

Remediation of direct blue 71 wastewater by salting out processes using inorganic salt solutions and seawater

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

This study investigates an alternative simple low-cost method of removing a hazardous dye, direct blue 71 (DB71), by changing the ionic strength of the aqueous solution (salting-out) via addition of various salt solutions of different concentrations as well as using seawater. This led to formation of dye aggregations which can be filtered. Investigation with inorganic salts revealed high removal efficiency with 0.6 M monovalent salts (KNO_3 , KCl and NaCl), while for divalent salts ($\text{Mg}(\text{NO}_3)_2$ and CaCl_2) only 0.001 M was required. High removal efficiency of 93% was achieved with 40x diluted seawater. Scanning electron microscopy reveals thread-like structure of the aggregated DB71.

KEYWORDS

Direct blue 71; dye aggregation; ionic strength; salting-out effect; seawater

1. INTRODUCTION

Among the industries, the textile and finishing industries resulted in the highest pollution of freshwater resources. Textile industry is very water intensive and an average size textile mill that produces 8000 kg fabrics per day consumes approximately 1.6 million liters of water, while the dyeing section contributed 15-20% of total textile effluents (Kant, 2012). The resultant textile dye wastewater is a great concern. Direct discharge of dye wastewater into open water bodies lead to irreversible ecological destruction, which is still a practice in some low-income developing countries (Ahmed et al., 2012). Remediation of such wastewater can be costly; however the remediation cost can be lowered by selecting economic-feasible treatment methods.

Direct dyes are usually applied directly to cotton, silk, wool as well as cellulosic fibres such as viscose, linen, jute, raime and hemp, without the need of mordants. They have high affinity toward cellulosic

fibres due to their flat, narrow and linear molecules that can enter pores of water swollen cellulose and orient themselves along the crystalline regions. Direct dyes are relatively inexpensive and provide wide range of hues and shades. Direct dyes are water soluble sodium salt of azo dyes which contain sulphonic groups, which differ from acid dyes, because the sulphonic functional groups are not involved in the attachment of the dye molecules onto the fibers (Needles, 1986). Majority of the direct dyes are disazo, trisazo and polyazo types. Two examples of the direct dyes are Direct blue 71 (DB71) and Congo red.

In aqueous solution, direct dye molecules often exist as aggregates, rather than single molecule. The degree of aggregation of direct dye is dependent on their chemical structure, electrolyte concentration and temperature. It depends on the type of the charged groups such as sulphonate anions and protonated amino groups, the number of charged groups and the positions of these groups in the molecule (Acton, 2013). An example of a direct dye with high degree of

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aggregation is direct red 28 due to protonated amino group and sulphonate anions at opposite sides of the dye molecule, while direct blue 1 has lower aggregation tendency due to the two sulphonate anions being close to each other (Acton, 2013).

The aim of this study is to aggregate a selected direct dye, DB71 (Figure 1), in aqueous solution by increasing the ionic strength of the aqueous solution and allowing the dye aggregates to grow large enough to be easily removed by simple filtration using filter paper. The addition of electrolyte is also known to aggregate organic molecules such as the humic acid (Wang et al., 2013). The objectives of this study include the application of various concentrations of monovalent and divalent salt solutions as well as various dilution of seawater to investigate their effectiveness in aggregation of DB71.

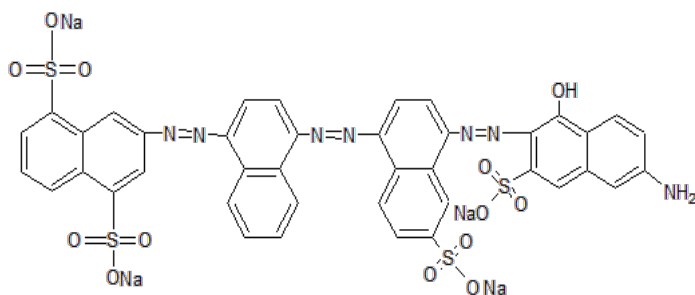


Figure 1. Molecular structure of direct blue 71.

According to the United States Geological Survey (USGS), 96.5% of global water are saltwater, located in the oceans, seas and bays, and are not suitable for drinking (United States Geological Survey, 2015). The major elements of the seawater (at 3.5% salinity) consist of 19400 mg/L Cl, 10800 mg/L Na, 1290 mg/L Mg, 904 mg/L S, 292 mg/L K, 411 mg/L Ca and 67 mg/L Br (Turekian, 1968). The idea of utilising seawater for remediation of certain dye wastes is an attractive idea due to the vast supply of such resources and global availability.

2. MATERIALS AND METHODS

2.1. Materials

Direct blue 71 ($C_{40}H_{23}N_7Na_4O_{13}S_4$, Mol.wt. 1029.87, 50% dye content) was obtained from Sigma-Aldrich and used without further purification. All the salts (NaCl, KCl, KNO_3 , $Mg(NO_3)_2$ and $CaCl_2$) were of analytical grade reagents and obtained from Merck and BDH limited.

