Photodegradation of Methylene Blue Dye by Using Hydroxyapatite-Cemented Titanium Dioxide Composite

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Abstract

The present research work was focused on the preparation, characterization and application of a hydroxyapatite-cemented titanium dioxide composite. Photodegradation of methylene blue dye solution by prepared composites in solar light and in the dark was conducted. The photodegradation capacities of composites were studied for the degradation of methylene blue from aqueous solutions with various parameters such as initial concentration of dye solution, contact time and reusability of the composite. The methylene blue dye sorbed composite was characterized by SEM-EDX techniques. As a result, a prepared hydroxyapatite-cemented titanium dioxide composite was applied to reduce textile effluent.

Keywords: Hydroxyapatite, photodegradation, textile effluent

Introduction

Hydroxyapatite (HA) is one of the inorganic materials and most methods to synthesize HA are based on the wet precipitation method of natural sources like sea shells, egg shells, fish bone and crab shells, etc. These natural resources are relatively abundant, cheap and easily available. 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 as reported by Rajesh *et al.*, 2007. The hydroxyapatite titanium dioxide composites were prepared by the homogeneous mixing of the hydroxyapatite and titanium dioxide powders using a ball-mill, followed by green compaction and then dried at the temperature studied by Basu and Ghosh, 2017. Hydroxyapatite-titanium dioxide composite has chemical stability and very high activity for photodegradation of organic compounds such as dyes, pesticides and fertilizer residues. Moreover, this composite may play an important role in controlling environmental pollution. It was done by Shidang *et al.*, 2009.

In the present study, crab shells were used as raw materials for the synthesis of hydroxyapatite and then the prepared hydroxyapatite was blended with titanium dioxide as a reinforcing phase and cement as a binder to form a hydroxyapatite-cemented titanium dioxide composite without sintering. The main aim of this research work is to study the hydroxyapatite-cemented titanium dioxide (HA-cemented TiO_2) composite for the photodegradation of dye solutions and textile effluent.

Materials and Methods

Materials

In this research work, waste crab shells were collected from the seafood industry in the Yangon Region, Myanmar. The commercial grade of diammonium hydrogen phosphate was purchased from Shwe Ma Chemical Store in Yangon. Cement was purchased from a local market.

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Method of Preparation of Hydroxyapatite-cemented Titanium Dioxide 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 for suspension in 100 mL of distilled water with a calcium concentration of 0.3 M. 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 a glass rod stirring for 5 min.

Photodegradation of Methylene Blue by Prepared Hydroxyapatite-cemented Titanium Dioxide Composite

To study the effects of important parameters like initial dye concentration, contact time and reusability of the composite on the photodegradation of methylene blue (MB), filtration experiments were conducted. 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 1 (a) and (b)] and exposed to the solar light for 1 h. After 1 h, the dye solutions were taken out and their absorbance was recorded at λ_{max} 450 nm 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 reusability of the composite was also conducted under solar light and dark. Firstly, the dye concentration (100 mgL^{-1}) was contacted with the composite for 1 h and then the remaining dye concentration was determined. Secondly, the used composite was cleaned and it was used for filtration again. Thirdly, a similar filtration procedure was carried out. The same procedures were carried out in the dark.

(a)

(b)

Figure 1 (a) Photograph of experimental filtration unit for the degradation of the methylene blue

Figure 1 (b) Photograph of prepared HA-cemented TiO_2 composite

Characterization of Hydroxyapatite-Cemented Titanium Dioxide Composite

SEM-EDX analysis

The Scanning Electron Microscope (Carl Zeiss SMT Co. Ltd, Germany) is a method and procedure designed for directly studying the surfaces of solid objects that uses a beam of focused electrons of relatively low energy as an electron probe that is scanned in a regular manner over the specimen, 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.

Results and Discussion

The calibration curve for methylene blue dye solution at λ_{max} 450 nm using spectrophotometer is presented in Table 1 and Figure 2.

