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Removal of Methylene Blue Dye from Textile Wastewater using Activated Carbon Prepared from Rice Husk

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ABSTRACT: Textile industry is one of those industries that consume large amounts of water during the manufacturing process and, also, discharge great amounts of effluents with synthetic dyes to the environment causing public concern. Azo dyes are applied in textile industries, are considered to be serious health-risk factors. Several physico-chemical and biological methods for dye removal from wastewater have been investigated in the last decades. But, these treatment techniques need posterior separation process which significantly affects the economic performance of the plant. On the other hand, adsorption is one of the efficient methods and needs low capital and operational costs. Thus, this study investigates the potential use of low cost activated carbon prepared from the rice husk for the removal of Methylene Blue wastes. The rice husk was collected form rice mill and washed repeatedly until the dirty was eliminated. Then, it was heated at 500 ^oC for 30 min and the activated carbon had been activated with H_2SO_4 in order to make the carbon porous. A batch experiments were carried out in order to investigate the effect of various parameters. Uv-visibile spectrometer was used for the analysis of final concentration of the effluent. Experimental results have shown that, the amount of dye adsorption increased with decreasing the initial concentration, adsorbent dosage, contact time and temperature. Over 99% removal efficiency were achieved for the given dosage. With respect pH, pH value of 8-10 was found to be the optimal value.

KEYWORDS: Water Pollution, Rice husk carbon, Methylene Blue, Adsorption Isotherms, Sear's method.

1 INTRODUCTION

Water pollution due to color dyestuff industrial waste becomes a major concern worldwide. Many industries including leather and textile industries use dyes extensively in different unit operation. Main pollution in textile industries came from dyeing and finishing section. These processes require a wide range of input chemicals and dyestuff, which is generally an organic compound of complex structures [1]. There are more than 100,000 commercially available dye and more than $7x10^5$ tones per year are produced annually [1], [2]. Wastewater containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to biological degradation and are stable to light. There are different methods for the removal of textile effluents. The technologies for color removal can be divided into three major categories: biological, chemical and physical processes. The conventional biological treatment is the most economically used methods compared to other physical and chemical processes. However, biological treatment is incapable of obtaining satisfactory color elimination for concentrated wastes. This is due to their complex chemical structure and xenobiotic nature [4], [5]. Other studies complete decolourization however can be attained when applying anaerobic digestion through further non biological process [6]. The other most frequently used waste treatment method is chemical process such as coagulation, Fenton's process. But, chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates further disposal problem [7].

Different physical treatment techniques are also successfully tested, such as membrane-filtration processes (nanofiltration, reverse osmosis, electro dialysis) and adsorption techniques. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale industries [7],[8],[9]. Nowadays; adsorption is the most effective method of dyes removal technique using low cost adsorbents as it will be reviewed in next section. Adsorption is a well known equilibrium separation process for water decontamination applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design and ease of operation as review [4], [10],[11]. A researcher studies the adsorption of Congo red on carbon prepared from Neem leaf litter and Raw Neem Leaf. According to the authors, adsorption of Congo red on Neem leaf litter showed the highest adsorption capacities compared to any other adsorbents [6]. It was observed that the adsorbent is effective for the removal of anionic dyes in a wastewater treatment process. [12],[13] study activated carbons prepared from teak leaf, maize corn and babool tree bark were used to study adsorption of red industrial dye under various experimental conditions. The authors demonstrated that the adsorbents were effective for the removal of Methylene red industrial dye. Thus, the objective of this work is to investigate the potential of active carbon derived from low cost local available rice husk for the removal Methylene Blue dye from textile wastes.

2 EXPERIMENTAL SECTION

2.1 CHEMICALS AND MATERIALS

Analytical grade Methylene blue Dye (purchased from AMBALA Cantt-India) was used as adsorbant. Distill water was used to prepare mother solution. Concentrated H_2SO_4 (purchased BDH Chemicals Ltd, poole England) for activation of row rice husk carbon, iron(III)Chloride salt (purchased from Finkem laboratory) for imprigination , HCl (0.1M) (purchased from Whitehouse Industrialstate,Runcorn Cheshire) or NaOH (0.1M) (purchased from Avishaker) for pH adjustment were used. The required materials/appratus are beakers, pH meter (model: MP220, Toledo GmbH, Switzerland), Uv-visible spectrophotometer (model:I-290,intech), infrared spectrophotometer, oven (model:OV25OC-England), muffle furnace(TI5A,stuart scientific),grinding machine, shaker (VRN-480,Gemmy industrial crop, Taiwan), meshes,Erlmleyer flasks.