Seawater was collected from the Tungku Beach in the Brunei-Muara District, Brunei Darussalam and was filtered using Whatman no.1 filter paper and stored in an amber glass container.

2.2. Procedures for aggregation of dye

A stock solution of 500 mg/L direct blue 71 (DB71) was first prepared. To investigate the effect of salt concentration on the aggregation of dye, various concentrations of salt solutions were prepared and mixed with the DB71 stock solution in glass vials. The final concentration of DB71 is 100 mg/L and the studied concentrations of salt ranged from 0.001 M to 1.0 M. The final volume of the dye-salt mixture is 10 mL. The mixture was agitated by hand and left to stand for 24 h. The mixture was then filtered with Whatman filter paper no 1. The filtrates were analysed for DB71 concentration using a Shimadzu UV-1601PC UV-visible spectrophotometer at wavelength of 594 nm. A similar procedure was adapted for the investigation of the effect of various dilution of seawater on aggregation of DB71.

2.3. Surface morphology analysis

The surface morphology analysis of the aggregated DB71 was carried out using Tescan Vega XMU scanning electron microscope (SEM). The aggregated dye caused by seawater was transferred to a petri dish and dried in an oven at 50°C. The sample was mounted on carbon conducting tape and gold-coated for 30 sec using SPI-MODULE™ Sputter Coater.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of salts and seawater on aggregation

Not all direct dyes form aggregates (Acton, 2013). The main reason for the ability of DB71 dye to form aggregate is due to the position of an amine group located at the end of the molecule, when protonated can interact and bond with any sulphonate anion groups of another DB71 molecule (Figure 1) (Acton, 2013).

The removal efficiency of DB71 from aqueous solution, based on the effect of the concentration of monovalent and divalent salts, are summarised in Figure 2a. The increase in the concentration of electrolyte decreases the thickness of the electric double layer surrounding the dye molecule and

this allows the dye molecules to move closer to each other and provides higher probability of the molecule overcoming the electric force that keeps them apart (Clark, 2011). This phenomenon is also known as the salting-out effect.

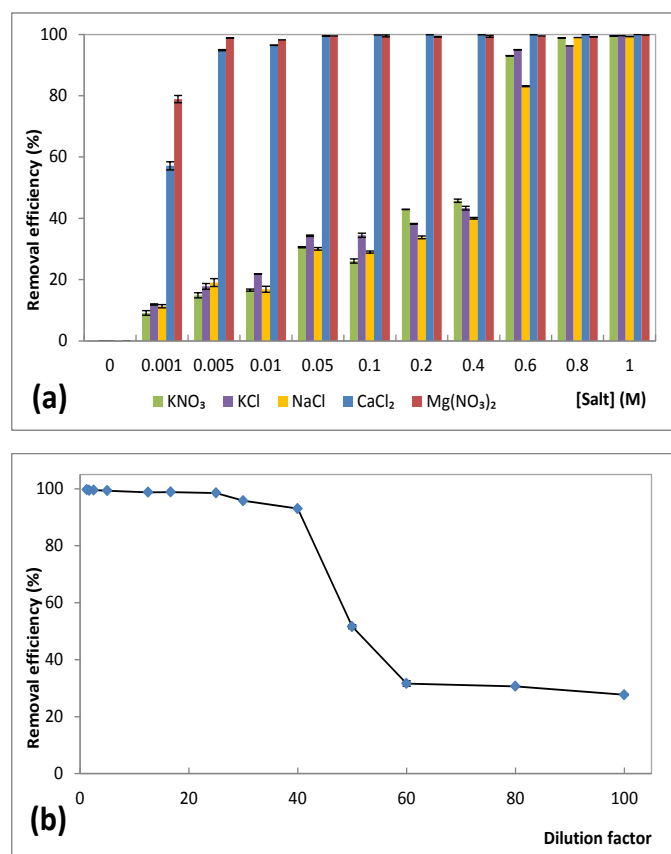


Figure 2. Removal efficiency of 100 mg/L DB71 based on the effect of (a) various concentration of salts and the type of salt, and (b) dilution of seawater.

Low concentrations of divalent salts at 0.005 M CaCl₂ and 0.005 M Mg(NO₃)₂ were able to cause aggregation large enough to be filtered off and resulted in removal efficiency of 94.9% and 98.8%, respectively. However, monovalent salts (KCl, KNO₃ and NaCl) required a relatively higher salt concentration of 0.8 M to achieve approximately the same level of removal efficiency. These results showed that divalent salts were more effective than monovalent salts in coagulation of dye aggregates. This behaviour can be explained by the ability of divalent cation to interact with the dye aggregates in two ways: by electrostatic attraction between positive charges of the cation and the sulphonate anion of the dye molecule, and complexation/bridging effect of divalent cations (Wang et al., 2013) leading to the formation of intra-molecular and inter-molecular ionic links between the anionic

group of the dyes (Shaffer and von Wandruszka, 2015). Divalent cations are also more effective in neutralising the charge of the dye aggregates, which lead to the reduction of surface charge of dye aggregate particles and thus reduce the electrical forces keeping particles apart and allow easier agglomeration (Binnie et al., 2002).

