

## Removal of acid blue 25 from aqueous solution by using common salts and seawater to induce the salting out effect

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### Abstract

This study used common salts (monovalent and divalent salts) and seawater to cause aggregation of an acid dye, AB25 to a particle size large enough to be removed by simple filtration using a filter paper. All the common salts (CaCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, KNO<sub>3</sub>, KCl, NaCl) were able to produce high removal efficiencies of AB25 (100 mg/L, unadjusted pH) at 99.4%, 90.3%, 98.4%, 99.3% and 99.3%, respectively, while a 2.5x dilution of seawater was successful in removing up to 93.8% of AB25. These findings proved the effectiveness of this method which is a much simpler and direct approach to dye wastewater remediation.

*Index Terms:* Acid blue 25, dye aggregation, ionic strength, seawater, salting-out effect

### 1. Introduction

In the past, all the dye materials were obtained from natural sources which include root, flower, barks, insects and minerals.<sup>1</sup> These practices gradually declined after the accidental discovery of the first synthetic dye in 1856, as the shift from natural to synthetic source make more economic sense for the thriving industrialising nations at that time.<sup>1</sup> Because of the vibrant colour, chemical and thermal stability of synthetic dyes, dye wastewater has become an environmental liability as its untreated form when discharged to rivers has devastating effects and is known to completely destroy an aquatic habitat,<sup>2</sup> and it may also seep into groundwater and contaminate potable water source.

The synthetic dyes are further classified into several categories depending on their chemical structures and functional groups. Some of the major dye classes are basic dyes (triphenylmethane and thiazine dyes), acid dyes (Ponceau S and acid blue 25), reactive dyes (reactive orange 16 and reactive blue 19), direct dyes (congo red, direct blue 71) and azo dyes (pigment yellow 12 and Brilliant Scarlet 3R). There are many methods of treating dye

wastewater. Some of the examples include phytoremediation,<sup>3,4</sup> reverse osmosis, electrolysis, chemical degradation, adsorption and others;<sup>5,6</sup> however each method has its own advantages and disadvantages.

Reverse osmosis is high in operating cost, and the removal efficiency depends on the type of membrane material and pore size.<sup>7</sup> It was reported that membrane used for removing basic dyes may not perform the same way with acid dye.<sup>7</sup> Another disadvantage of the reverse osmosis is the resultant of a concentrated effluent.<sup>5,6</sup> Chemical degradation uses either oxidising or reducing agents which are not low-cost and it can result in mineralisation.<sup>5</sup> In addition, the degraded products can sometimes be more toxic than its original forms.<sup>8</sup> Adsorption method is one of the most researched methods due to its low cost and ease of usage. However the efficiency of adsorption depends on the adsorbent type. Our past studies involving agro-waste materials (e.g. Tarap fruit waste) and plant biomasses (water fern, *Nepenthes* leaves, *Casuarina* plant parts) were highly effective in treating basic dyes particularly the triphenylmethane dye class (e.g. methyl violet

2B, rhodamine B). However with the acid dye, the removal efficiency was much lower.<sup>9-14</sup> The maximum adsorption capacity reported for the removal of methyl violet 2B using *Azolla pinnata*,<sup>14</sup> soya bean waste,<sup>15</sup> *Nepenthes* leaves<sup>9</sup> and tarap fruit waste<sup>11</sup> were 199.4, 180.7, 194 and 263.7 mg/g, respectively, while the removal of acid blue 25 (AB25) using *Azolla pinnata* and soya bean waste were 50.5 and 38.4 mg/g, respectively.<sup>13</sup>