Table 1 Absorbance for Different Concentration of Methylene Blue Solution at λ_{max} 450 nm

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

λ_{max} = 450 nm

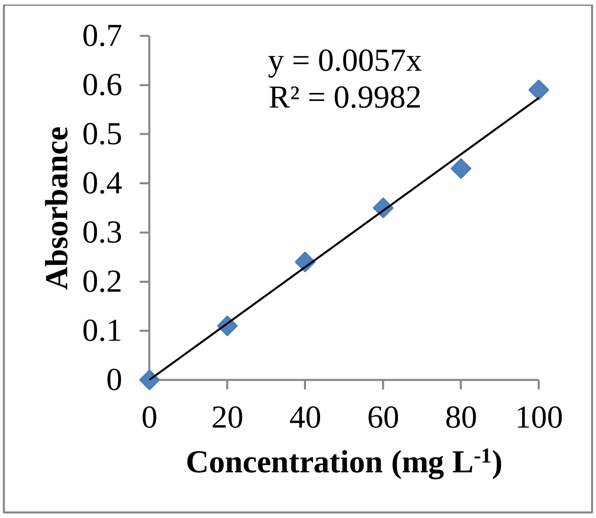

Figure 2 Calibration curve for methylene blue solution

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 3 showed 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, dye concentration in aqueous solution decreased, so the molecules of the dye had more chance to react with the available active site on the composite.

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 (%)	
		Light	Dark	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

Initial concentration = 100 mg L^{-1}, contact time = 1 h

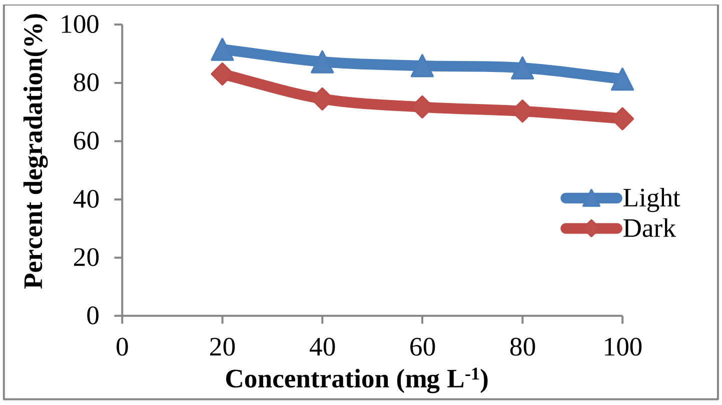

Figure 3 The percent degradation of MB by HA-cemented TiO_2 composite at different initial concentrations (Solar Light and Dark)

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 to become slow with the increase of contact time equilibrium, which corresponds to Figure 4.

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 (%)	
		Light	Dark	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 $mg\ L^{-1}$, contact time = 1 h

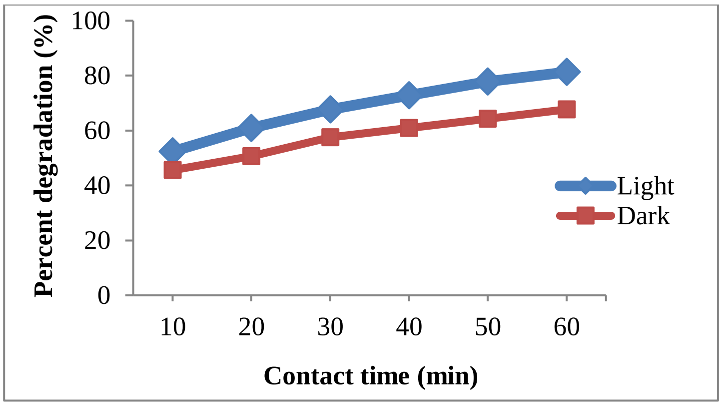

Figure 4 The percent degradation of MB by HA-cemented TiO_2 composite at different contact times (Solar Light and Dark)

The results are shown in Table 4 and Figure 5. It can be seen that the HA-cemented TiO_2 composite still maintained relatively preferable photodegradation after three cycles. Under solar light, the methylene blue solution degraded by 81.29 % in 60 min. Therefore, the HA-cemented TiO_2 composite exhibited good integrated photodegradation performance toward MB. However, the equilibrium degradation capacity in the dark was somewhat weakened. The degradation capacity of the third cycle was somewhat decreased by about 11.79 % relative to the first cycle. This was presumably attributed to the possibility that it was hard for the simulated solar light to irradiate adsorbed methylene blue deep inside the HA-cemented TiO_2 composite to initiate their photodegradation.

