Regeneration Feasibility of Bentonite by Sodium Persulfate

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Abstract Among natural materials, clays occupy a prominent position being low cost, available in abundance, environmentally friendly, and having good adsorption properties. Bentonite, which has strong affinity towards cationic dyes such as methylene blue (MB) is able to remove dye effectively. It is very economical if the spent adsorbent can be recovered and reused for many cycles. Hence, this study investigated the ability of sodium persulfate (Na₂S₂O₈) (SPS) to regenerate bentonite loaded with MB. The modification of raw bentonite with SPS was also investigated. The results showed that after added with SPS, the bentonite and MB adsorbed and flocculated together to form large flocs that were firm and compact. The process adsorption and flocculation was very efficient and equilibrium was reached within one hour. However, the modification of raw bentonite may not be a good option as the flocs formed were loose and less compact. High water retention of the flocs would cause disposal issue during dewatering process. The flocculation mechanism of MB-loaded bentonite can be explained in macroscopic and microscopic level. In macroscopic level, charge neutralization and bridge formation are the main mechanism while in microscopic level, increase in interlayer spacing and extensive cation exchange with MB are the one that contribute to flocs formation. Besides that, dimerization and trimerization also contribute to total MB adsorption which also allow bigger flocs formed. However, the ability of SPS to degrade MB adsorbed to bentonite through oxidation process does remain uncertain. Instead of regeneration, flocculation of MB-loaded bentonite upon addition of SPS occurred to remove the dye effectively. For reusability study, the MB-loaded bentonite can be used up to 3 cycles with percentage removal of 95%. Hence, SPS, as a flocculation promoting agent can be further studied and investigated, to be used in large scale in colour wastewater treatment.

Keywords: Regeneration, Bentonite, Sodium Persulfate, Methylene Blue

1. Introduction

At current times, the regeneration method of low-cost adsorbents is still not well-developed. Limited studies were carried out especially on the regeneration of bentonite clay. Regeneration is essential to recover the capacity to ensure a continuous usage of adsorbent instead of disposal after one-time usage. It is economical to have regeneration on the adsorbents, thus saving a lot of cost. There are few regeneration methods that remove solutes from adsorbent such as thermal regeneration, pressure swing regeneration, vacuum regeneration, microwave regeneration, etc. Each regeneration method has its pros and cons and thus a solution should be investigated further.

Sodium persulfate (Na₂S₂O₈) (SPS) is a relatively new oxidant which has the potential to remedy the textile effluent issue. It dissociates in water to form persulfate anion (S₄O₆²⁻). The persulfate (PS) anion with a high redox potential with E⁰ = 2.01 V can be thermally or chemically activated to form the sulfate radical (SO₄⁻) which is a stronger oxidant with redox potential, E⁰ = 2.4 V. The reactions are as follows:

\[ S_2O_8^{2–} + 2e^- \rightarrow 2SO_4^{2–} \quad E^0 = 2.01 \text{V} \] (1)

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Thermal activation: \( S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-} \)  

Chemical activation: \( S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-} \cdot +Fe^{3+} + SO_4^{2-} \)

\[ SO_4^{-} \cdot +e^{-} \rightarrow SO_4^{2-} \quad E^0 = 2.40 \text{ V} \]

Persulfate is a strong oxidant but it does require higher reaction activation energy than other oxidants like permanganate. It was reported that an activation energy of 98 kJ/mol is required for persulfate to oxidise trichloroethylene (TCE) as compared to 35 kJ/mol required by potassium permanganate [1]. This shows that although persulfate has a higher redox potential than permanganate \( (E^0 = 1.68 \text{ V}) \), chemical degradation of TCE with persulfate without supplemental activation is relatively slow. Therefore, persulfate maybe thermodynamically stable in the subsurface [15]. Redox potential of persulfate is also higher than hydrogen peroxide (1.8 V) [2].

In addition, persulfate is a non-selectively reactive and relatively stable at room temperature. It has relatively long lifetime in water, as compared to hydrogen peroxide. However, due to the fact that the reaction of organic compounds with persulfate ions is kinetically slow, thus they are generally activated to generate intermediate sulfate free radicals to enhance the oxidation process under heat or light conditions.

