 1 h (Basu and Ghosh, 2017). Hydroxyapatite-titanium dioxide composite has chemical stability of and very high activity for degradation such as dye, pesticides and fertilizer residues. Moreover, this composite may play an important role in controlling environmental pollution (Shidong *et al*., 2009).

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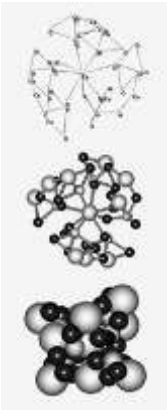


Figure 1. Structure of hydroxyapatite (HA)

The term "Langmuir–Hinshelwood mechanism" has often been used to describe the mechanism of photocatalytic reaction in suspension systems. In the field of catalysis, the reaction of two kinds of molecules proceeds on a surface on which both molecules are adsorbed at the same surface adsorption sites, with the surface reaction being the rate-determining step. The general rate equation for the L–H mechanism includes two sets of parameters for two kinds of molecules, and when one set of parameters is neglected, the equation is for a monomolecular reaction, similar to the photocatalytic reaction of a substrate adsorbed in Langmuirian fashion (Ohtani, 2011).

In this study, the hydroxyapatites were prepared from waste crab shell by using a wet precipitation technique. The prepared hydroxyapatite and titanium dioxide with cement have been fabricated by blending to form a HA-cemented TiO_2 composite. The different ratios of TiO_2 have been chosen to improve the mechanical strength and compatibility of the developed composite. The aim of the research work is to prepare the HA-cemented TiO_2 composite for the photodegradation of dye solutions and to study the photocatalytic degradation kinetics data that are fitted to the Langmuir-Hinshelwood model.

Materials and Methods

Preparation of HA-Cemented TiO_2 Composite

In the processing of composites, hydroxyapatite is prepared by reacting calcium precursor with phosphate at a Ca/P molar ratio of 1.67. Calcium oxide (CaO) was obtained as a result of calcinating crab shell powder at 900 °C and then made into a suspension in 100 mL of distilled water with a 0.3 M calcium concentration. The suspensions reacted dropwise with a 0.2 M solution of $(NH_4)_2HPO_4$. Afterward, the autoclave was quenched down through the wet precipitation method. And then trap closed chemical glass using aluminum foil to produce a suspension until pH10. The solution was then stirred for 5 h at 90 °C with a magnetic stirrer. The precipitate was filtered through filter paper and dried at 110 °C for 15 h. The pure hydroxyapatite was obtained by sintering the dried precipitate at 900 °C for 2 h. The hydroxyapatite-cemented titanium dioxide composite was performed at room temperature as follows: The fixed amount of hydroxyapatite and titanium dioxide was mixed with a glass rod for 5 min. And then cement weighing 3 g was dissolved in nearly 5 mL of distilled water by stirring with a glass rod for 5 min.

Preparation of Stock Solution of Methylene Blue

A stock solution of 100 mg L^{-1} of methylene blue (MB) solution was prepared by dissolving 0.1 g of dye in 1 L of distilled water. By serial dilution, the dye solutions of methylene blue within the concentration range of 20 to 100 mg L^{-1} were prepared. Analyses were carried out by the

colorimetric method using a UV-visible spectrophotometer and a calibration curve of methylene blue solution was plotted.

Photodegradation of Methylene Blue by Prepared HA-Cemented TiO_2 Composite

Filtration experiments were conducted to study the effect of important parameters like initial dye concentration and contact time of the composite on the photodegradation of methylene blue (MB). For each experimental run, 50 mL of different concentrations of the dye solution (20 mg L^{-1} to 100 mg L^{-1}) were contacted with the prepared HA-cemented titanium dioxide composite in the filtration unit [Figure 2 (a), (b) and (c)] and exposed to the solar light for 1 h. After 1 h, the dye solutions were taken out and their absorbance was recorded using a spectrophotometer. Similar procedures were carried out in the dark. In the contact time experiment**,** dye solution (100 mg L^{-1}) was filtrated at different time intervals (10, 20, 30, 40, 50 and 60 min) and the remaining dye concentrations were determined. The same procedures were carried out in the dark.

