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Photodegradation of methylene blue dye using bentonite as a catalyst

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ABSTRACT

This study involves removal of methylene blue (MB) dye using the photodegradation process. Raw and activated bentonite has been considered as a photo-catalyst. Generally, complete removal of MB by bentonite alone or UV-radiation alone could not be achieved, as demonstrated in this study. However, MB could be successfully decolorized and degraded when using the UV and bentonite combination. Use of hydroxyl-Fe-pillared bentonite has been investigated and found to result in a complete phot-degradation of MB. The effects of different operating parameters on the MB degradation using this process have been investigated. These include initial MB concentration, bentonite concentration, pH of the slurry system, presence of electrolyte, addition of ferric sulphate and effect settling curve. Also, the rate degradation processes was investigated at these different conditions and parameters; and to certain extent were reasonably fitted to a pseudo-first-order kinetic model. Increasing initial concentration of MB, at a constant concentration of bentonite or hydroxyl-Fe-pillared bentonite (H-Fe-P-B), increases the time of degradation. The time for decolorization MB when using UV-hydroxyl-Fe-pillared bentonite slurry system is lower than that when using the UV-bentonite slurry system. The optimum pH for the removal of MB using UV-bentonite slurry process is 4.0. The presence of ferric sulphate salt reduces the photodegradation of MB.

Keywords: Methylene blue; Bentonite; Photodegradation; Pillaring

1. Introduction

Effluents from the textile dyeing and finishing industries contain high levels of environmental contaminants, strong color, suspended solid, surfactants, some heavy metals and have unstable pH, temperature and COD [1]. These effluents should be treated before disposal as they face hard governmental and standard regulations. Although not strongly hazardous, methylene blue (MB), one of the well-known dye materials, can have various harmful effects. Precipitation, adsorption and biological treatment are among the methods used for treating textile and dying effluents. [2]. The disadvantage of precipitation methods is the sludge formation. The disadvantage of adsorption is that the adsorbent needs to be regularly regenerated. This is associated with additional costs and some times time-consuming procedures. Biological treatment is ineffective in cases where complicated aromatic compounds are present.

Ultraviolet and Fenton reaction began to be used at the end of 1970s for the treatment of non-biodegradable organic compounds, such as herbicides [3]. Advanced UV oxidation processes have also been implemented, which include use of oxidizing agent, such as H_2O_2, to generate powerful hydroxyl radicals (OH*) that non-selectively attack organic compounds. The advantage of H_2O_2/UV processes is that they prevent any possible sludge

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formation during the treatment process [4,5]. Extensive studies are available in literature on the use of several oxidizing agents when using UV in degradation of dye compounds. For example, Kang et al. [6] evaluated the treatment of textile effluents by UV/ H_2O_2 oxidation combined with osmosis (RO) membrane separation for water reuse in textile dyeing processes. The results of Pake and Chang [7] showed that the photo-catalytic oxidation rate, in the presence of Fe/MgO as a catalyst, increased with increasing hydrogen peroxide and catalyst dosage. Perkowski and Ledakwicz [8] studied the decomposition of anthraquinone dye (polan blue E2R) in an aqueous solution in the presence of ozone, hydrogen peroxide or UV radiation with the aim to investigate the effect of ozone dose and concentration, as well as temperature on decolorization of different initial dye concentrations. Meric et al. [9] investigated the removal of reactive black 5 (RB5) from wastewater using the Fenton oxidation process (FOP). This study was performed in a systematic approach searching optimum values of $FeSO_4$ and H_2O_2 concentrations, pH, and temperature. Daneshvar et al. [10] studied the critical effect of hydrogen peroxide concentration on the photochemical oxidative degradation of C.I. Acid Red 27 (AR27). Meric et al. [9] designed experiments to decolorize and to reduce chemical oxygen demand (COD) using Fenton oxidation process in a mixture of four reactive dyes, namely Remozal Brilliant Blue (RB), Remozal Yellow 84 (RY), Remozal Black 5 (RB5), and Remozal Red RB (RR). The authors found that higher concentrations of dyes require greater proportions of $FeSO_4$ and H_2O_2. Banat et al. [11] studied photodegradation of MB dye by the UV/H_2O_2 and UV/acetone oxidation processes.

