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Treatment of Dye Wastewater by Functionalization of Bentonite-Methylene Blue with Sodium Persulfate

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Abstract

Bentonite has been effectively used in many studies for the removal of methylene blue (MB) laden waste waters. This is due to its high swelling ratio, good adsorptive properties and environmentally friendly characteristics. In spite of this, prolonged use renders the BMB non-functional and cause for discard. Sodium persulfate (SPS), has been reported to be an excellent flocculating agent for the functionalization of spent adsorbent due to some of its unique properties. In this study, the functionalization of spent bentonite-methylene blue (BMB) adsorbent in dye wastewater treatment was carried out using SPS at varying temperature conditions. Results revealed that the addition of SPS to MB-loaded adsorbent demonstrated efficient adsorption, high flocculation efficiency as well as faster equilibrium (60 min). The BMB loaded adsorbent showed 95% removal efficiency up to three cycles. A plausible mechanism was proposed and discussed on the basis of the results. Thus, exhausted BMB was found to be effectively used for treatment of coloured wastewater on an industrial scale.

Keywords: Bentonite; Methylene blue; Sodium persulfate; Dye wastewater; Functionalization.

1 Introduction

The textile industry utilises enormous volumes of water as a medium range mill uses about 1.6 million litres of water per day (1). Textile wastewater has become a major cause of water pollution due to the increasing the demand of textile products as well as the utilization of synthetic dyes (2). Owing to the high stability and extreme conditions, huge quantities of dyes are not eliminated during conventional wastewater treatment processes and remain in the ecosystem (3). Azo dyes from the textile industry are reported to be recalcitrant during their biodegradation and often perceived as xenobiotic (4). In spite of this, environmental legislation has made it mandatory for industries to eliminate colour from their dye effluents before discharge (5). Therefore, the textile industries have received considerable attention in the recent years (6) with regards to effective removal methods. Triarylmethane (triphenylmethane) a universally used textile dye, makes up approximately 30%–40 % of the overall dye consumption (7) and have been extensively applied on wool, cotton, silk and nylon (8). It is used for coloring food, paper, leather, plastics, waxes and a host of other industrial applications as well (9). Triarylmethane is also very useful in the laboratories for staining purposes in microbiology and histo-pathological techniques.

In recent times low-cost adsorbents are being sought after as the alternative for activated carbon in waste water treatment (8, 10). These adsorbents are most often natural materials, biosorbents and agricultural or industrial waste materials. Amongst all other natural materials, clay occupies a prominent position due to low costs, easy availability, good sorption properties and environmentally safe (10, 11). Adsorbents of clay origin (diatomite, kaolinite, bentonite and fullers earth) are utilized because of the presence of organic and inorganic molecules (12). Bentonite, composed of montmorillonite clay of the aluminum phyllosilicates group is a well-known adsorbent used in wastewater treatment due to its unique properties such as high porosity, surface area and of high adsorption capacity (13, 14). The adsorption of methylene blue on clay is controlled by the ion-exchange processes. This implies that the adsorbing capacity fluctuates with pH variation (15).

Removal of organic pollutants, phenol and dyes is already an extensively studied area of waste water research (16-18). However, investigation on regeneration and recovery of adsorbed molecules on the adsorbent surface is an area which needs to be explored. The reuse of adsorbent is paramount to ensure an economical and environmentally friendly process (19). Adsorbents can be

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regenerated by chemical, thermal, solvent, and biological methods (20). Regeneration is a method of adsorbent recovery that ensures sustainable re-use of the bentonite for at least 4 cycles. Regeneration or recyclability of low-cost adsorbents is still not well-developed. Organic dyes that are strongly adsorbed onto the adsorbent (bentonite) is unfavourable for desorption. Sodium persulfate ($Na_2S_2O_8$) (SPS), has been recently found to be a potential remedy for regenerating the adsorbents in textile effluents (21). It dissociates in water to form persulfate anion ($S_2O_8^{2-}$). The persulfate (PS) anion has a redox potential (E^0 = 2.01 V) and is chemically /thermally activated to the sulfate radical ($SO^{4-}\bullet$), with a stronger oxidant with redox potential, E^0 = 2.4 V (22).

Persulfate has the potential to degrade organic contaminants (ethylene blue) and the recovery of bentonite to ensure its reusability and long term usage. Most treatment processes involve advanced oxidation processes (AOP) however, this study employed the thermal activation of sodium persulfate to remove the coloured pollutant (MB). Pollutants attached to bentonite are expected to be fully degraded by this method which is a significant contribution in the realm of coloured waste water treatment.