(a) **(b)** **(c)**

Figure 2. Photographs of (a) experimental filtration unit for the degradation of the methylene blue (b) methylene blue before and (c) after sorbed on HA-cemented TiO_2 composite

Effect of Initial Concentration on the Degradation Rate of Methylene Blue Solution by HA-Cemented TiO_2 Composite (Solar Light and Dark)

Different initial concentrations of methylene blue solution were prepared ranging from 20 to 40 mg L^{-1}. HA-cemented titanium dioxide composite was brought into contact with a fixed volume of each methylene blue solution at 50 mL prefixed for 1 h in the sunlight. After 1 h, the residual methylene blue solutions were determined by a spectrophotometer. The degradation rate of methylene blue by HA-cemented titanium dioxide composite in the dark was also determined by the above procedure. The experimental results seem to be consistent with the following equation:

$$R = -\frac{dc}{dt} = \frac{k_r K_a C_0}{1 + K_a C_0}$$

where r, k_r, K_a and C_0 are the rate of the reaction, the rate constant of the reaction of the surface-adsorbed substrate with electron, the adsorption equilibrium constant, the limiting amount of surface adsorption, and the concentration of substrate in the bulk at equilibrium, respectively. The reciprocal of initial rate ($1/R_0$) disappearance against the reciprocal of the initial concentration ($1/C_0$) was plotted by using Langmuir-Hinshelwood model equation.

Examination of Surface Morphology by SEM Technique

A scanning electron microscope (SEM) uses a beam of focused electrons of relatively low energy as an electron probe, operating at an acceleration voltage of 10 kV in vacuum with a filament current of 50 mA. The SEM studies were performed on powder sample morphology and size. These properties were based on appearance.

Photocatalytic degradation of fish pond water

The water quality parameters of water samples from near Shwedagon Pagoda, such as pH, temperature, dissolved oxygen, chemical oxygen demand, biological oxygen demand, total alkalinity, total suspended solids, chloride, sulfate, nitrite nitrogen, and ammonia nitrogen, were examined at the water and soil examination laboratory, Freshwater Aquaculture Research, Aquaculture Division, Department of Fisheries. And then, in the filtration unit, 100 mL of fish pond water sample was filled, and a prepared HA-cemented titanium dioxide composite was introduced for 2 h in solar light. The water sample's qualities were determined after 2 h.

Results and Discussion

The calibration curve for methylene blue dye solution using a spectrophotometer is presented in Table 1 and Figure 3.

Table 1. Absorbance for Different Concentrations of Methylene Blue Solution

No.	Concentration (mg L^{-1})	Absorbance
1	20	0.11
2	40	0.24
3	60	0.35
4	80	0.43
5	100	0.59

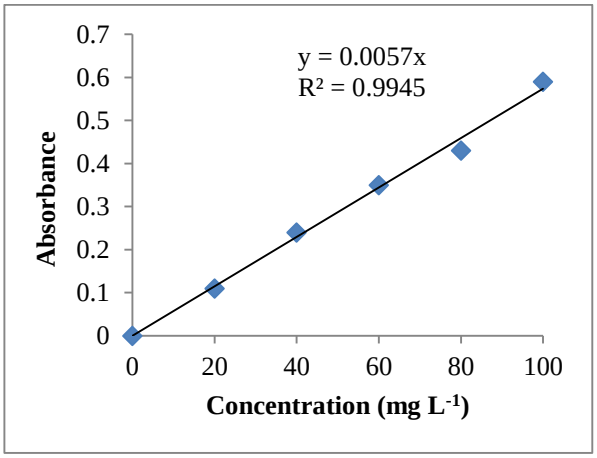


Figure 3. Calibration curve for methylene blue solution

The effect of the initial concentration of methylene blue dye on the photodegradation efficiency of the hydroxyapatite-cemented titanium dioxide composite was evaluated at different concentrations of 20, 40, 60, 80, and 100 mg L^{-1}. Table 2 and Figure 4 show that with the increase of the initial concentration from 20 mg L^{-1} to 100 mg L^{-1}, the percent degradation of dye was reduced from 91.50 % to 81.29 % in the solar light and from 82.99 % to 67.69 % in the dark. In the present study, with the decrease of the dye concentration in aqueous solution, the molecules of the dye have a better chance to react with the available active site on the composite, and as a result, the percent degradation is increased.