The use of clay as an oxidizing agent in UV process has also been considered by Sun et al. [12]. Those authors studied the photocatalytic degradation of cationic azo dye by TiO_2/bentonite nanocomposite. The effect of the addition of H_2O_2 was also discussed for enhancement of azo dyes. According to the authors results, TiO_2 could be intercalated into the inter layer of bentonite clay by the method of acid-catalyzed sol-gel process. In this case, the photodegradation of azo dyes using TiO_2/bentonite nanocomposite as a catalyst can be considered as a promising alternative to wastewater purification. Also Chen and Zhu [13] studied the catalytic degradation of orange II by UV-Fenton with hydroxyl-Fe-pillared bentonite in water. The focus was on the UV-Fenton process for degradation of azo-dye with hydroxyl-Fe-pillared bentonite as a catalyst. The effect of initial pH on UV-Fenton process as well as the stability of catalyst was studied in detail. The catalytic activity of raw bentonite was also detected in order to explore the catalytic stability of different iron configurations in hydroxyl-Fe-pillared bentonite.

In this work, bentonite as a catalyst was considered for the photo-treatment of MB colored solutions. MB photodegradation using raw bentonite or Fe-pillared bentonite as catalyst and effect of different operating parameters on this process has not been investigated before. It is the objective of this work to study the effects of doses of raw bentonite and doses of activated bentonite, oxidation time, pH, addition of salts, and ferric sulphate.

2. Experimental

2.1. Materials

Methylene blue (MB) was used as a model compound of dying materials. MB, $C_{16}H_{18}ClN_3SCl$, is a synthetic organic dye; it can be classified with regard to its chemical structure in the group of azindyes. The maximum wavelength (λ_{max}) of light that can be absorbed by MB is 662 nm; its molar adsorption coefficient, which appears in Beers-Lambert law (ϵ), is about 19 M^{-1} cm^{-1} at 254 nm [5]. The MB used in this work is of analytical grade (Net Tech, UK).

Bentonite was purchased from Fischer Scientific Chemicals (USA). It is primarily Ca^{+2}–montomorillonite with the chemical formula $Ca_{0.39}Na_{0.02}K_{0.02}$ $(Si_{7.91}Al_{0.09})$ $(Al_{2.51}Fe_{0.45}Mg_{1.10})$ O_{20} $(OH)_4$ nH_2O. The cation exchange capacity of bentonite used in this work is 108.4 mM 100 g^{-1} [14]. It was mechanically ground with a mortar and pestle to less than 200-mesh (0.074 mm).

2.2. Apparatus

The apparatus consists of a 2-L vessel which is connected by a pipe to a centrifugal pump. At the beginning, the vessel contains the MB solution at a given concentration. The pump fed the solution to a low-pressure mercury UV lamp with a 10 W output. The effluent from the UV cell was returned back to the feed vessel. Samples were continuously collected from the tank at different periods of time for the purpose of MB measurements.

2.3. Procedure

A stock solution of MB dye was prepared. The pH of the solution was adjusted using HCl or NaOH. A certain amount of bentonite was added to the solution according to the dose required. The flow rate was adjusted at 50 ml/s for all experimental runs.

Raw bentonite was treated to produce hydroxyl Fe-pillared bentonite. The procedure given by Feng et al. [5] has been followed. This was done as follows: (a) preparing an aqueous bentonite suspension; (b) preparing Fe^{3+} pillaring solution by adding $NaCO_3$ to $Fe(NO_3)_3$ aqueous solution; (c) adding the Fe^{3+} pillaring solution obtained in step (b) to the aqueous bentonite suspension obtained in step (a) with stirring to form bentonite Fe^{3+} pillaring solution mixture; (d) agitating the mixture at room temperature or at 100 °C for 48 h; (e) centrifugation and washing the mixture to obtain a catalyst precursor precipitate; and (f) calcining the catalyst precursor to form intercalated bentonite iron oxide catalyst nanoparticles [15].

2.3.1. Analysis

In each experimental run, 10 samples of 10 ml each were collected at a pre-specified time intervals. The samples were centrifuged and the supernatants were taken for analysis. The concentration of MB was measured spectrophotometrically.

2.3.2. Bottle point test

The bottle point test was used to study the kinetics of MB sorption onto bentonite. Known weights of bentonite were transferred into dark glass bottles containing 30 ml of aqueous solutions of methylene blue dye at specified concentration, such that the adsorbent concentration was made as 1 g/l. The mixtures were agitated in a shaker and samples were taken at fixed time period in order to study the kinetics of the adsorption process onto bentonite. The solution was separated from the samples via centrifugation. The concentration of MB was determined using a Spectronic spectrophotometer. All measurements were done at the wavelength corresponding to the maximum absorbance at 662 nm using distilled water as a blank.