The aim of this research work is to investigate an alternative method for the removal of a selected acid dye (AB25) from aqueous solution by using a low-cost and sustainable method. Briefly, acid dye is one of the major classes of dye with wide applications in textile and cosmetic industries. The AB25 was chosen as the model acid dye for this experiment due to its harmfulness to the environment and it is also a very commonly studied acid dye. In this study, we proposed the use of seawater and various salts to cause aggregation of AB25 in aqueous solution. The proposed method is based on the concept of protein purification by the salting out effect, where salt concentration is increased which led to the decreased solubility of the protein.<sup>16</sup> The general explanation of this effect is that the high salt concentration allows more salt ions to interact with the water molecules, thus reducing the interaction of water molecules with the charged part of the protein, thereby leading to more protein-protein interactions.<sup>17</sup>

As for the case of the dye, the increase in the concentration of salts leads to the reduction of the thickness of the electric double layer surrounding the dye molecules. This forces the dye molecules to move closer to each other and provides higher probability of the molecules overcoming the electric force that keeps them apart.<sup>18</sup> In our previous study, we achieved a great success with a direct dye (direct blue 71) with a removal efficiency of 93% using a 40 times diluted seawater.<sup>19</sup>

The objectives of this study include studying the effects of various concentrations of monovalent salts, divalent salts and various dilutions of

seawater on the aggregation and removal of AB25 dyes from aqueous solution.

## 2. Experimental

### 2.1 Sample preparation and chemicals

Acid blue 25 (AB25) ( $C_{20}H_{13}N_2NaO_5S$ ,  $M_r$  416.38 g/mol, 45% dye content, Sigma-Aldrich) was used without further purification. The salts (NaCl, KCl,  $KNO_3$ ,  $Mg(NO_3)_2$  and  $CaCl_2$ ) (analytical grade) were obtained from BDH limited.

The seawater was collected from the Tungku Beach along the Muara-Tutong Highway in the Brunei-Muara District, Brunei Darussalam. The seawater was subjected to filtration using a Whatman No.1 filter paper to remove sand and other particles and the filtrate was then kept in an amber glass container away from sunlight.

### 2.2 Procedures for the aggregation of acid dye

A stock solution of 500 mg/L AB25 was first prepared, followed by preparing various concentrations of the salt solutions ranging from 0.001 M to 1.0 M. A total of 2 mL of the 500 mg/L AB25 was first transferred to a glass vial (final concentration of AB25 is 100 mg/L), followed by addition of distilled water with the salt added last whereby the total final volume of dye-salt mixture was 10 mL. The vials containing the dye-salt mixture were sealed using screw caps, hand-shaken and left to stand for 24 h. Duplicate were carried out for each salt. Similar procedures as mentioned above were used to investigate the effect of various dilutions of seawater on aggregation of AB25. After 24 h of standing, the dye-salt mixture was filtered using a Whatman filter paper No 1, and the filtrates were analysed at wavelength of 597 nm using a Shimadzu UV-1601PC UV-visible spectrophotometer.