Thermally activated persulfate (TAP) is currently a new novel method that emerges as an excellent choice of advanced oxidation processes (AOPs) for the treatment of organic solvents. AOPs involves the hydroxyl radical precursors and they are very quickly depleted in oxidants. Thus, TAP system emerges as the alternative method as it has longer lifetime and it is able to produce sulfate radicals \( SO_4^+ \) directly as well as hydroxyl radicals \( \text{OH}^- \) indirectly. Both radicals play important roles in oxidizing organic contaminants (OCs). However, \( SO_4^+ \) being more selective represents a higher reaction stoichiometric efficiency (RSE). RSE is the number of moles of OC degraded divided by the number of moles of Sodium persulfate (SPS) consumed over a specific time interval \( ([\text{OC}]/[\text{SPS}]) \) [3].

In light of the ability of persulfate to degrade organic contaminants and methylene blue, there is a potential of persulfate oxidation applied in the recovery of bentonite to ensure its reusability and long term usage. Instead of employing AOPs to treat the colour wastewater directly, the present work uses the process to remove the coloured pollutants (Methylene Blue) adsorbed to the surface to recover bentonite after use.

However, an intrinsic short coming of oxidation by heated persulfate is the necessity of an energy consuming thermal bed (30 - 99 °C). Accordingly, it is of practical importance to find out the optional operational parameters for the oxidation of each compound or class of compounds. A survey of published data regarding oxidation by heated persulfate suggests that the transferability of achieved results is a difficult task. Relevant operational parameters included the activated temperature, pH, buffer nature, concentration of the contaminant and concentration of SPS as well.

Organic dyes that are strongly adsorbed onto the adsorbent like bentonite is unfavourable to undergo desorption. No regeneration of clay is possible in the sorption of dyes, since strong chemical bonding occurs between bentonite and the sorbed dyes [4]. As a result, bentonite is not recyclable. Hence, this current work is attempted to regenerate and recycle bentonite clay after use for adsorption by thermal activation of sodium persulfate. Pollutants attached to bentonite are anticipated to be degraded successfully if the regeneration technique is working well. Indeed, the success of bentonite regeneration will become a great breakthrough in coloured wastewater remedy.

2. Materials and Methods

The cationic dye, Methylene Blue (MB) is a commercial grade supplied by Merck Millipore, Germany. It is used as an adsorbate to simulate industrial wastewater in order to evaluate the adsorption capacity of the adsorbent coating, used as received without further modification. The MB selection is guided by its strong adsorption onto solids also for its high solubility in water. MB dye is made up in stock solution of concentration 1000 mg/L and is diluted to the required concentrations of 100 mg/L. Distilled water is employed for preparing all the solutions and reagents. Bentonite is a type of clay mineral source that is laboratory graded purchased from Sigma Aldrich, USA. It is used without any modification except when tested with SPS. Bentonite has different particle grain size with an average particle size of 20-30 nm. It is stored in dry place to prevent any contamination. A total of 0.3 g was used for each sample of experiment. Three types of phosphate buffer solution (Sodium persulfate (SPS) oxidant, \( Na_2S_2O_8 \), Sodium dihydrogen phosphate dihydrate (\( NaH_2PO_4 \cdot 2H_2O \)) and Disodium hydrogen phosphate anhydrous (\( Na_2HPO_4 \)) used and all those three chemical were supplied by Chem-Lab (Belgium), Fluka (Netherlands) and Merck (Germany), respectively.

UV visible spectrophotometer (HACH DR-5000, Canada) is used to measure the absorbance of dye solution. Absorbances at different concentrations of dye were calibrated for 0-12 mg/L using UV-vis spectrophotometer at 664 nm. The linear relationships between absorbance \( A_{664} \) and MB dye concentration were plotted Zetameter (model Malvern iDB Zeta Sizer Nano Series, England) is used to identify the particle size of the flocs formed.

2.1. Decolorization of Methylene Blue in Aqueous Solution

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Phosphate buffer (PB) stock solution was prepared in a 100 mL volumetric flask by mixing 3.2025 g Na₂HPO₄ (213.5 mM) and 5.3038 g NaH₂PO₄·2H₂O (323.4 mM) salts in order to get a PB solution of neutral pH (pH~7.0). Then, adequate volumes of MB and PB stock solutions were added together to a predefined volume of deionized water in order to get the desired concentration of each reactant into the beaker. There are 5 mL of MB solution of 100 ppm and 5 mL of PB solution. After that, 5 mL of sodium persulfate (SPS) of 100 mM was added after immersion of MB solutions in the thermostated water bath until reaching the desired temperature (70 °C). The decolourisation of MB in the aqueous solution and its colour change was observed over 75 min.