The removal efficiency of 100 mg/L DB71 based on various dilution of seawater is summarised in Figure 2b. Dilution factor ≥ 50 led to a huge decrease in removal efficiency. Between seawater dilutions from 60x to 100x, the removal efficiency changed slightly from 31.6% to 27.7%. The undiluted seawater resulted in removal of 99.6% of 100 mg/L DB71 and 40x diluted seawater maintained high removal efficiency of 93.0%. These data indicate that 1 part seawater can be added to 39 parts of dye wastewater and yet achieve high removal efficiency. The high efficiency of seawater is most likely due to its high ionic strength which promotes aggregation of particle to size that can be easily filtered. It may also be due to the presence of trivalent cations, such as Fe(III) and Al(III), which are known to be able to be more effective than monovalent cations up to 1000 times (Binnie et al., 2002).

There were few other remediation methods reported for the remediation of DB71 wastewater, which include adsorption (Bulut et al., 2007), Fenton's oxidation (Ertugay and Acar, 2013), catalytic degradation (Tabatabaee et al., 2011) and bioremediation using bacteria (Jin et al., 2009). Adsorption may be one of the most popular techniques which is one of the most researched methods in the last decade, covering a wide range of adsorbents for a wide range of pollutants (Wang et al., 2011). This technique may be good for removal of certain class of dyes such as basic dyes (Dahri et al., 2014; Kooch et al., 2016b; Kooch et al., 2016a; Chieng et al., 2015), however it is not effective especially for direct dyes. The adsorptive removal of 100 mg/L DB71 by using wheat shell achieved adsorption capacity of only 9.62 mg/g (Bulut et al., 2007). Fenton's oxidation reported an approximately 53% decolourisation of 100 mg/L DB71 (Ertugay and Acar, 2013), while catalytic degradation of 50 mg/L DB71 using lucunary heteropolyanion reported 87% decolourisation (Tabatabaee et al., 2011). Bioremediation using selected strain of *Escherichia coli* reported removal efficiency of approximately 82% for 150 mg/L DB71 (Jin et al., 2009). The removal efficiency of all these methods was still lower than the inorganic salt or seawater methods.

As mentioned earlier, seawater method is only applicable for dyes of functional groups similar to DB71,

due to the positions of the amine and the sulphonate groups. This work can be applied to many other dyes with the mentioned functional groups located at convenient positions. Congo red is another dye where high removal efficiency can be achieved by using seawater-aggregation method (preliminary data not shown). Details on the selection of highly aggregating dye species are available in the literature (Acton, 2013) and remediation of such dyes by adsorption, chemical oxidation and degradation methods may have little merits.



Figure 3. The aggregated mesh-like DB71 using undiluted seawater that settle at the bottom of glass vial before filtering with distilled water.

3.2 Surface morphology analysis

Figure 3 showed the suspended aggregated DB71 caused by seawater which had settled at the bottom of the glass container after 24 h. Formation of multiple thread-like appearances of the dye aggregates was observed with some suspended in the salt solution. The SEM image is as shown in Figure 4 which further confirms the formation of thread-like structure. The mechanism for the formation of this thread-like structure is not known and is outside the scope of this study.

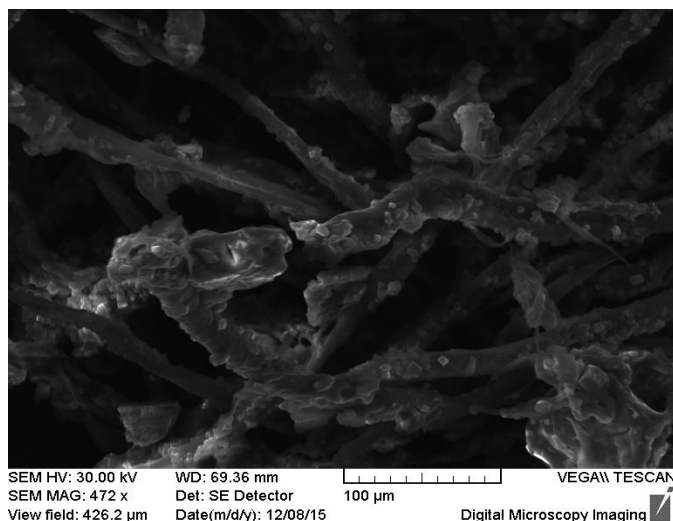


Figure 4. SEM image of aggregated DB71 with thread-like appearance at magnification of 472x.

4. CONCLUSIONS

The results of the present study indicated that efficient removal of DB71 was achieved by changing the ionic strength of the aqueous solution via addition of salt solutions, and allowing the aggregated dye to be filtered. High removal efficiency was achieved with 0.6 M monovalent salts (KNO_3 , KCl and NaCl), while divalent salts ($\text{Mg}(\text{NO}_3)_2$ and CaCl_2) only required 0.001 M. With 40x diluted seawater, a high removal efficiency of 93% was achieved. This method is perceived as a much simple, direct and more economically feasible when compared to other alternatives.

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