3. Results and discussion

3.1. Adsorption of methylene blue dyes on bentonite

The results for the kinetics of the MB uptake by bentonite using traditional bottle point tests are shown in Fig. 1 at different initial concentrations of MB, namely 8.0, 10.0 and 12 ppm. As of the traditional trend, MB uptake increases with the increase in the initial MB concentration. It can be observed that regardless of the initial concentrations, the sorption process terminates after the first 12 min, indicating equilibrium. According to these results, complete removal of MB by bentonite, at the indicated conditions, cannot be attained. For example, only 3.1% of MB can be removed when the initial concentration was 12 ppm.

3.2. Photocatalytic decomposition of MB

The decay of color, with respect to contact time, at different initial MB concentrations, namely 8, 10, 12 ppm, and different doses of bentonite, namely 0.0, 0.2, 0.5, 0.7, 1, 1.2 g/L, have been investigated and are shown in Fig. 2A–C. The results are presented as C/C_0 vs time, where C_0 refers to the initial MB concentration while C is the MB concentration at time t. Again, the results demonstrate that UV alone (i.e. at bentonite concentration of 0.0 g/L) is unable to decolorize MB completely. In a previous investigation, the authors also demonstrated that substantial decolorization of the dye can be reached only when using UV/H_2O_2, where neither UV nor H_2O_2 alone was appreciably able to decolorize any of the dyes [11]. Since there is certain contribution of MB removal when using bentonite alone and when using UV alone, it is expected that a combination of bentonite/UV would result in a better decoloration process. This is because of the increase in hydroxyl radical production, which would enhance the decoloration reaction of MB in the presence of bentonite. In other words, it is possible in this case to assume that bentonite acts as a catalyst for the production of free radicals. The decoloration at a given dose of bentonite and different initial MB concentrations can also be deduced from the results of Fig. 2; as the initial MB concentration increased, the time of decoloration is increased, e.g. at a bentonite dose of 0.7 g/l.

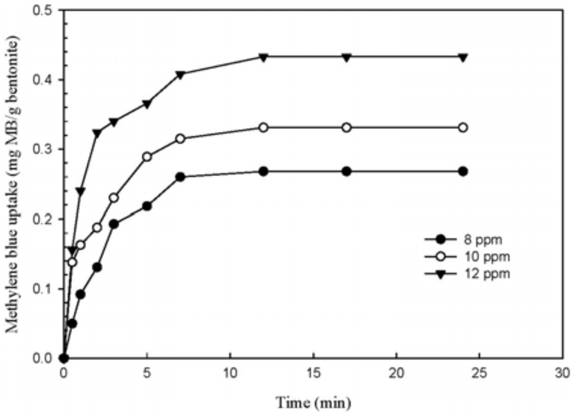

Fig. 1. Uptake of methylene blue (MB) by bentonite vs contact time at various MB concentrations. Bentonite concentration: 1 g/L.

It can be seen (Fig. 2) that as the dose of bentonite increases the time of decoloration becomes shorter and larger amounts of MB are removed. This could be explained in terms of the reaction of bentonite with UV to produce hydroxyl radicals (OH^-); hydroxyl radicals produced from the reaction are increased as the amount of bentonite increased. Since hydroxyl radicals are the dominant in the decoloration process, the time of the decoloration would be shorter. It is proposed that two types of oxidizing species are involved in the photocatalytic process: hydroxyl radicals, generated by oxidation of adsorbed water molecules, and positive holes [13]. The overall process can be illustrated by following sequence of reactions:

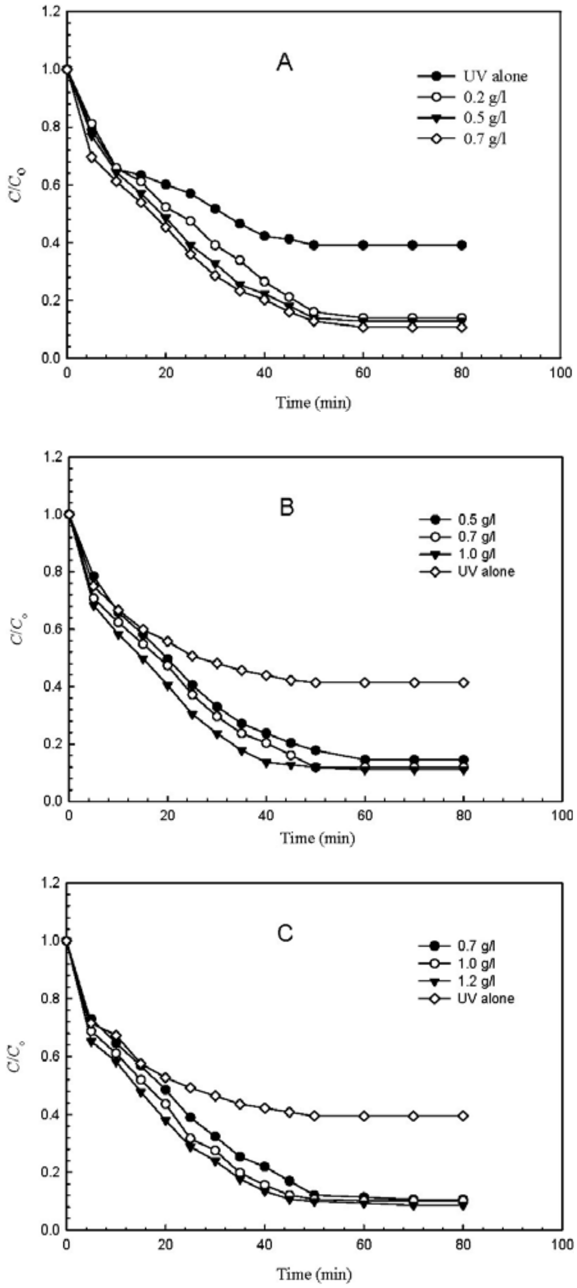

Fig. 2. Photodegradation of methylene blue using different concentrations of bentonite in a UV-slurry system. Initial MB concentrations: A 8 ppm; B 10 ppm; C 12 ppm.

bentonite + hv (UV) → bentonite-e^- + bentonite-h^+

bentonite-h^+ + H_2O → bentonite + H^+ + OH*

bentonite-h^+ + OH^- → bentonite + H_2O

O_2 + bentonite-e^- → bentonite + *O_2^-

OH* + dye → degradation of the dye

h^+ + dye → oxidation of the dye

During experimentation, it was observed that bubbles were released especially at the end of the experiments. These bubbles were expected due to be carbon dioxide, CO_2, produced from mineralization of MB. This can be demonstrated by the following stoichiometric oxidation reaction [14]:

$$C_{16}H_{18}ClN_3S^+ + (51/2)\,O_2 \rightarrow 16CO_2 + 3NO_3^- + SO_4^{-2} + 6H^+ + 6H_2O$$

The major kinetic pathway of MB photodegradation can be represented by the following well-know equation:

$$\frac{dC_{MB}}{dt} = -k_1 C_{MB} C_{OH^-} \tag{1}$$

where C_{MB} and C_{OH^-} are the dye and hydroxyl radical concentrations (mol/L), respectively. According to the pseudo-stationary hypothesis, the C_{OH^-} remains constant in the presence of excess bentonite; thus, the above-mentioned rate expression can be written as:

$$\frac{dC_{MB}}{dt} = -kC_{MB} \tag{2}$$

Accordingly, the parameter k can be obtained by linear plotting of the experimental values of $\ln C_{MB}$ vs time at given experimental conditions. Applying this to the data of Fig. 2, the k values were calculated at different bentonite and initial MB concentrations. These are shown in Table 1 with the corresponding value of R^2; all R^2 values in this table are higher than 0.97, indicating reasonably high correlation. At a fixed dose of bentonite, the reaction rate constant k (min^{-1}) decreases with the increase in MB dye concentration; while at a given MB concentration, it increases with the increase in bentonite doses (Table 1).

3.3. *Effect of initial pH*

Because of water dissociation equilibrium and the nature of surface charge of bentonite, pH plays a significant role in a UV-irradiated bentonite slurry system. The effect of pH on the degradation of MB using UV-bentonite slurry has been investigated using MB solutions of different initial pH values, namely 4.5, 7.0 and 9.0. The results (Fig. 3) show that MB was degraded most efficiently by UV-bentonite when using an MB solution with an initial pH value of 4.0. The pseudo-first-order kinetic rates obtained from the slopes, as obtained from the results of Fig. 3, are displayed in Table 2 at different pH values. It is seen that the value of k varies from 0.0713 min^{-1} to 0.0221 min^{-1} when the initial pH increased from 4 to 9.