2.2. Decolorization of Methylene Blue Adsorbed to Bentonite

After adsorption over 1 hour with initial concentration of MB of 100 ppm, the MB-loaded bentonite was centrifuged at 3000 rpm using Centrifuge Hettich Model EBA 20 and transferred into a 250 mL beaker. Phosphate buffer (PB) stock solution with 213.5 mM of Na₂HPO₄ and 323.4 mM of NaH₂PO₄·2H₂O was prepared. Then, 100 mL of PB stock solutions was added into the beaker. After that, 100 mL sodium persulfate (SPS) of 100 mM was added after immersion of MB solutions in the thermostated water bath until reaching the desired temperature (70 °C). The decolourisation of MB and regeneration ability of bentonite was observed.

The degradation and regeneration was tested with four different conditions: (1) heated at 70 °C for 6 hours (#A1), (2) heated at 70 °C for 24 hours (#A2), (3) not heated (at room temperature which is the ambient temperature of 30 °C) for 6 hours (#A3), and (4) as a control (no added SPS into the bentonite loaded with MB and leave it at room temperature) for 6 hours (#A4).

2.3. Modification of Raw Bentonite with Sodium Persulfate

The same procedures were employed as in section 3.7 except there is no 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 till 70 °C (#B1) and (2) at room temperature (#B2) for 6 hours. Then, the modified raw bentonite was put into fresh MB solutions with concentration of 100 ppm for MB removal.

2.4. Reusability of Spent Bentonite

The experiment was conducted in order to investigate the performance of MB removal by bentonite up to 3 cycles. The reusability study was prepared using MB solution of 100 ppm. The same regeneration procedures were employed as in section 3.7. The procedures were repeated until the third cycle.

3. Result and Discussion

3.1. Decolorization of Methylene Blue by Heated Persulfate in Aqueous Solution

Advanced oxidation process based on thermally activated sodium persulfate (Na₂S₂O₈) (SPS) is used in this work to degrade methylene blue (MB) in aqueous solution. This experiment was carried out to reassure the decolourisation ability of SPS towards MB as reported by Ghauch et al., (2012b) [5]. They reported that reactions running at neutral and acidic conditions are more improved (with higher observed degradation rate constants) showing full decolourisation as compared to basic condition. Furthermore, MB solution is buffered to (1) not to allow serious pH drop and (2) to mimic natural effluent conditions. Thus, by conducting the experiment at neutral pH (pH ~ 7) in buffered MB solutions, results showed complete MB decolorisation at 70 °C over 60 min of reaction.

Figure 1 shows the decreasing trend of MB in the aqueous solution with time. At 60 min, the concentration of MB is almost equal to zero and the percentage removal is up to 99.99%. Concentration of MB from 60 to 75 min remain the same with percentage removal of 99.99%. As a result, the whole decolourisation process takes 1 hour to complete it. Figure 2 shows the colour variation of MB solutions ([MB]₀ = 100 ppm) during oxidation with 100 mM SPS at different times. The colour variation started with dark blue > dark green > pale green > yellow > colourless.
Figure 1. Graph of concentration of MB in the aqueous solution against time. At time = 60 min, the concentration of MB is almost equal to zero.

Figure 2. Colour variation of MB solution ([MB]₀ = 100 ppm) during oxidation with 100 mM SPS at different times showing complete decolourisation over 60 min of reaction. Experimental condition: pH ~ 7.0, temperature = 70 °C.

[5] illustrated the proposed degradation mechanism for MB dye via thermally activated persulfate based on the intermediate products detected and their subsequent disappearance as well as through literature survey [5-8]. The reaction started with the abstraction of an electron from one of the benzene rings of MB and followed by the formation of a MB radical cation. The resulting [MB]⁺ will exhibit some internal arrangement so as facilitating demethylation, N-dealkylation and hydroxylation in aqueous solution. Demethylation is followed by sulfonation at any available carbon of the benzene cycle yielding therefore MB intermediates. All intermediates exhibit further oxidation upon persulfate heating and will be converted to smaller molecules (eg. aldehyde, carboxylic acid) to finally give carbon dioxide, nitrate, sulfate and water. As a result, when the small molecules are formed as the final products, it means that MB has been degraded successfully and turn the solution from initially dark blue to colourless. Therefore, thermally activated SPS is able to oxidise and degrade MB into colourless products.

3.2. Decolorization of Methylene Blue Adsorbed to Bentonite

In light of the ability of sodium persulfate (SPS) to degrade MB in aqueous solution, the present work used SPS to degrade MB that had been adsorbed to bentonite. Bentonite clay is a widely used adsorbent to remove dyes due to its excellent adsorption capacity and ability. Relatively good removal abilities of clays group towards MB uptakes has been demonstrated by many researchers [9-13].