Removal efficiency (RE) was calculated based on the following equation,

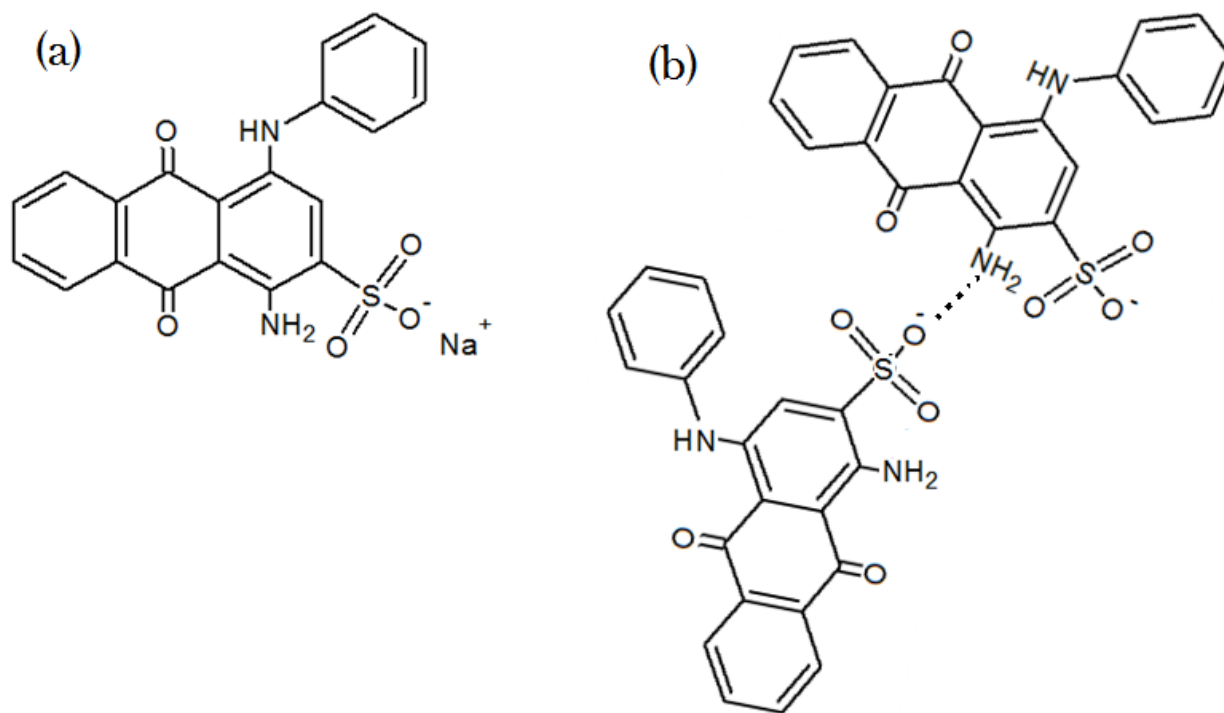
$$RE = \frac{(C_i - C_f) \times 100\%}{C_i} \quad (1)$$

where  $C_i$  is the initial dye concentration while  $C_f$  is the final dye concentration.

### 2.3 Surface morphology analysis

The aggregated dye obtained from the seawater treatment were collected, transferred to a glass petri-dish and dried in a desiccator. The dried sample was subjected to surface morphology analysis using a Tescan Vega XMU scanning electron microscope (SEM). The sample was gold-coated for 30 sec using a SPI-MODULE<sup>TM</sup> Sputter Coater.

## 3. Results and Discussions



**Figure 1.** (a) a typical depiction of the molecular structure of AB25 dye (b) possible interaction between two AB25 molecules.

**Figure 2** summarises the REs of AB25 (unadjusted pH, 100 mg/L dye) from aqueous solution by using various concentrations of monovalent and divalent salts. It can be observed that the increase of salt concentrations leads to the increase of the RE of AB25. At  $\text{CaCl}_2$  concentrations of 0.01 M and 0.1 M, the RE values increased rapidly at 53.6% and 83.7%, respectively. Beyond 0.1 M  $\text{CaCl}_2$ , there was a slower increase in RE, where the maximum was

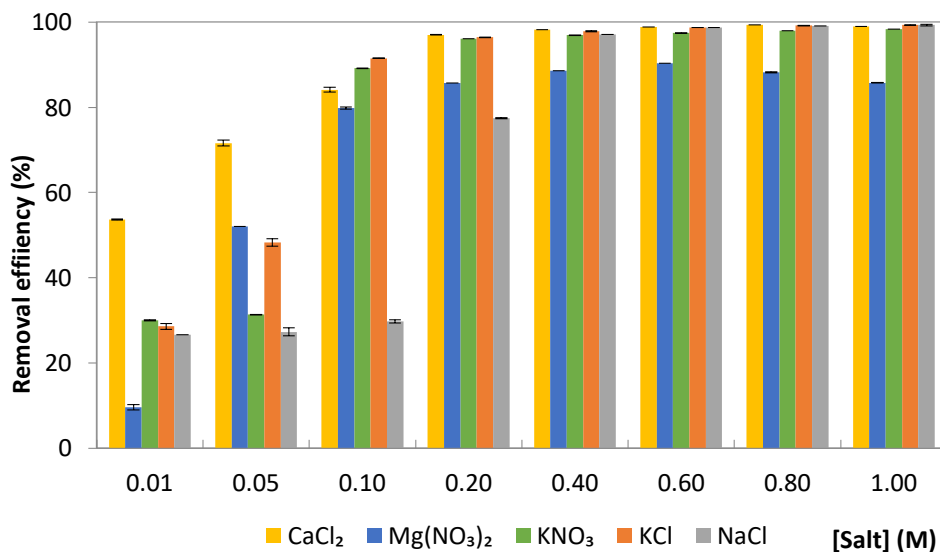
### 3.1 Effect of different concentrations of salts and seawater on AB25 aggregation