2 Materials and methods

Figure 1 gives an annotated description of the proposed method to be used in this experiment. The chemicals used in this study were Methylene Blue[adsorbate], Bentonite[adsorbent], Sodium persulfate (SPS) oxidant ($Na_2S_2O_8$) of [99% purity], Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$) [>99% purity] and Di-sodium hydrogen phosphate anhydrous (Na^2HPO^4). The UV visible spectrophotometer (HACH DR-5000 Hach, Colorado, USA) was utilized to measure the absorbance of dye solution. Particle size of the flocs were determined by a Zetasizer Nano Series (Malvern Instruments Ltd, UK) and Hach pH meter for the pH measurements.

2.1 Preparation of solutions

Commercial grade cationic dye Methylene Blue (MB) was used to prepare the stock solution (1.0 g of MB in 1 L distilled water) and diluted to the required concentrations at room temperature (27±2ºC). Absorbance curve for different concentrations (0-15mg/L) of dye were calibrated at 664 nm using UV-Vis Spectrophotometer.

2.2 Decolourisation of Methylene blue in aqueous solution

100mL of phosphate buffer (PBS) was prepared by mixing Na_2HPO_4 (3.2025 g) and $NaH_2PO_4{\cdot}2H_2O$ (5.3038g) to obtain a neutral pH. 100 ppm MB was thereafter added to PBS (5 mL each) to attain the desired concentration of each reactant at 70 °C. The decolourisation of MB in the aqueous solution was observed in 75 min.

2.3 Decolourisation of MBloaded bentonite

After adsorption of MB (1h), the MB-loaded bentonite was centrifuged at 4000 rpm and transferred into a beaker (250 mL). To 50 mL of PPB stock solution, 100ppm sodium persulfate (SPS) was added and immersed into a water bath at 70 °C. The decolourisation of MB and regeneration ability of bentonite was tested at four different conditions:

(1) heated for 6 hours (#A1),

(2) heated for 24 hours (#A2),

(3) not heated (without SPS) (#A3), and

(4) as a control (without SPS into the bentonite loaded with MB at room temperature) (#A4).

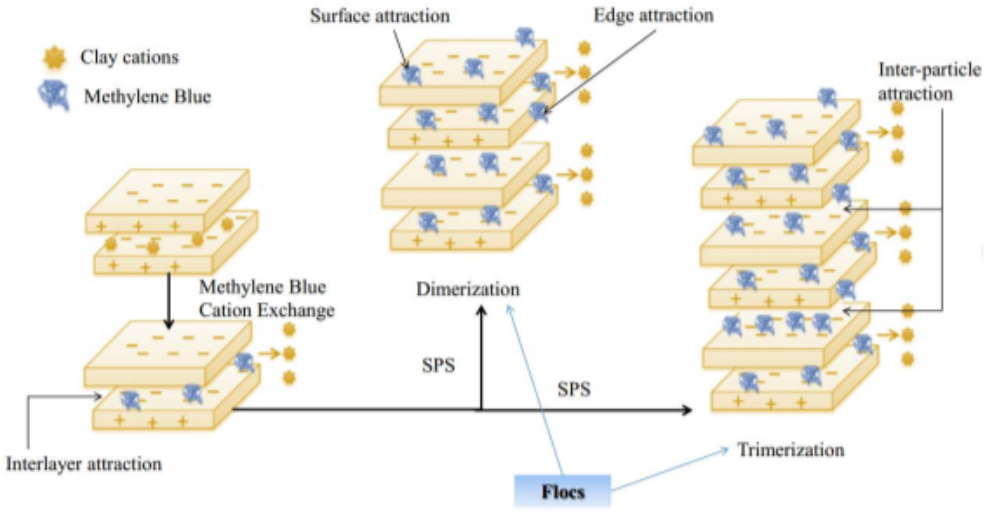

Figure 1: A proposed Scheme for the adsorption of MB and coagulation on bentonite by the addition of SPS.

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2.4 Modification of Bentonite with sodium persulfate

The same procedures were followed as above without the adsorption prior to the addition of SPS to identify whether SPS can modify or activate raw bentonite to improve its performance on MB removal. Two conditions were tested with raw bentonite: (1) heated upto 70 °C (#B1) and (2) at room temperature (#B2) for 6 h. Then, the modified raw bentonite was put into MB solutions (100 ppm).

2.5 Reusability of bentonite

The reusability study was carried out using 100 ppm MB solution. The procedures were repeated for three cycles.

3 Results and Discussion

Degradation of methylene blue (MB) was examined using thermally activated (SPS) and PBS at pH 7. The results revealed complete decolourization of MB at 70°C in 60 min. Decline in color efficiency of MB aqueous solution with time (as shown in Fig. 2) demonstrated almost 99.99 % removal capacity was achieved in 60 min. Concentration of MB from 60 to 75 min also remained the same (99.99 % removal). As a result, complete decolourisation took place in 1 h. Change in colour of MB solutions during oxidation with SPS (100 ppm) at different times is shown in Fig. 3. The colour variation covered trend as: dark blue > dark green > pale green > yellow > colorless.