Table 2. The Percent Degradation of MB by HA-Cemented TiO_2 Composite at Different Initial Concentrations (Solar Light and Dark)

No.	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})		Percent degradation (%)	
		Solar light	Dark	Solar light	Dark
1	20	1.70	3.40	91.50	82.99
2	40	5.10	10.20	87.23	74.50
3	60	8.50	17.00	85.83	71.66
4	80	11.90	23.80	85.12	70.25
5	100	18.71	32.31	81.29	67.69

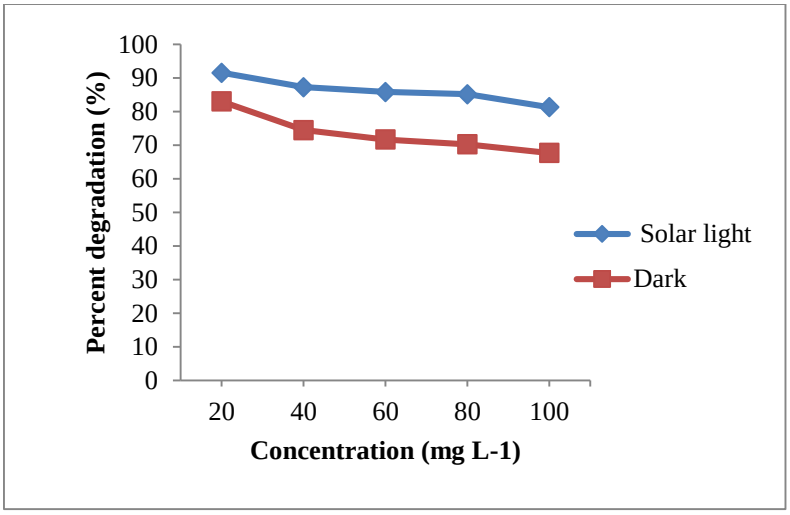


Figure 4. The percent degradation of MB by HA-cemented TiO_2 composite at different initial concentrations (solar light and dark)

From the results of Table 3, it was evident that the maximum adsorption occurred at 81.29 % in solar light and 67.69 % in the dark at 60 min. The degradation of methylene blue by HA-cemented TiO_2 composite was found to be rapid at the initial period of contact time and then slow with increasing contact time; the system reached equilibrium after 60 min. This was due to the availability of active sites that were occupied (Figure 5).

Table 3. The Percent Degradation of MB by HA-Cemented TiO_2 Composite at Different Contact Times (Solar Light and Dark)

No.	Contact time (min)	Final concentration (mg L^{-1})		Percent degradation (%)	
		Solar light	Dark	Solar light	Dark
1	10	47.62	54.42	52.38	45.58
2	20	39.11	49.32	60.89	50.68
3	30	32.31	42.52	67.69	57.48
4	40	27.21	39.11	72.79	60.89
5	50	22.11	35.71	77.89	64.29
6	60	18.71	32.31	81.29	67.69

Initial concentration = 100 mg L^{-1}

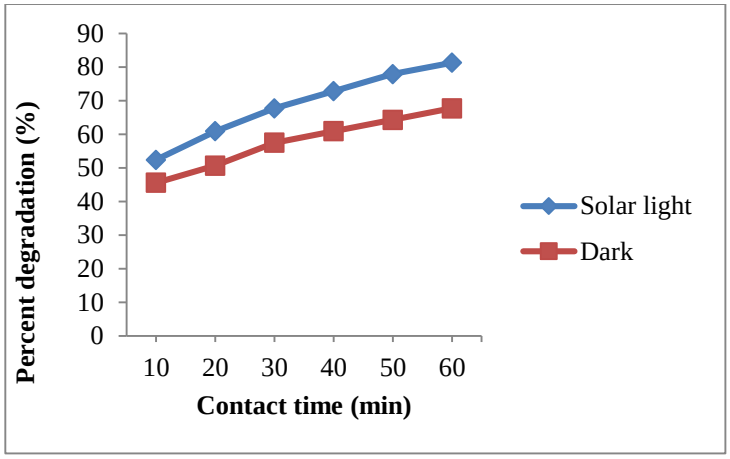


Figure 5. The percent degradation of MB in solar light and dark by HA-cemented TiO_2 composite at different contact times

Kinetic Study on Photodegradation of Methylene Blue Solution by HA-Cemented TiO_2 Composite with Langmuir-Hinshelwood Model

The kinetic study on the photodegradation of methylene blue solution by hydroxyapatite-cemented TiO_2 composite in solar light and dark was performed, and the results were fitted into the simple Langmuir-Hinshelwood mechanism. The reaction of two types of molecules on a surface in which both molecules are adsorbed at the same surface adsorption sites, with the rate-determining step being the surface reaction. Two parameters are calculated from the linear plot. One is the limiting rate of the reaction at the infinite concentration that gives maximum adsorption, that is k_r and the other is the adsorption equilibrium constant, K_a. The former parameter is a product of the rate constant and adsorption capacity of a photocatalyst, and this may be a photocatalytic activity. From this equation and plot, the value of k_r was obtained from the intercept, and then K_a was evaluated from the slope. The value of k_r in solar light was 4.885 mg L^{-1} min^{-1} and in the dark was 2.241 mg L^{-1} min^{-1}, respectively. The adsorption constant K_a for solar light was 0.0038 L mg^{-1} and 0.0070 L mg^{-1} in dark. The results are shown in Tables 4, and 5, and Figure 6.