Table 1
Pseudo-first-order rate constant at different initial concentration of MB photodegradation

Bentonite (g/l)	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
	8 ppm		10 ppm		12 ppm	
0.2	0.03267	0.9877				
0.5	0.03840	0.9921	0.03605	0.9886		
0.7	0.04766	0.9822	0.04398	0.9901	0.04205	0.9834
1			0.04913	0.9798	0.04725	0.9766
1.2					0.05353	0.9891

Table 2
Pseudo-first-order rate constant at different pH values. Initial MB concentration: 10 ppm; bentonite dose: 1.0 g/l

pH	k (min^{-1})	R^2	Color removal at 60 min (%)
4.0	0.0713	0.9865	92.3
7.5	0.0492	0.9840	88.7
9.0	0.0221	0.9723	86.4

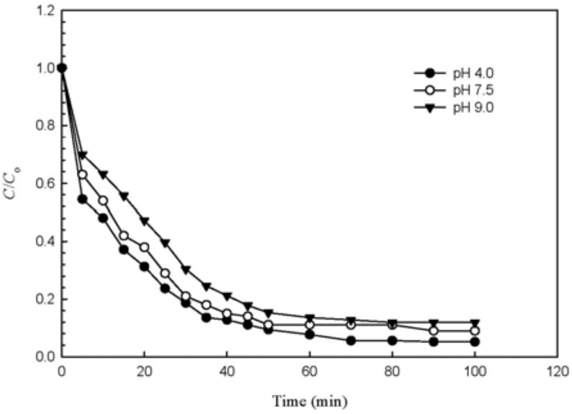

Fig. 3. Effect of initial pH on photodegradation of MB using bentonite-UV slurry system. Initial concentration of MB: 10 ppm; bentonite concentration: 1 g/l.

It was assumed that the surface hydroxyls of bentonite have acidic-basic properties [13]. The charge imbalance is offset by exchangeable cations (Ca^{+2}, K^+, Na^+) on the surface layer [13]. In the acidic aqueous solution, the exchange between cations (Ca^{+2}, K^+, Na^+) in the bentonite interlayer and the H^+ in the solution result in an increase in the pH value. However, in the alkaline aqueous solution, part of the base will be consumed by the surface hydroxyls of bentonite which leads to a decrease in the pH value.

3.4. Effect of electrolyte

The effect of electrolyte on the efficiency of MB removal has been investigated by the addition of NaCl salt at two concentration levels, namely 0.5 and 1.0 g/L. It was noticed (Fig. 4) that the presence of electrolyte in the UV-bentonite slurry reduces the efficiency of the oxidation treatment process. This trend can be explained by the fact that electrolytes decreases total absorbance, where absorbance indicates the quantity of the incoming radiation that is being absorbed by the molecules of the substance. These will lead to less generation of free radicals [16].

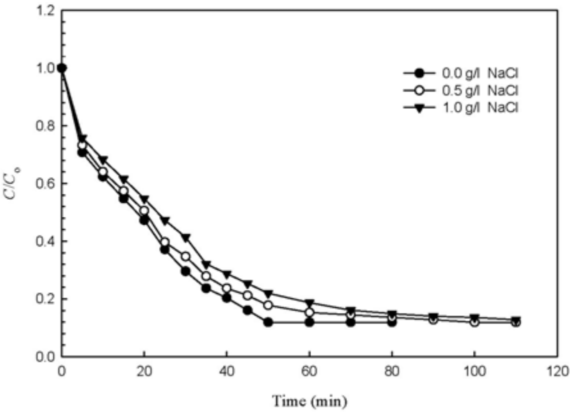

Fig. 4. Effect of electrolyte on photodegradation of MB using bentonite-UV slurry system. Initial concentration of MB: 10 ppm; bentonite concentration: 0.7 g/l.

3.5. Effect of ferric sulphate

The effect of ferric sulphate was studied using 0.7 g/L of bentonite, 10 ppm initial concentration of MB and different concentrations of ferric sulphate (0.5, 1.0 g/l). As shown in Fig. 5, MB removal decreases as the amount of ferric sulphate increases. This is because the sulfate ions can remain partially adsorbed at the surface of bentonite. The effect of temporal evolution of SO_4^{-2} ions as a result of complete oxidation of the MB dye, indicating that SO_4^{-2} ions are initial products, directly resulted from the initial attack on the sulfonyl group [14].