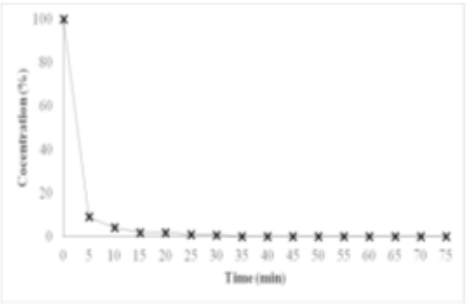

Figure 2: Concentration of MB in the aqueous solution with respect to time. At time = 60 min, the concentration of MB is almost equal to zero.

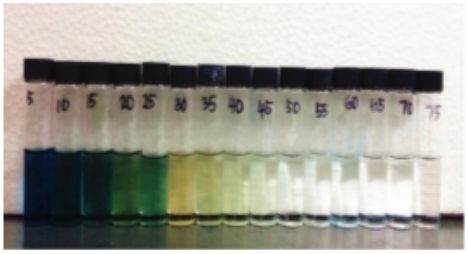

Figure 3: Changes in colour of MB solution (100 ppm) by the oxidation of SPS (100 mM) with respect to different times showing complete decolourisation inr 60 min. Experimental condition: pH ~ 7.0, Temperature = 70 °C.

Initially, there was a reduction in the concentration of MB (100 % at 0 min.) to 2.25 % (at 5 min.) which gradually decreased. Up to 97.8%, color removal efficiency of MB was attained in 5 min which corroborates other studies on the efficiency of adsorption of MB onto bentonite. This is owing to the basic structure of bentonite montmorillonite consisting of two tetrahedrically aligned sheets of silicon ions surrounded by an octahedrically synchronized sheet of aluminum ions (13). This permits the isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+}/Fe^{2+} for Al^{3+} in the octahedral sheet resulting in the negatively charged surface of bentonite. Thus, MB is a cationic dye that is adsorbed onto bentonite demonstrating a strong affinity towards heteroaromatic dyes (24). Electrostatic attraction between cations (dye molecules) and negatively charged montmorillonite (anions) surfaces result in the adsorption of MB onto bentonite. It also occurs via cation exchange. (25). In the study, adsorption of MB onto bentonite decreased over time, with the same initial MB concentration (100 ppm) (Fig. 4). For all samples the percentage removal of MB up to 99.9 % was achieved after an hour. Interestingly, flocculation of MB was observed instead and only adsorption for #A1, #A2, and #A3. The bentonite and MB coalescence resulted in the formation of flocs. After 10 min of stirring and 1h settling, a colour was obtained. A clear solution was obtained for each sample.

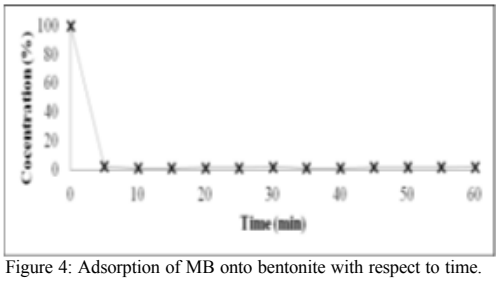

Figure 4: Adsorption of MB onto bentonite with respect to time.

On the other hand, no observable formation of flocs was found for #A4. The bentonite and MB agglomerated and settled down together, however, still remained in powdery form. Figure 5 shows the transparent colour solution when the flocs formed settled down at the bottom of beaker for #A1, #A2, and #A3 whereas a relatively bluish-clear solution for #A4 when powdery bentonite and MB had settled down. There is a quick SPS of MB and bentonite after the regeneration using SPS which implies that the addition of SPS to bentonite led to flocculation. Thus, the regeneration process with SPS promotes the flocculation of bentonite and MB which is explained by the high adsorptive capacity of bentonite (13). Regeneration of bentonite with SPS occurs superficially within the interlayers of bentonite (26). This increases the quantity of MB adsorbed which results in formation of bigger flocs-molecules. In addition, it also involves charge neutralization among the individual molecules which further enhances bonding between MB and bentonite (27).