Among the researchers, Azha et al. (2014) has done research on the effect of different clays used in adsorbing MB [13]. The clays used were bentonite, kaolinite, and zeolite. It was reported that bentonite gave the best performance as compared to other clays which was 100% MB removal in 100 ppm MB solution. The percentage of MB removal achieved by kaolinite and zeolite were just 40% over 6 hours of the whole experiment. Thus, although they are from the same family of clay mineral sources, they do differ in adsorption ability and bentonite stands out the best adsorbent among all.

Bentonite clay has small particle size, high porosity, and high cation exchange capacity [14]. However, the adsorptive capacity of bentonite decreases with time until all the free and available sites are occupied. Bentonite is said to be saturated. In order to make this method more environmental friendly and economical, regeneration of bentonite is very important to recover bentonite for subsequent usage. SPS is a strong oxidizing agent that is able to oxidise various types of organic contaminants as reported by many researchers [15-17]. To the best of researchers’ work, SPS has never been tested on MB
solutions until Ghauch et al. (2012b) reported it [5]. Thus, the present work is conducted to investigate the ability of SPS to degrade MB that has been adsorbed into bentonite instead of MB in aqueous solution. In another words, this study is carried out to study the ability of SPS to regenerate bentonite loaded with MB for subsequent usage, as many cycles as possible.

Figure 3 shows that the adsorption of MB onto bentonite with concentration of MB solutions decreases over time, with initial MB concentration of 100 ppm. Initially, it shows a drastic reduction of concentration of MB solution from 100% at 0 min to 2.25% at 5 min. After 5 min, the drop is not drastic but gradual. The percentage removal of MB up to 97.8% within 5 min can be achieved. This showed that the adsorption of MB onto bentonite is rapid and efficient. The basic structural unit of montmorillonite that has two tetrahedrically coordinated sheets of silicon ions surrounding an octahedrically coordinated sheet of aluminium ions allows the isomorphous substitutions of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sheet and Mg$^{2+}$, Fe$^{2+}$, etc. cations for Al$^{3+}$ in the octahedral sheet. This results in a net negative surface charge on the clay that enables the exchange of cations. Thus, MB which is a cationic dye is able to be adsorbed onto bentonite, exhibiting a strong affinity for heteroaromatic cationic dyes [18]. The adsorption of MB onto bentonite is not only through cation exchange but also via the electrostatic attraction between the dye cations and negatively charged surface of montmorillonite [19].

![Figure 3. Graph of concentration of MB solution against time.](image)

After first time adsorption, the bentonite was mixed with SPS and phosphate buffer to identify whether the MB adsorbed onto bentonite can be degraded successfully by SPS. The degradation was tested with four different conditions: (1) heated at 70 °C for 6 hours (#A1), (2) heated at 70 °C for 24 hours (#A2), (3) not heated (at room temperature which is the ambient temperature of 30 °C) for 6 hours (#A3), and (4) as a control (no added SPS into the bentonite loaded with MB and leave it at room temperature) for 6 hours (#A4). After that, the so called regenerated bentonite was put into fresh MB solution with the same initial concentration for second time adsorption. In control sample, the MB-loaded bentonite does not undergo regeneration with SPS and was not buffered with phosphate buffer. They just performed second time adsorption after first adsorption.

Figure 4 shows that the adsorption of MB onto bentonite with concentration of MB solutions decreases over time, with the same initial MB concentration of 100 ppm. It showed the same trend of decreasing concentration of MB over time as the first time adsorption. Rapid and efficient MB removal can be achieved within first 5 min. The percentage removal of MB up to 99.9% can be achieved at the end of one hour of experiment for all samples.

![Figure 4. Graph of concentration of MB solutions against time using the regenerated bentonite.](image)
From the experimental observation, adsorption was not the only process happening during the testing. Interestingly, flocculation of MB was observed instead of purely adsorption itself for #A1, #A2, and #A3. The bentonite and MB coalesced together, results in formation of flocs. After stirring for 10 min, stirring was stopped and let the flocs to settle down over 1 hour. An obvious colour change from initially dark blue to transparent can be observed. A clear solution was obtained for each sample.

On the other hand, for #A4, there is no formation of flocs that can be observed. The bentonite and MB agglomerated and settled down together but still remained in powdery form. Figure 5 shows the transparent colour solutions 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.