Table 4. Effect of Initial Concentration on the Degradation Rate of MB solution by HA-Cemented TiO_2 Composite (Solar Light)

No.	C_0 (mg L^{-1})	C_t (mg L^{-1})	R_0 (mg L^{-1} min^{-1})	$1/R_0$ (mg^{-1} L min)	$1/C_0$ (mg^{-1} L)
1	20	1.4	0.310	3.225	0.050
2	25	1.9	0.385	2.631	0.040
3	30	2.64	0.465	2.193	0.033
4	35	3.38	0.527	1.897	0.028
5	40	5.08	0.582	1.718	0.025

Table 5. Effect of Initial Concentration on the Degradation Rate of MB solution by HA-Cemented TiO_2 Composite (Dark)

No.	C_0 (mg L^{-1})	C_t (mg L^{-1})	R_0 (mg L^{-1} min^{-1})	$1/R_0$ (mg^{-1} L min)	$1/C_0$ (mg^{-1} L)
1	20	3.40	0.227	3.610	0.050
2	25	4.662	0..339	2.949	0.040
3	30	6.9	0.385	2.597	0.033
4	35	7.728	0.454	2.202	0.028
5	40	10.20	2.021	2.012	0.025

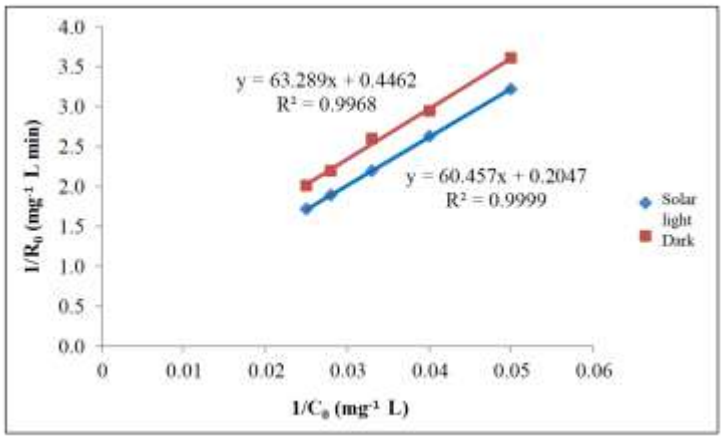


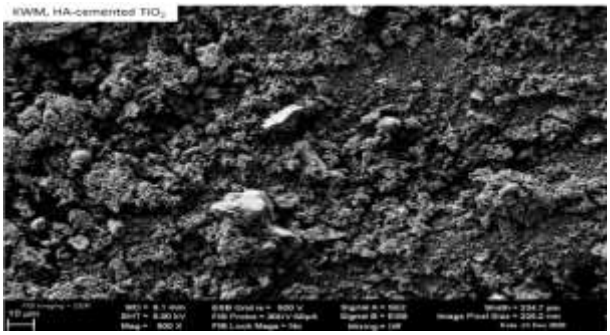
Figure 6. Plot of the reciprocal of the initial rate of MB disappearance against the reciprocal of initial concentration relevant to Langmuir-Hinshelwood model equation

Characterization of HA-Cemented TiO_2 Composite

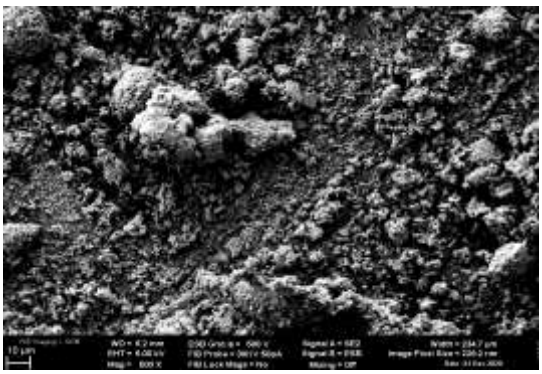
SEM analysis

The surface morphology of the HA-cemented TiO_2 composite was examined by SEM. Figure 7 (a) shows that cement, which was used as a small granule binding source, and TiO_2, identified as anatase crystals, were deposited on HA-like crystals.

From the SEM micrographs of methylene blue-sorbed HA-cemented TiO_2 composite in solar light and dark, it can be seen that the surface of the composite is densely covered with numerous dye molecules in Figure 7 (b). Figure 7 (c) clearly shows that the dye molecules are deposited on the surface of the composite.