Not all acid dyes can form dye aggregates. For the dye to be able to aggregate, the dye needs to possess a positively charged amine group at the position which can interact with the negatively charged sulphonate anion group of another dye molecule without causing any steric hindrance.<sup>20</sup> The molecular structure of AB25 is as shown in **Figure 1a**, while **Figure 1b** shows the possible interaction between the sulphonate group of one AB25 and the  $-\text{NH}_2$  group of another AB25 molecule.<sup>21</sup>

achieved at 99.4% at 1 M  $\text{CaCl}_2$ . A similar pattern of the increase in RE was observed for the other divalent salt,  $\text{Mg}(\text{NO}_3)_2$ , but the RE was lower and peaked at 90.3%. The aggregated AB25 using  $\text{Mg}(\text{NO}_3)_2$  was also observed to be very fine particles as compared to those obtained using  $\text{CaCl}_2$  and other monovalent salts and they were able to pass through the Whatman No.1 filter paper. Similar patterns of the increase of RE were also observed with the increase in

concentration of the monovalent salts ( $\text{KNO}_3$ ,  $\text{KCl}$  and  $\text{NaCl}$ ), where their maximum REs were at 98.4%, 99.3% and 99.3%, respectively. When comparing among the three studied monovalent salts,  $\text{NaCl}$  was not as effective as  $\text{KNO}_3$  and  $\text{KCl}$  salts and it requires a higher concentration to achieve the same level of RE. Comparing between the divalent and monovalent salts,  $\text{CaCl}_2$

was able to achieve higher RE at lower salt concentration when compared to the other salts. This may be due to the capability of divalent cations to neutralise the charge of the dye aggregate more effectively (when compared to monovalent salts) and reducing the electrical forces keeping particles apart and allow easier agglomeration<sup>22</sup>.

