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REDUCTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION USING ZERO VALENT IRON

Gayatri. Pujar

Dept. of Environmental Engineering, KLE DR. M. S. Sheshgiri College of Engineering & Technology, Belagavi , karnataka, India

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Abstract - *The present investigation assesses the applicability of Zero valent iron for the removal of the toxic dye methylene blue from aqueous solution. The adsorption characteristics and dye removal efficiency of iron has been determined by investigating factors such as effect of contact time, concentration of the dye, amount of adsorbents, and pH. Up to 94.92% dye removal was attained by increasing the dose of adsorbent. Maximum 94.92% dye removal was achieved after 20 min, on adding 1 mg of iron to dye solution of MB having concentration 50 mg/L of 50ml dye solution. 99.46% dye removal was attained by increasing pH to 12 (alkaline range) by adding 1 g dosage in 15mg/L dye solution of 50ml.*

Key Words: **Methylene blue, reduction, iron particles, spectrophotometer, zero valent iron.**

1. INTRODUCTION

The wastewater generated from textile dyeing is a high-volume discharge having a high concentration of inorganic and organic compounds, as well as residual dyes. The presence of dyes in effluents might be a major source of worry due to their negative impact on a variety of organisms [1]. More than 1, 00,000 commercially accessible dyes are projected to be available, with over $7x10^5$ tons of dye material generated yearly. It's widely acknowledged that the public's impression of water quality is swayed by a variety of factors [2].The textile industry is responsible for a long list of negative environmental consequences. The release of volatile organic compounds, oxides of Sulphur and Nitrogen, particulate and dust resulting in pollution of air. Surplus quantities and undesirable composition, including high loads of organic materials, micronutrients, and heavy metals creating problem by textile sludge remained. The textile dyes color not only prevents penetration of light through water, resulting in a drop in photosynthetic rate but also effects [3]. Methylene blue may be one of the most well-known Redox indicators and also known as Tetramethylthionine chloride is a cationic Thiazine dye with the chemical name Tetramethylthionine. It is a deep blue with a distinctive hue change the oxidized state; Leukomethylene Blue (LMB) is a colorless simpler version of the compound. Triarylmethane, a caption dye with a net charge that leads to tumors, skin issues, and genetic diseases, it is quite hazardous. Thus, it is of significant importance to get removal of such hazardous caption dyes of contaminated water in order to protect marine life and reduce pollutants [3].

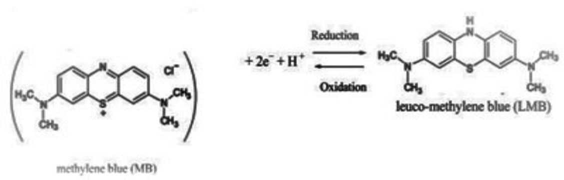
Iron particles have core that provides reducing power for reactions and an iron oxide coating that provides sites for adsorption and creation of chemical complexes. When ZVI and oxygen are present in the acidic solution, Hydrogen peroxide is formed, followed by Fenton reaction which produces the extremely reactive hydroxyl radical [4]. Zero valent iron (Fe^0) has established itself as a filtration system in ecological cleaning and sewage treatment can benefit from the use of this substance as filler over the last two decades.[5]

1.1 Reduction

The reduction of dye as well as oxidation of Fe^0 both process includes in organic removal by zero valent iron. By dissolution of zero valent iron, electrons are emitted.

$$Fe^{\circ} \rightarrow Fe^{+2} + 2e \text{ ....} \quad (1)$$

Organic contaminants are reduced using emitted electrons. Zero Valant Iron is known to convert MB to colorless LEUCO-METHYLENE BLUE (LMB), whereas LMB may be easily oxidized back into MB [6].



……(2)

As a result, the colorless product produced by Methylene Blue reduction likely is LMB. Followed by subsequent decolourization, the colorless solution was significantly recolored by aeration, as indicated below. As a result, the reduction of Methylene Blue to LMB is characterized as "Reduction" [6].