(a)



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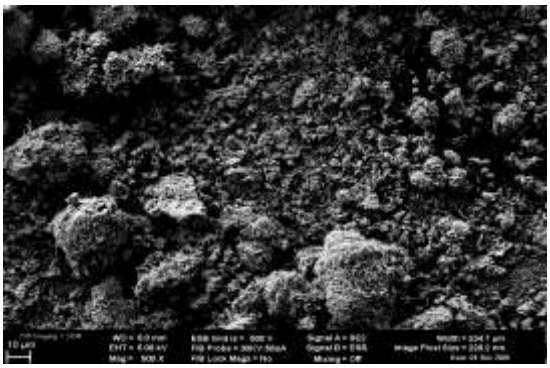

(c)

Figure 7. SEM micrographs of (a) HA-cemented TiO_2 composite (b) after MB sorbed HA-cemented TiO_2 composite (solar light) and (c) after MB sorbed HA-cemented TiO_2 composite (dark)

Treatment of Fishpond Water by HA-Cemented TiO_2 Composite

Suspended solids lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged into the aquatic environment. Nutrients (P, N and C) can lead to the growth of undesirable aquatic life. The water sample was collected from a fishpond near Shwedagon Pagoda and the collected water sample was treated with HA-cemented titanium dioxide composite under solar light. The quality of the collected water sample was determined before and after treatment for 2 h. Among the parameters of the water sample, before the treatment with HA-cemented titanium dioxide composite, the total suspended solid (TSS) value was 10 mg L^{-1}, and then, after treatment for 2 h, the value of TSS was reduced to 2.5 mg L^{-1}. This could be because suspended solids in the water sample were adsorbed onto the composite's surface. Therefore, the contaminants contained in water samples can be reduced by the HA-cemented titanium dioxide composite after treatment for 2 h.

Table 6. Results on Treatment of Fishpond Water by HA-Cemented TiO_2 Composite

Parameter	Unit	Before HA-cemented TiO_2	After HA-cemented TiO_2	Maximum EPA guideline*
pH	-	6.8	7.3	6.5 to 9.5
Temperature	°C	30	30	25 to 32
Dissolved oxygen	mg L^{-1}	2.75	3.25	>5
Total alkalinity	mg L^{-1}	94	92	50 to 150
Total suspended solid	mg L^{-1}	10	2.5	<25
Chemical oxygen demand	mg L^{-1}	3.31	2.21	<50
Biochemical oxygen demand	mg L^{-1}	0.50	0.50	150
Chloride	mg L^{-1}	39.99	24.99	31-50
Sulphate	mg L^{-1}	1.90	1.00	250
Nitrite nitrogen	mg L^{-1}	0.04	0.03	0 to 1
Ammonia nitrogen	mg L^{-1}	0.09	0.09	0 to 2

*USEPA, 2019

Conclusion

This study is primarily concerned with the development of an efficient photocatalyst, a hydroxyapatite-cemented titanium dioxide composite for the photodegradation of kinetic data that are fitted to the Langmuir-Hinshelwood model equation. The blending method was used to create a hydroxyapatite-cemented titanium dioxide composite with weight ratios of (40 %) titanium dioxide and hydroxyapatite and (20 %) of cement. The photodegradation of methylene blue by a prepared HA-cemented titanium dioxide composite was determined according to the parameters; initial concentration and contact time test. The effect of initial concentration on photodegradation was investigated. The maximum percent degradation of methylene blue was 81.29 % in solar light and 67.69 % in the dark for 1 h. The effect of contact time on the degradation of methylene blue solution revealed that the degradation was completed within 1 h. From this study, it is clearly seen that the percent degradation increases with increasing contact time. The kinetic study on the photodegradation of methylene blue was performed at optimum conditions. The photodegradation was found to follow the Langmuir-Hinshelwood model equation. By using this model equation, Langmuir-Hinshelwood parameters such as k_r and K_a were evaluated. The value of k_r in solar light was 4.885 mg L^{-1} min^{-1} and 2.241 mg L^{-1} min^{-1} in the dark, respectively. The contaminated water sample was collected from a fish pond near Shwedagon Pagoda. The qualities of the collected water sample parameters (pH, temperature, total alkalinity, TSS, DO, BOD, COD, chloride, sulphate, nitrite nitrogen and ammonia nitrogen) were determined before and after water treatment by using an HA-cemented titanium dioxide composite. According to the results, HA-cemented titanium dioxide composite can be effectively used for the treatment of wastewater samples.

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