3.6. Photocatalytic decomposition of MB using hydroxyl-Fe-pillared bentonite

Hydroxyl-Fe-pillared bentonite, with different doses, namely 0.2, 0.5, 0.7, 1.0 and 1.2 g/L, have been tested via

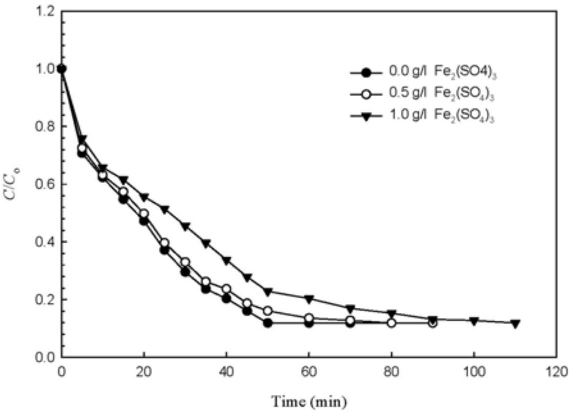

Fig. 5. Effect of ferric sulphate on photodegradation of MB using bentonite-UV slurry system. Initial concentration of MB: 10 ppm; bentonite concentration: 0.7 g/l.

this UV-slurry process for MB degradation. The results are shown in Fig. 6A, B, and C for initial MB concentrations 8, 10 and 12 ppm, respectively. The enhancement in the removal process of MB indicates that hydroxyl-Fe-pillared bentonite is a better catalyst than the raw bentonite. It is seen (Fig. 6) that as the hydroxyl-Fe-pillared bentonite dose increases, the decolouration time decreases and also the MB removal percentage increases. It is also seen that complete removal of MB using UV and this form of modified bentonite can be achieved. This indicates that the pillaring process has a beneficial effect on the characteristics of bentonite. The interlamellar distance (d_{001}) of hydroxyl-Fe-pillared bentonite (H-Fe-P-B) is 5.45 nm while for bentonite it is 1.52 nm [13]. The latter is the critical interlamellar distance of Ca^{+2}. This means that the microscopic area of bentonite increased remarkably after pillaring. Since the content of iron increased in bentonite after pillaring Fe-pillaring treatment for bentonite, it can be proposed that the iron ions intercalated the bentonite successfully.

3.7. *Effect on settling*

In order to demonstrate the contribution of bentonite toward this photodegradation process, settling tests were performed with bentonite-MB suspension samples without UV exposure and with bentonite-MB samples after being exposed to UV radiation. This was done using 10 ppm of MB solution and 1.0 g/L of bentonite. The samples were maintained in graduate cylinders and the level of clear suspension was recorded while bentonite settling takes place. The initial level of suspensions in all cylinders was maintained at 30 cm. The height which separate cloudy liquid from that of clear liquid was recorded as a function of time from the bottom of the cylinder. This is defined as the height of sludge-liquid interface, or H_c; thus the upper part would represent the clear water. The results at different periods of UV exposure are shown in Fig. 7.