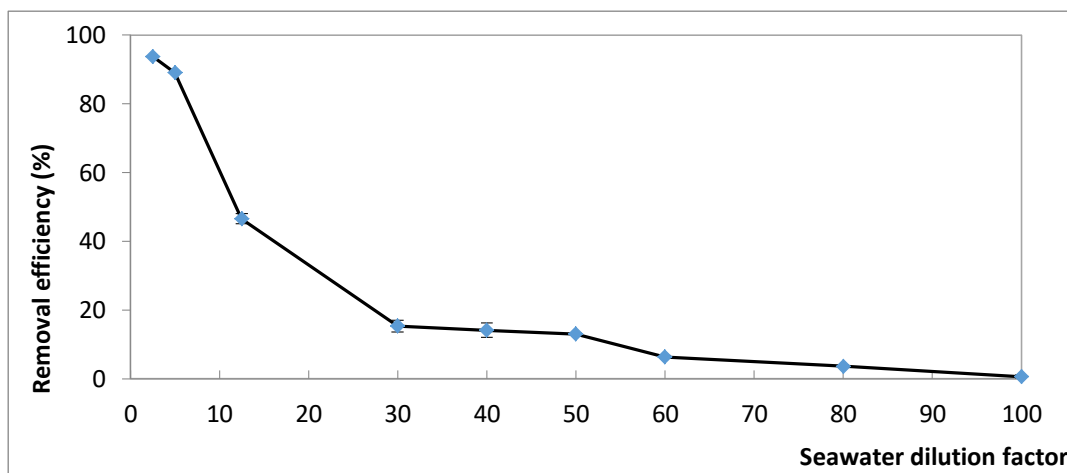


**Figure 2.** Removal efficiencies of AB25 (unadjusted pH, 100 mg/L dye) from aqueous solution by using various concentrations of monovalent and divalent salts.

The REs of 100 mg/L AB25 using various dilutions of seawater are as shown in **Figure 3** which shows a decrease in RE with increasing dilution of the seawater. A dilution factor (DF) of more than 50 did not result in significant removal of AB25 while the DF at 50x, 40x and 30x resulted in RE at 13.0%, 14.1% and 15.3 %, respectively. DF at 12.5x resulted in significant increase with RE at 46.5%. DF at 5x and 2.5x produced high RE at 89.0% and 93.8%, respectively. These data indicate that 1 part seawater can be added to 4 parts dye wastewater and yet achieve high removal efficiency. The high efficiency of seawater is most likely due to its high ionic strength that leads to the aggregation of AB25 to a particle size that can be easily filtered. Another possibility is the presence of trivalent cations in seawater, such as  $\text{Fe}(\text{III})$  and  $\text{Al}(\text{III})$ , that are known to be more effective as coagulants than monovalent cations up to 1000 times.<sup>22</sup> Therefore the combination of all

monovalent, divalent and trivalent salts in the seawater may enhance the overall process.

Comparing our proposed salting out method with other water treatment methods (photolysis, redox mediator and adsorption) as reported in the literatures the RE of using direct UV irradiation of AB25 (100 mg/L dye, pH 5.7) was estimated to be around 90%, however decolourisation reached 100% when  $\text{H}_2\text{O}_2$  was added.<sup>23</sup> The uses of redox mediators (laccases derived from fungal sources: *Myceliophthora thermophila*, *Polyporus pinisitus* and *Trametes versicolor*) (20 mg/L dye, pH 5.5 ) reported RE at 53.3%, 59.8% and 88.4%, respectively.<sup>24</sup> The adsorption of AB25 using *Azolla pinnata* (100 mg/L dye, pH 2.0)<sup>13</sup> and diatomite (100 mg/L dye, pH 2.0)<sup>25</sup> obtained RE at 40.8% and 60.0%, respectively. In summary, by using seawater method the RE is on par with the photolysis method (direct UV irradiation), but it performs better than the redox mediator and adsorption methods.



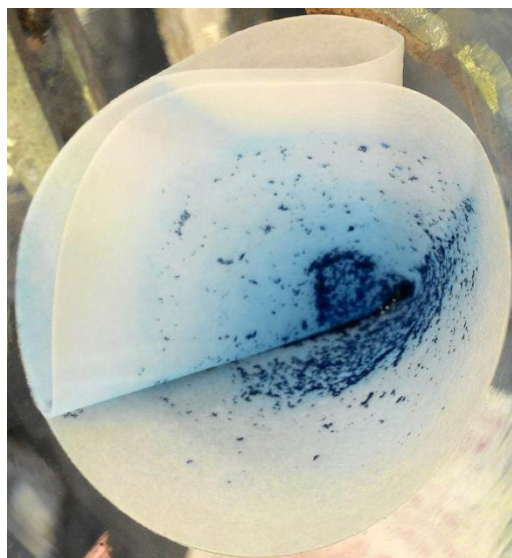
**Figure 3.** Removal of AB25 from aqueous solution using various dilutions of seawater.