Table 4 Effect of Reusability of Composite on the Degradation Percent of MB (Solar Light and Dark)

Reuse	Final concentration (mg L^{-1})		Percent degradation (%)	
	Light	Dark	Light	Dark
First	18.71	32.31	81.29	67.69
Second	25.31	35.81	74.69	64.19
Third	30.50	38.01	69.50	61.99

Initial concentration = 100 mg L^{-1}, contact time = 1 h

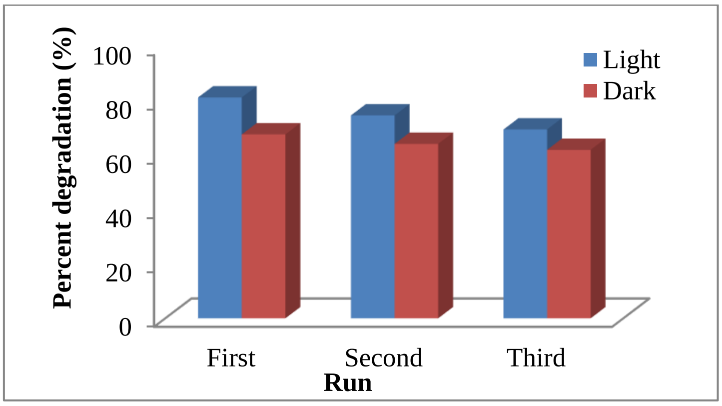

Figure 5 Applied reusability on composite as a function of percent degradation of methylene blue (Solar Light and Dark)

Characterization of Methylene Blue Sorbed on Hydroxyapatite-Cemented Titanium Dioxide Composite

SEM-EDX analysis

From the SEM micrographs of the 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 and clearly shows that the layer of dye is deposited on the surface of the composite.

From EDX analysis, the photochemical oxidation process, calcium and oxygen in the composite in solar light were slightly higher than in darkness. The composite surface was uniform, which indicates that TiO_2 was uniformly dispersed in the mixture. The four elements are observed for the HA-cemented TiO_2 composite, which corresponds to Ti, Ca, Si and O as shown in Figures 6, 7 and Table 5.

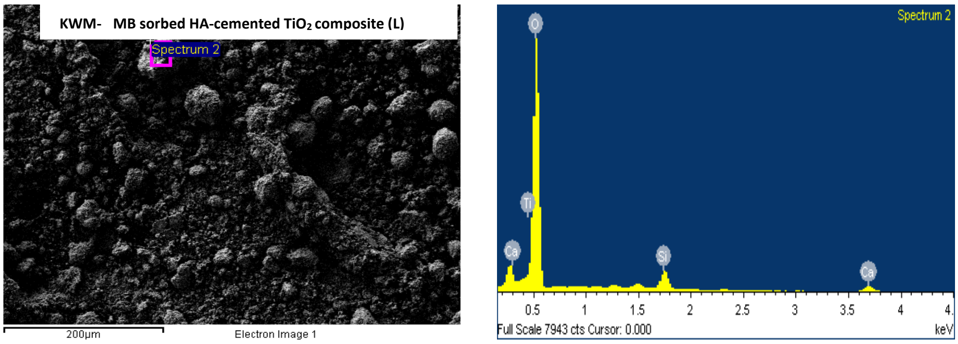

Figure 6 SEM-EDX analysis of MB sorbed HA-cemented TiO_2 composite (Solar Light)