![Figure 5. Colour change from dark blue to transparent for #A1, #A2 and #A3 and to a relatively bluish-clear solution for #A4 after MB adsorption for 1 hour.](image)

As illustrated in Figure 5, the aggregates of MB and bentonite happened after the regeneration process carried out with SPS. This means that after bentonite was mixed with SPS, flocculation occurred. Thus, the regeneration process with SPS promoted the flocculation of bentonite and MB. This can be explained through structure of bentonite that enables it having excellent adsorptive capacity. Regeneration of bentonite with SPS allows the bentonite to carry out adsorption not merely on surface, but also within the interlayers of bentonite. The interlayer adsorption of MB into bentonite significantly contributes to the total MB adsorption [20]. Adsorptive surface of bentonite has been greatly increased, more MB can be adsorbed into it. When MB can be adsorbed into bentonite from outer and interlayer surface, rapid cation exchange and formation of electrostatic attraction between the dye cations and negatively charged surface which results in formation of bigger molecules – flocs. In addition, it also involves charge neutralization among the individual molecules which further enhance the bonding between MB and bentonite [21].

Besides, looking at the structure of SPS, there are two negatively charged sites available as shown in Figure 6. Bridging is possible to occur as the negatively charged persulfate anion is attracted to the positively charged surface of MB attached to bentonite due to electrostatic attraction. Since after the first time adsorption, bentonite has become less negatively charged when it is loaded with MB that is positively charged. Its zeta potential becomes more positive. As a result, coagulation by charge neutralization destabilizes bentonite and transfers small particles into large aggregates (bridge formation) and adsorbs MB onto the aggregates by an adsorption mechanism which can later be removed by filtration and sedimentation. Adsorbed macromolecules tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends dangle and get adsorbed by another particle forming a bridge between particles [22]. Hence, flocculation is interpreted as being a result of charge neutralization and bridging of SPS with bentonite. Thus, SPS plays the role as a bridging agent.

![Figure 6. Two sodium cations and one persulfate anion.](image)
For control, the aggregates of the particles could be explained in microscopic as well as in macroscopic level. In macroscopic level, the negative charges predominate the surface of bentonite and therefore like-charged molecules will exhibit repulsive forces. The surface becomes more positive when the number of MB cations adsorbed onto the surface increases. Thus, zeta potential becomes less negative. At one point, when the negatively charged surface is completely neutralised by MB cations, zeta potential of bentonite becomes zero. This is called as isoelectric point (pI) when the negative and positive charges cancel, repulsive electrostatic attraction forces are reduced and the attraction forces predominate. The attraction forces will cause agglomeration and precipitation of the particles. Hence, as observed, the control sample agglomerate and able to settle down. The importance of the concept of isoelectric point can be analysed from the study of proteins especially in the purification/separation process. The proteins separate based on their relative content of acidic and basic residues. Isoelectric point precipitation is also very often used to precipitate contaminant proteins [23].

On the other hand, in microscopic level, it can be explained through the swelling behaviour of bentonite. When the bentonite is immersed in water for a long period of time, swelling of bentonite occurs. The c-spacing, or the degree of expansion of the layer planes (as shown in Figure 7) increases depending on the cations located in the interlayer region, i.e. on the basal cleavage. Since the interlayer cations are mono-valent and strongly hydrated (Na+), the inter-platelet repulsion is stronger and the degree of platelet separation is larger. Since the surface is hydrophilic, large uptake of water between platelets can be explained [18, 24] However when compared to water, the nature of organic cation MB+ has more affinity and selectivity to the negatively charged mineral surfaces as reported by Li et al. (2011a) [20]. When MB+ substitutes the interlayer cations, the departure of the smaller hydrated inorganic cations results in simultaneous removal of water. As a result, bentonite and MB were weakly attracted and no flocs were formed in the control sample. They remained in powdery form and settled down at the bottom of beaker, giving a relatively bluish-clear solution.

![Figure 7. Representation of a three-layer expanding clay lattice](image)

All the samples were analysed with Zeta Sizer to determine the floc size formed. The floc size of each sample is shown in Table 1.