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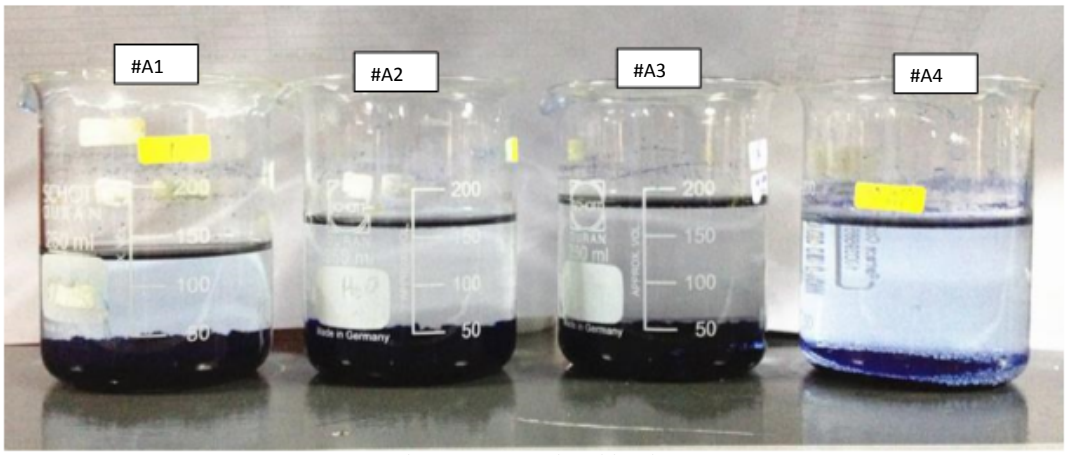

Figure 5: Treatments heated for 6 h

In the control (#4), the aggregation of the particles is achieved by the swelling behaviour of bentonite, since the surface is hydrophilic, large uptake of water between platelets can be explained (24, 27). Organic cation (MB^+) has more affinity to attract negatively charged surfaces as compared to water (26). The inorganic cations are eliminated as a result of the substitution of the interlayer cations with MB^+ thus simultaneously removing the water molecules. As a result, bentonite and MB were weakly attracted and there was no formation of floc in the control sample. They remained in powder form and settled down at the bottom of beaker, giving a relatively bluish-clear solution.

It can be inferred from Table 1 that bentonite and MB in #A1 has the biggest floc size (5993±0.01nm) among all whereas the size of particles in #A4 were the smallest (2450 ± 0.06nm) owing to the formation of powdery agglomerates instead of flocs. This indicates that flocculation occurs only in MB-loaded bentonite with SPS. However, based on the result obtained the floc size in #A1, #A2, and #A3 ranges from 3000 – 6000 nm.

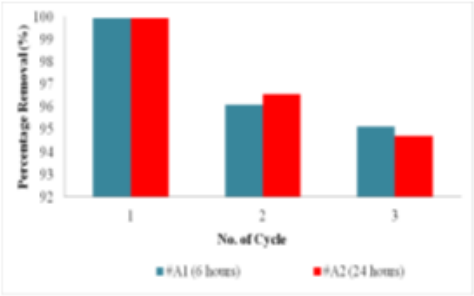

Figure 6: Percentage removal of MB with SPS after three cycles

The percentage removal for all cases was found relatively same after 1 h (99.9 %) which is an achievement in comparison with 85% after first cycle to 47% after 4th cycle in Pandey's study (15) using bentonite beads. MB removal was still effective by using the bentonite with SPS as the regenerating agent, irrespective of the regenerating conditions (Fig. 6). However, the control shows a drastic decrease in percentage removal of MB from 99.9 % in the first cycle, drops to 32.7 % in the second cycle and lastly to 12.4 % in the third cycle. This proved that the SPS plays significant role to enhance flocculation of MB and bentonite until optimum dye adsorption.

4 Conclusion

This is a preliminary study that highlighted the regeneration ability of MB-loaded bentonite using SPS. Regenerated bentonite has been effectively used for MB removal in MB solutions. Flocculation of bentonite and MB was observed instead of degradation of dye using oxidation process. The process of adsorption and flocculation was found to be very fast and equilibrium was reached in 1 hour with 99% removal efficiency. However, by last cycle the efficiency reduced to 12.4%. This study proved that SPS has great potential in extending the life of the bentonite loaded with MB. Therefore, more studies need to be carried out to validate all possible errors in the process. The study would go a long way in reutilizing the MB-bentonite, thereby ensuring sustainability in the textile waste water treatment process.

Conflict of Interest

The authors have declared no conflict of interest.

Acknowledgments

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Table 1: Floc size of all samples (#A1- 4).

Sample	#A1	#A2	#A3	A#4
Floc Size (nm)	5993± 0.02	3084±0.01	3678±0.08	2450±0.06

#A1: heated for 6 hours
#A2: heated for 24 hours
#A3: not heated (at room temperature)
#A4: SPS not added (at room temperature) [serves as control]

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List of symbols

1. Persulfate anion = ($S_2O_8^{2-}$)
2. Redox potential = E0
3. Sulfate radical = SO_4^{-} •
4. Sodium persulfate = SPS