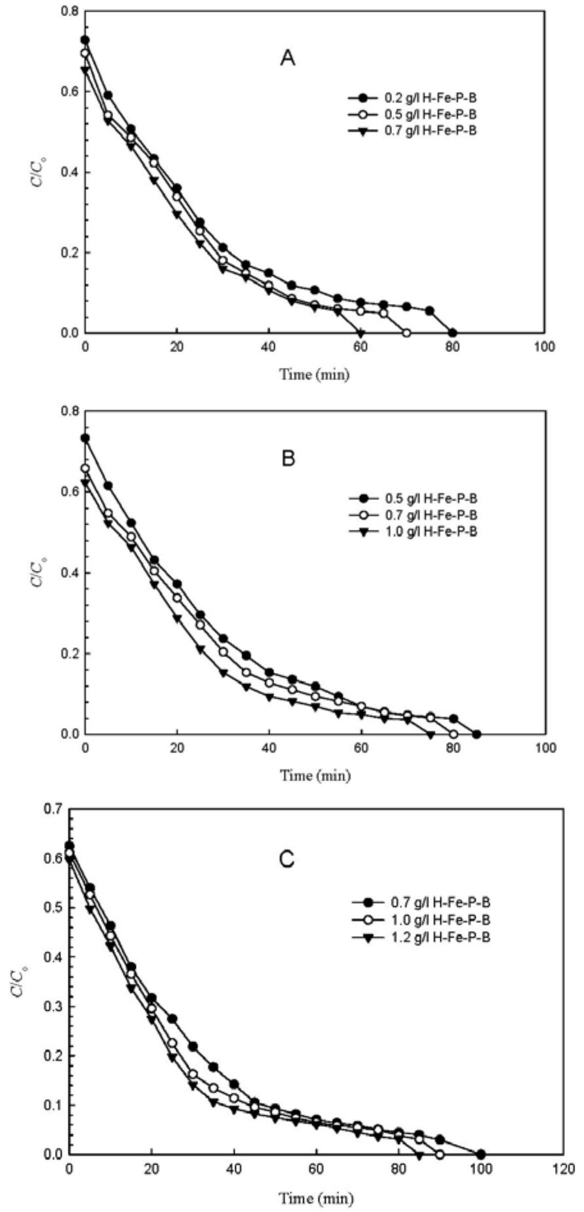

Fig. 6. Photodegradation of methylene blue using different concentrations of hydroxyle-Fe-pillared bentonite in a UV-slurry system. Initial MB concentrations: A, 8 ppm; B, 10 ppm; C, 12 ppm.

Without UV exposure, it is seen (Fig. 7) that almost the entire cylinder is cloudy over the period of the settling test; i.e. the height of the interface was 28.8 cm after 5 h settling period which left only 2.2 cm of clear water. However, the use of bentonite being exposed to UV radiation in the settling test improved the settling curve significantly, Fig. 7. The results also indicated that the prolong exposure to UV radiation resulted in a faster settling rate. For example, the height of the interface

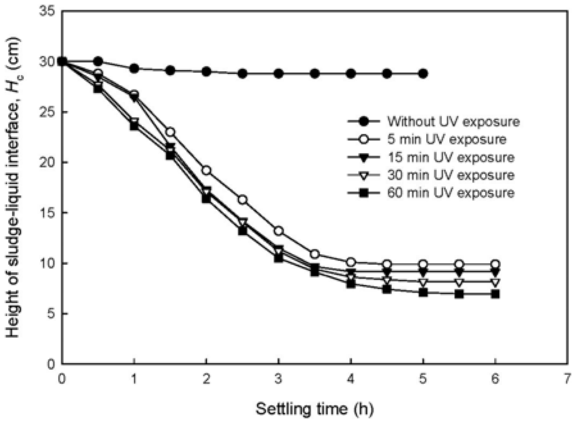

Fig. 7. Effect UV exposure on bentonite settling curve. MB concentration: 10 ppm; bentonite dose: 1 g/l.

decreased from 9.17 to 6.97 cm after 6 h settling when using bentonite exposed to 15 min and 60 min UV radiation, respectively; this would result in 20.87 and 22.03 cm of clear water layer. This could be due to accumulation of MB at the surface of bentonite which makes it heavier for settling specially at prolong time of UV exposure. These were surprising results and would indicate that bentonite can act as a very good catalyst in the photodegradation process of MB.

4. Conclusions

UV-radiation along with bentonite as a photocatalyst can be used for degradation of MB blue in a colorized medium. Use of hydroxyl-Fe-pillared bentonite (H-Fe-P-B) based photocatalyst at room temperature resulted in complete degradation of MB. Longer time is required for degradation of MB when increasing initial concentration of MB at a constant concentration of bentonite or hydroxyl-Fe-pillared bentonite (H-Fe-P-B). The time for decolorization MB when using UV-hydroxyl-Fe-pillared bentonite slurry system is lower than that when using UV-bentonite slurry system. The kinetics of MB degradation obeys a pseudo-first-order kinetic. Degradation time for MB was also influenced by the presence of electrolyte such as NaCl. The presence of ferric sulphate salt reduces the photodegradation of MB. The settling behavior of MB solution is significantly improved given that the bentonite-MB suspension is being pre-exposed to UV radiation. Since photocatalytic decomposition of MB by using hydroxyl-Fe-pillared bentonite is more effective than using raw bentonite, more studies are needed to focus on using hydroxyl-Fe-pillared bentonite.

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