**Table 1.** The result floc size of all samples (#A1-4) by using Zeta Sizer.

| Sample # | A1   | A2   | A3   | A4   | Bentonite |
|----------|------|------|------|------|-----------|
| Average Floc Size (µm) | 5.993 | 3.084 | 3.678 | 2.450 | 0.7476 |

From the result obtained, all samples of MB-loaded bentonite have sizes greater than (> 0.7476 µm) purely bentonite. This has proven there is increase in particle size in all the samples. MB-loaded bentonite in #A1 has the biggest floc size among all which is 5.993 µm whereas the size of particles in #A4 are the smallest because powdery agglomerates were formed instead of flocs. This indicates that regenerating MB-loaded bentonite with SPS in any of the condition flocculation occurs. However, based on the result obtained, although the floc size in #A1, #A2, and #A3 ranges from 3.0 – 6.0 µm, the percentage removal for all cases were relatively the same after 1 hour which is up to 99.9%. Hence, since the MB-loaded bentonite can still achieve percentage removal of MB of 99.9% in second time adsorption after being regenerated without any heating, thus it will be employed as the best regeneration condition. Another contributing factor to effective removal of MB of 99.9% can also be due to bentonite itself which still has vacant site available for the positively charged MB to be attached on it. They are still unsaturated after the first adsorption, therefore cation exchange on the surface is still possible. Hence, from the result obtained, it can be deduced that there is possibility of MB adsorbed onto bentonite is oxidized to smaller molecules. MB-loaded bentonite is regenerated to provide more free sites for cation exchange to occur. However, more studies need to be done to identify the mechanism behind the degradation process to understand the whole process.

The increase in particle size is also further verified by using microscope model Olympus BX53 to identify the particle size of MB-loaded bentonite. The particle sizes are irregular and hence by taking the average for each sample, the size is tabulated as shown in Table 2.
Table 2. The result floc size of all samples (#A1-4) by using microscope Model Olympus BX53

| Sample # | A1   | A2   | A3   | A4   |
|----------|------|------|------|------|
| **Average Floc Size (µm)** | 10.88 | 12.60 | 8.08 | 5.47 |

From Table 2, it also shows that the particle size of all samples of MB-loaded bentonite are greater than (> 0.007 µm) purely bentonite. This has further assured the occurrence of flocculation and agglomeration during the experiment.

3.3. Decolorization of Raw Bentonite with Sodium Persulfate

Raw bentonite was added with sodium persulfate to identify whether any possibility of modification on bentonite can be further explored to improve its performance on MB removal. Two conditions to modify raw bentonite: (1) heated till 70 °C (#B1) and (2) at room temperature (#B2) for 6 hours. Then, the modified raw bentonite was put into fresh MB solutions with concentration of 100 ppm for MB removal.

Figure 8 shows that a similar decreasing trend can be observed. The concentration of MB solution decreases drastically from 100% at 0 min to 1.9% at the 5 min for case #B1, while decreases to 2.8% for case #B2, and then decreases gradually after 5 min for both cases. The final concentration percentage for case #B2 is 1.58% which is relatively higher than case #B1 which gives only 0.08%. This showed that by heating the raw bentonite with SPS at 70 °C, the bentonite can remove more MB as compared to raw bentonite without any heating.

![Graph of concentration of MB solutions against time using modified raw bentonite over 1 hour.](image)

Figure 8. Graph of concentration of MB solutions against time using modified raw bentonite over 1 hour.

Figure 9 shows that the final colour of MB solution at 60 min for case #B1 is less bluish than #B1, indicating higher amount of MB was removed in beaker 1 than beaker 2. Comparing two cases, it showed that the effect of temperature on the cation exchange ability of MB on bentonite contributing slightly on MB removal. As temperature increases, water is transferred from the interlayer region to the pores between the clay aggregates (macropores) [25]. The swelling capacity of the clay was obvious but slightly decreases at sample in higher temperature. Thus, MB⁺ is able to undergo cation exchange directly with the negatively charged surface of bentonite with less hindrance imposed by water molecules.

![Final colour of MB solutions from dark blue to less dark blue for raw bentonite modification at two conditions: (1) heated till 70 °C (#B1) and (2) at room temperature over 6 hours (#B2).](image)

Figure 9. Final colour of MB solutions from dark blue to less dark blue for raw bentonite modification at two conditions: (1) heated till 70 °C (#B1) and (2) at room temperature over 6 hours (#B2).
Nevertheless, both modified raw bentonite removed MB not only by adsorption, but also by flocculation as formation of flocs can be observed for both cases. Flocculation can be explained through the occurrence of not only adsorption but also charge neutralization among the individual molecules. The flocs formed in #B1 and #B2 were analysed with Zeta Sizer. The flocs formed in #B1 have an average size of 2.211 µm whereas the flocs formed in #B2 have an average size of 1.443 µm. Thus, the flocs formed in #B1 are bigger than in #B2, indicating that more MB was adsorbed into bentonite in #B1 which gave higher percentage removal of MB.