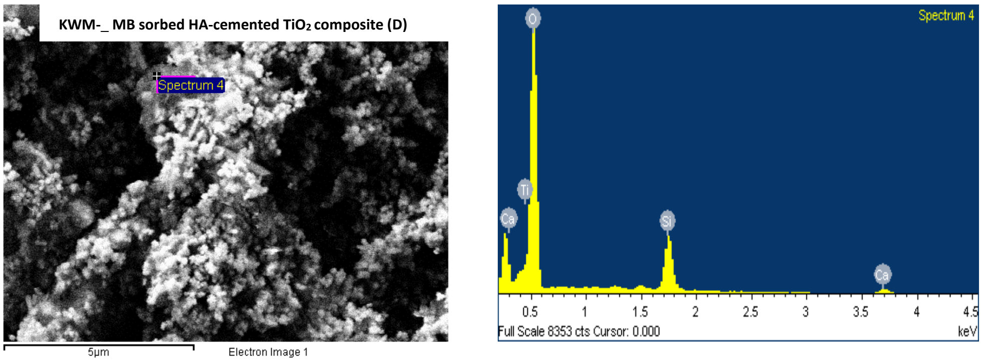

Figure 7 SEM-EDX analysis of MB sorbed HA-cemented TiO_2 composite H (Dark)

Table 5 SEM-EDX Analysis of MB Sorbed HA-Cemented TiO_2 Composite (Solar Light and Dark)

Element	Weight (%)	
	Light	Dark
O	37.30	31.34
Si	3.31	7.15
Ca	22.77	12.28
Ti	36.62	49.23
Total	100.00	100.00

Color degradation of textile dyeing wastewater samples by HA cemented TiO_2 composite

The residual dyes from different sources (e.g., textile industries, paper and leather industries) are considered a wide variety of organic pollutants introduced into the natural water resources. Photodegradation of HA-cemented TiO_2 composite was used for the degradation of textile wastewater samples collected from a textile printing site in South Okkalapa Township. Degradation of textile wastewater was carried out by HA-cemented TiO_2 composite in a filtration unit under optimum conditions. Table 6 illustrates the residual color of wastewater samples in terms of spectrophotometer. The dye concentrations and absorbance in wastewater textile effluent was measured using a spectrophotometer at λ_{max} of 540 nm. Moreover, the percent degradation of textile effluent was 91.38 % in the solar light and 81.03 % in the dark. From these results, almost all the color of the wastewater samples was depleted after treatment for 2 h. In the degradation of dye wastewater samples, it was observed that the percent degradation of textile wastewater was markedly reduced by the HA-cemented TiO_2 composite in the solar light.

Table 6 Color Degradation of Textile Dyeing Wastewater Samples by HA-Cemented TiO_2 Composite

Color	Initial color (Absorbance)	Residual color (Absorbance)		Percent degradation (%)	
		Light	Dark	Light	Dark
Textile effluent	0.58	0.05	0.11	91.38	81.03

λ_{max} for textile effluent = 540 nm, contact time = 2 h, volume of solution = 100 mL

Conclusion

In the present investigation, the preparation of an effective photocatalyst, hydroxyapatite-cemented titanium dioxide composite for the photodegradation of model methylene blue solution. The photodegradation of methylene blue by a prepared HA-cemented titanium dioxide composite was determined according to the parameters; initial concentration, contact time and reusability test. The effect of initial concentration on photodegradation was investigated. The maximum percentage degradation of methylene blue was 81.29 % in the 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 percentage degradation increases with increasing contact time. The degradation efficiency of the prepared HA- cemented titanium dioxide composite in the recycling usage of water treatment was carried out with methylene blue solution. It is clearly observed that the prepared HA- cemented titanium dioxide composite can be used three times effectively because its degradation efficiency decreases significantly. The degradation efficiency of HA- cemented titanium dioxide composite was used for the degradation of textile dyeing wastewater samples collected from the textile printing site at South Okkalapa Township. The residual color in textile wastewater was measured by a UV-visible spectrophotometer. The percent degradation of textile wastewater was 91.38 % in the solar light and 81.03 % in the dark after 2 h of treatment.

Acknowledgement

We gratefully acknowledge the Director General, Dr. Daw Phyu Phyu Win, of the Department of Research and Innovation for allowing this research work and also for all the necessary research facilities provided. We would like to express our special thanks to our co-supervisor, Dr. Win Pa Pa for her kind guidance and supervision, valuable advice and constant encouragement throughout this research. We would like to thank Professor Dr. Ni Ni Than, Head of the Chemistry Department, Yangon University, for her encouragement and permission to conduct this research. We would like to extend special thanks to members of the Research Project Board of the University of Yangon for screening and reviewing this project work.

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