The zero valent iron surface adsorbs the dye molecule in the first step of dye degradation. In the second step, C_4H_5NS which is reductive cleavage of chronophers in MB is induced resulting in decolourization and mineralization continues.

$$MB + ne \rightarrow Intermediates + ne \rightarrow CO_2 + H_2O + Mineralization\ Products \text{ ....} \quad (3)$$

These processes take place on the Zero Valant Iron surfac and involves electron transfer via an iron oxide layer tha has developed just on surface. ZVI donates electrons to MI while Fe^0 reacts with H_2O to produce H atoms, which caus the chromospheres to cleave. ZVI treatment generates som of the reduced intermediates which are mineralize sequentially to CO_2, H_2O along with mineralization product To achieve complete mineralization of MB, the reductiv degrading capacity of Zero valent iron might not be stron enough [6].

2. MATERIALS AND METHODOLOGY

2.1 Preparation and calibration of synthetic dye solution

Methylene Blue Dye (MBD) powder($C_{16}H_{18}N_3SCl$) of molecular weight 319.85g/mol, Stock solution was prepared of concentration 100Mg/l by dissolving 0.1gram of MBD in 1 liter distilled water(Conductivity< 10 µS/cm). Stock solution is stored in air tight container to avoid UV degradation. Zero valent iron (ZVI) which is used for color reduction is brought from the cast iron factory of Udhyambag, Belagavi.

2.2 Batch Experiments

Several batch experiments were performed to know the removal efficiency of iron waste. The experiments were carried out with storage capacity 60ml plastic vials. 7 set experiments carried out at different concentration of methylene blue solution (50ml) with different dosages of iron waste, at different time intervals. The first set was carried out by adding 0.5gram ZVI in 50ml MBD solution of initial concentration 15mg/l with two samples and 1 control. Later, remaining experiments were carried out with 1gram dosage with different initial concentrations 15mg/l.25mg/l, 50mg/l at time intervals from 5mins to 60 min. Each set was rotated at 50RPM for different time intervals in vial rotor. At the end of reaction the samples was filtered and centrifuged for 10 min about 4000RPM. Concentration is determined by UV spectroscopy. The pH values of all the samples noted. One set of experiment repeated by adjusting pH to 12 by adding NaOH of 0.125 M (5 g) to 15mg/l.

2.3 Methodology

Standard solution of Methylene blue dye prepared by diluting 0.1 gm of MBD in 1L Distilled water for 100 mg/L stock. Calibration is done for different concentrations using UV-VIS spectrophotometer.

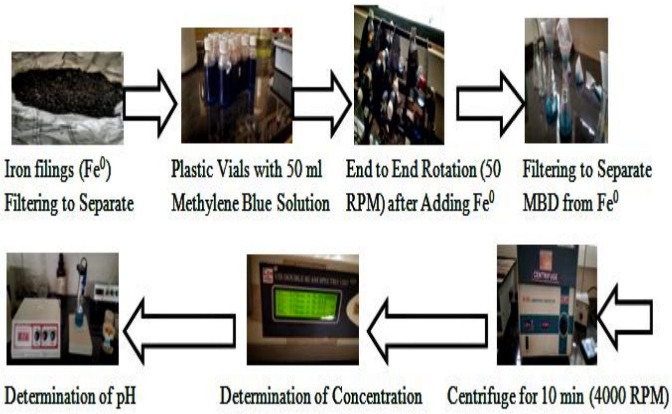


Fig -1: Step by step procedure of batch experiment

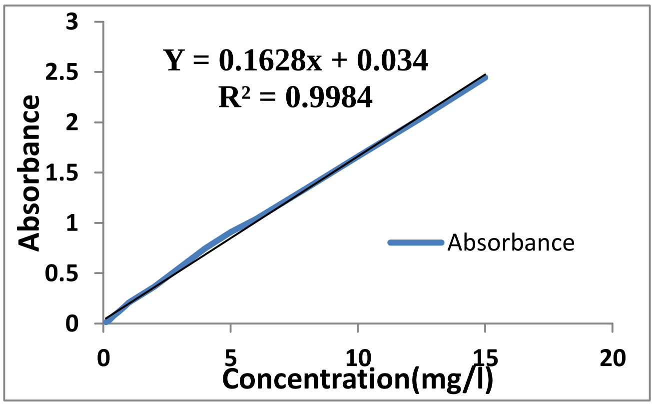


Fig -2: Standard curve of MBD from higher to lower concentration (150-0.1mg/L)