### 3.2 Surface morphology analysis

Surface morphology analysis was carried out to characterise the aggregated AB25 (using seawater) collected on the filter paper as shown in **Figure 4**. The SEM image, as shown in **Figure 5**, helps to provide visualisation of the sample at higher magnification and resolution. The aggregated AB25 was observed to be irregular without definite shape and the surface appeared to be rough and folded. The mechanism for the formation of this structure is not known and is outside the scope of this study.

### 4. Conclusion.

This study used common salts and seawater to cause aggregation of AB25 to particle size large enough to be removed by simple filtration using filter paper. All the salts and seawater were able to produce high removal efficiencies proving that this method is effective and also a much simpler approach as compared to other methods as mentioned above.



**Figure 4.** Aggregated dye obtained using seawater was collected on a filter paper.

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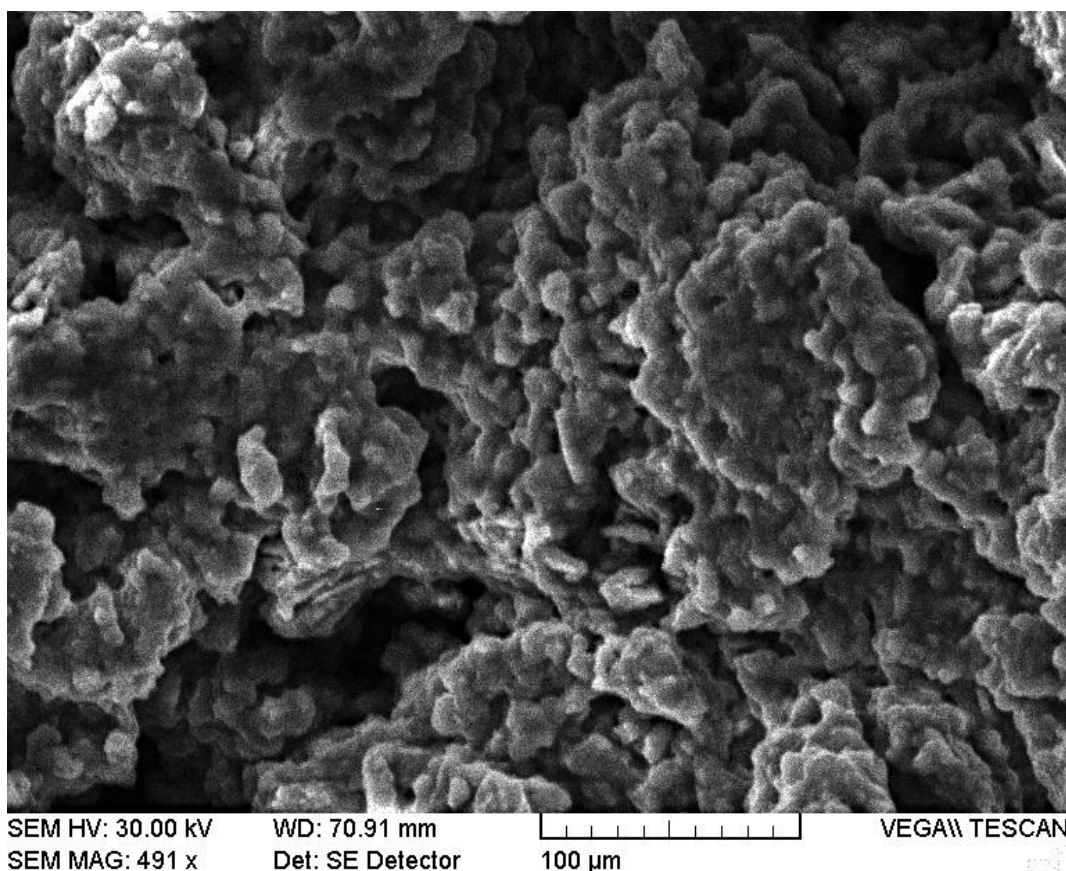


Figure 5. SEM image of the aggregated AB25 obtained using seawater under magnification of 491x.

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