3.4. Comparison of the Structure of Flocs

The same regeneration procedure was applied on the MB-loaded bentonite (#A1) and MB-loaded modified bentonite (#B1). They were mixed with SPS and phosphate buffer and heated at 70 °C for 6 hours. After that, they were centrifuged and dried. Both samples were tested in 100 ppm MB solutions for dye removal.

Flocculation of bentonite and MB can be observed as shown in Figure 10. Comparing the floc size of #A1 and #B1, the floc size of #A1 on average is slightly larger than that of #B1. This was shown when both samples were analysed with Zeta Sizer. The floc size of #A1 is 5.993 µm in average whereas #B1 has an average floc size of 2.211 µm. Particle size estimates based upon volume are particularly useful for settlement purposes. The settlement of flocs is a particularly important operational parameter because increased rates of floc settlement results in better solids removal in settlement tanks [26]. Large compact flocs have a high settling rate and can be removed effectively through settlement. Therefore, from Figure 11, the flocs formed in #A1 are more compact than those in #B1 and thus, are able to settle faster. The flocs formed in #B1 have loose structure and enables higher amount of water retention. High water retention is a disadvantage as it brings disposal issue in dewatering application. Also, they took a relatively longer time to settle down. Hence, large and porous flocs aid filtration but not settling due to high permeability [27]. As a result, by comparing the floc size formation, modification of raw bentonite is not a good option for effective MB removal.

Figure 10. Formation of flocs

Figure 11. Floc structure of (a) #A1 (compact) and (b) #B1 (loose).
3.4. Mechanism of MB Adsorption and Flocculation on Bentonite upon Addition with Sodium Persulfate

From previous section, SPS is found to be the flocculation-promoting as well as the bridging agent. This can be explained through application of SPS. SPS is a specialized oxidizing agent in chemistry, and it is commonly used as soil conditioner, and soil remediation as well as in manufacture of dyestuffs. As a soil conditioner, it is added to soil to improve the soil’s physical qualities, especially its ability to provide nutrition for plants. The four main purposes of a soil conditioner are (1) to improve soil structure by keeping the soil loose, (2) to enrich the soils by adding nutrients essential for plant growth, (3) to increase the cation exchange capacity of soils, and (4) to improve water retention in dry, coarse soils which are not holding water well [28]. Due to the ability of SPS especially in improving cation exchange, this results in extensive exchange of MB which is cationic with the negatively charged surface of bentonite. Together with charge neutralization, bigger flocs form together and rearrange themselves. The structure change continually because that flocs internal bonds break under shear and re-form at more favorable points where the attractive force is greater or the repulsive force is lower [29], when the balance between the rate of aggregation and the rate of breakage for a given shear condition is reached, flocs formation completes and the size of flocs reach a steady plateau [30]. According to the process, flocs aggregation process mainly depends on flocculation mechanism.

Flocculation mechanism of bentonite and MB in macroscopic level includes charge neutralization and bridge formation. The negatively charged surface of bentonite is neutralized by the cationic MB\(^+\) and become MB-loaded bentonite. MB loaded on bentonite is attracted to the two ends of persulfate anion and bridge is formed. More particles are dangled together and bigger particle can be formed which results in flocs formation as shown in Figure 12.

Due to the structure of bentonite, it can become swollen and increases its interlayer spacing when hydrated with water. This is the nature of bentonite to have swelling behaviour. Figure 13 shows the structure of bentonite in hydrated and non-hydrated conditions. Hence, in microscopic level, since the surface is hydrophilic, there is large uptake of water between platelets. A lot of MB\(^+\) substitutes the interlayer cations including water. As a result, bentonite and MB were weakly attracted and bigger size of MB-loaded bentonite is formed.

![Figure 12. Macroscopic level: The proposed mechanism of MB adsorption and coagulation on bentonite upon addition of SPS.](image)

In previous research done by Li et al. (2011b) and Cenens and Schoonheydt (1998), four reactions were accounted when MB came in contact with bentonite: ion exchange, protonation, dimerization, and trimerization. However, the relative amounts of these four forms of MB depend not only on the loading but also on the type of clay and on the exchangeable cation [11,32]. Li et al. (2011a) reported that protonation of MB is considered as a reaction with water only, rather than with clays. Hence, protonation is not taken into consideration in the interaction between bentonite and MB [20].
For a synthetic clay, laponite, Schoonheydt and Heughebaert (1992) reported that the adsorption of MB on laponite is dominated by monomers at low loading levels, while dimers and trimers (or higher aggregates) are formed as the loading level increases [33]. Meanwhile, trimers were formed only at the external surface. Thus, adsorption of trimers can make a significant contribution to the total MB adsorption. The aggregation state of MB on the surface is independent from the aggregation state in the initial solutions [34], but dependent on the final equilibrium concentration, which is high in the dimer and trimer range near the MB adsorption maxima.