3. RESULTS AND DISCUSSION

3.1 Effects of initial concentration

The Fig 3 given below shows the reduction of methylene blue dye using dosage of ZVI of 0.5 g. The color reduced from 15mg/L to 2.3 mg/L. After 20 min there was no change in color reduction up to 60 min. Similarly 25mg/L reduced to 3.12mg/L in 20 min. 50mg/L reduced to 3.74mg/L. The pH was at 8.

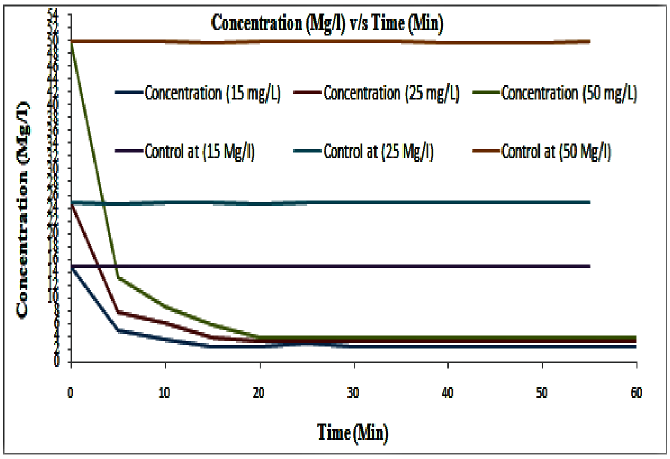


Fig -3: Effect of initial concentration of 0.5gm

The Fig 4 given below shows the reduction of methylene blue dye using dosage of ZVI of 1grams. The color reduced from 15mg/L to 2.24mg/L at optimum time 20 minutes. After 20 min there was no change in color reduction up to 60min. Similarly 25mg/L reduced to 2.36mg/L in 20 min 50mg/L reduced to 2.54mg/L. The pH was at 8.

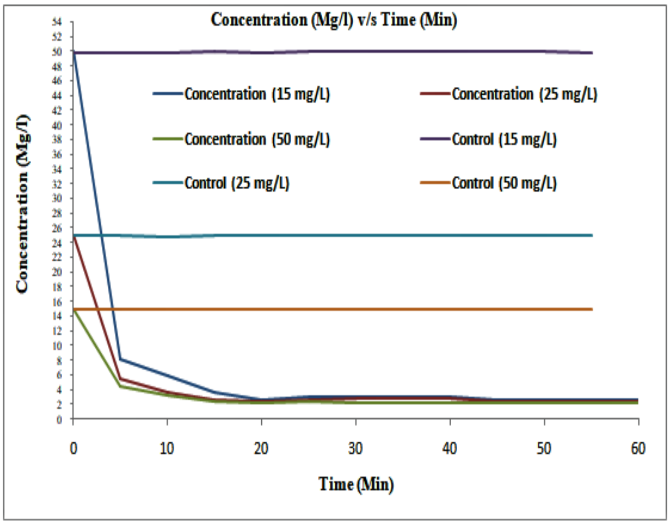


Fig -4: Effect of initial concentration of 1 gm dosage

3.2 Effects of dye removal efficiency

The effect of removal efficiency of methylene blue dye was studied by varying concentration 15, 25, 50 mg/L using scrap iron waste of 0.5 g at constant pH 8. From Fig 5, it can be observed that for 15mg/L, dye removed at about 84.66%. For 25 mg/l, showing reduction of 87.52 %. Lastly, for 50 mg/l shows color reduction of 92.52%.

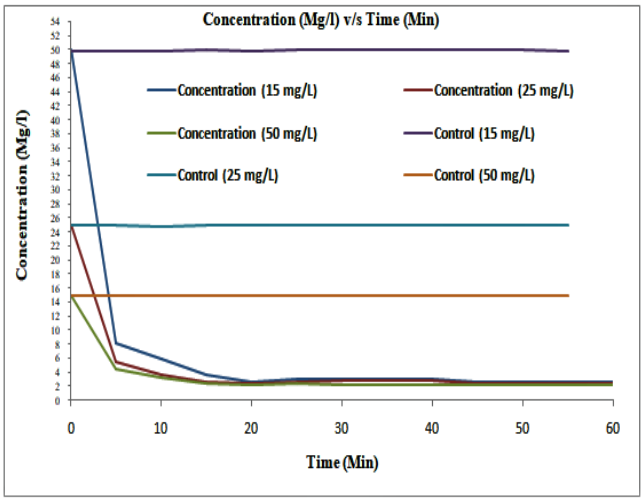


Fig -5: Dye removal efficiency of 0.5gm

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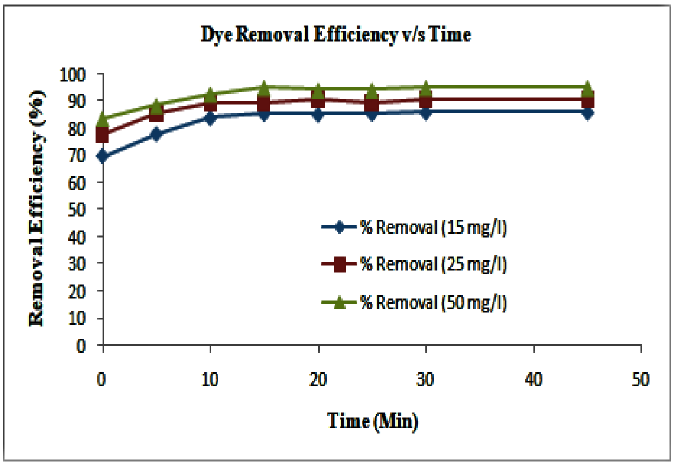

Fig -6: Effect of dye removal efficiency of 1 gm dosage

3.3 Effects of pH

The effect of pH on reduction Percentage was studied by varying the pH range from 8 to 12 by adding NaOH (0.125M) into MB solution. Initial concentration of methylene blue dye solution of 15mg/L and Dosage of reactant surface (iron waste) of 1 gram is used. From Fig 7, it can be seen that the percentage of removal efficiency of dye increased 99.46% with increase in pH. From experimental observation, it is noticed that though the reduction of color of dye is 99.46%, the color has turned from blue to purple blue as shown in Fig 7.

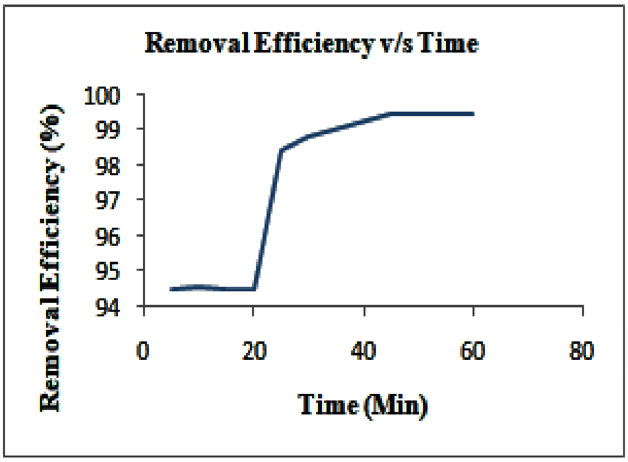

Fig -7: Effect of pH of 1 gm dosage

4. CONCLUSIONS

Methylene blue dye has been efficiently removed from its aqueous solution by a Fe^0 (iron filings) using batch techniques. Investigations on influence of various parameters such as contact time, Fe^0 dose, pH, and initial dye concentration on removal of MB have been carried out.

The removal efficiency was up to 92.88 % at pH 8 and 99.46% at pH 12 (alkaline range) for the contact time 60 min. From all the experimental results, it can be concluded that the reduction mechanism is responsible for dye reduction using Fe^0

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