As a result, it is believed that the bentonite behave similarly as laponite as reported by Veroni (1995), the chief difference between laponite and bentonite is the high degree disorder and delamination of laponite, which also persists in the pillared form [31]. Thus, it enhanced adsorption in comparison with montmorillonite results from an increased accessible surface area and may also be related to more hydrophobic character of the bare silicate surface.

In a nutshell, flocculation of MB-loaded bentonite can be explained in macroscopic and microscopic level. Furthermore, adsorption of MB onto bentonite which involves the cation exchange interaction such as surface attachment, edge attachment, interlayer interaction, and inter-particle interaction, it possibly brings into dimerization and trimerization of each individual molecules after SPS is added into bentonite and MB. This is because SPS which improves cation exchange capacity of bentonite, increases the amount of cationic MB adsorbed into bentonite, thus results in formation of big flocs. Flocculation phenomenon is thus explained. Figure 14 shows the proposed mechanism of MB adsorption and coagulation on bentonite upon addition of SPS.

In fact, this work has found a great breakthrough to current wastewater treatment technology because formation of large and compact flocs eases the removal of flocs due to its high settling rate using the addition of SPS. Dye can be removed effectively by such a simple method.

Figure 14. Microscopic level: The propose mechanism of MB adsorption and coagulation on bentonite upon addition of SPS.

### 3.4. Reusability of Spend Bentonite

The spent bentonite was regenerated under same conditions for another 3 cycles. Wastewater treatment will be economical if the spent adsorbent can be recovered and regenerated. The process of adsorption and flocculation are very fast and equilibrium was reached within 1 hour. Figure 15 shows that the percentage removal of MB decreases with number of cycle. All the cases had percentage removal up to 95% even until third cycle.
MB removal was still effective by using the bentonite with SPS as the regenerating agent, irrespective of the regenerating conditions. 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 did play some role in enhancing the flocculation of MB and bentonite until maximum dye adsorption is achieved. However, whether the SPS degrade and decolourise MB adsorbed onto bentonite, more research and work need to be done.

4. Conclusion

This study highlighted the regeneration ability of MB-loaded bentonite by SPS. When regenerated spent bentonite was used for further MB removal in MB solutions, flocculation of bentonite and MB can be observed instead of degradation of dye that has been adsorbed to bentonite through the oxidation process (as proven that MB in aqueous solution is able to be degraded by thermally heated SPS). The process adsorption and flocculation was very fast and equilibri um was reached within one hour.

In this study, no detailed mechanism of flocculation of bentonite and MB was studied, but a proposed mechanism that the adsorption of trimers can make a significant contribution to the total MB adsorption. Flocculation mechanism can be explained in macroscopic and microscopic level. In macroscopic level, charge neutralization and bridge formation are the main mechanism while in microscopic level, increase in interlayer spacing and extensive cation exchange with MB are the one that contribute to flocs formation. SPS was the flocculation promoting and bridging agent due to its nature of application of being a soil conditioner that improves the cation exchange capacity of the clays. Persulfate anion is able to form bridge with the cationic MB⁺ which in turn produce bigger flocs. However, the ability of SPS to degrade MB adsorbed to bentonite through oxidation process does remain uncertain. Instead of regeneration, flocculation of MB-loaded bentonite upon addition of SPS occurred to remove the dye effectively. Hence, further experimental and theoretical investigations are required to improve the understanding on the mechanism of the degradation process of MB loaded on bentonite.

This study also investigated the modification of raw bentonite by SPS. There is modification of raw bentonite as it straight away perform flocculation instead of purely adsorption once it is added with MB solution. Removal of dye is taken place by flocculation instead of adsorption. However, raw bentonite modification with SPS may not be a good option due to the structure of flocs formed are loose and high water retention. Removal of flocs through settling is difficult due to its low rate of settling and there will be an issue during dewatering process.

The study also investigated the effect of reusability of spent bentonite. The bentonite added with SPS has a high prospective in colour wastewater treatment as the percentage removal of MB remained around 95% even until the third cycle. This is indeed economical as the spent adsorbent can be recovered and reused as much as it can. SPS has greatly ensure the reusability of bentonite and more studies can be carried out to improvise the process.
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