2.2 SOLUTION PREPARATION

An accurately weighed 1g of the dye dissolved in distilled water was used to prepare stock solution (1000 ppm). Solution used in the experiment for the desired concentration was obtained by successive dilutions. Dye final concentration was determined by using absorbance values measured before and after the treatment, at 668 nm with Uv-Visible Spectrometer (model: I-290, intech) [14].

2.3 BACH ADSORPTION EXPERIMENTS

The pH of the solutions was varied from 2 to 10, by adding 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) solutions for pH adjustment and measured using a pH meter(MP220.toledo, GmbH, siwtzerland). All the chemicals used were analytical grade. Batch mode experiments were conducted at a temperature of 25±2 ^{0}C by shaking 1g of adsorbent rotary shaker (VRN15OC-England) in 50 ml of Methylene blue solution of the desired concentration in 100 ml Erlenmeyer flasks. The flasks were agitated on a rotary shaker at 200 rpm for 2 h to ensure equilibrium. The influence of pH (2.0, 4.0, 6.0, 8.0, and 10.0), contact time (30, 60, 90, 120, and 150 min) and initial Methylene blue concentration (10, 15, 20, 25, 30mg⁄ l) on the performance of the rice husk carbon were evaluated. The Methylene blue concentration in the supernatant solution after the adsorption process was analyzed using a Uv– visible spectrophotometer(model:I-290,intech) by recording the absorbance changes at a wavelength of maximum absorbance (668 nm).The removal percentage (R%) of Methylene blue was calculated for each run using the following expression.

$$R(\%) = \left[\frac{C_i - C_e}{C_i}\right] \times 100 \ (1)$$

C_i and Ce were the initial and final concentration of Methylene blue in the solution. Under the experimental conditions, the adsorption capacity for each concentration of Methylene blue at equilibrium was determined by the following expression.

$$q_e\left(\frac{mg}{g}\right) = \left[\frac{C_i - C_e}{m}\right] V \ (2)$$

V is the volume of solution (in liters) and M is the mass of adsorbent (in grams) used.

2.4 CHARACTERIZATION OF ADSORBENTS (RHC)

Determination of pH Zero point charge: pHzpc was determined to investigate the surface charge of RHC. For the determination of pH_{zpc}, 0.01M NaCl was prepared and its pH was adjusted between 2.0 and 12.0 by using 0.01M NaOH/HCl. 100mL of 0.01MNaCl was taken in to 250mL Erlenmeyer flasks and 0.20 g of activated carbon was added to the solutions. These flasks were kept for 48 h and the pH of the solutions was measured by using a two-point calibration pH meter (model: MP220, Toledo GmbH, Switzerland). The results were then plotted between “pH final versus pH initial”. The point of intersection of the curves of “pH final versus pH initial,” is the pH_{zpc} of ARHC [15].

Determination of Surface area of Rice Husk Carbon: Surface area per gram of the ARHC and ARHC-Fe were obtained using Sear’s method, Sear’s 1956. For this 1.5 g of carbon sample was mixed with 100 ml of water and 30 g NaCl for both adsorbents. The mixture was stirred for five minutes. To this, 0.1 N HCl was added to make final volume of 150 ml and final pH of 4.0. It was then titrated against 0.1N NaOH. The volume (V ml) of 0.1N NaOH required to raise the pH from 4.0 to 9.0 [16]. The specific area (i.e. area per gm) was obtained using the formula:

$A = 32.V - 25$ (3)

Where A = Surface area of RHC per gram (in m^2/g)

V = volume of 0.1N NaOH required to raise the pH from 4.0 to 9.0.

3 RESULT AND DISCUSSION

3.1 CHARACTERIZATION OF ADSORBENT

Determinations of ph zero point charge: determination of pH_{zpc} was performed to investigate the surface charge of RHC. The result is presented in fig.1. As it can be seen in this particular study the pH_{zpc} is found to be 8.35. It is well reported that adsorption of cation is favored at ph > pH_{zpc}, while the adsorption of anion is favored at ph < pH_{zpc} was noted J. T. Nwabanne and M. I. Mordi, (2009).

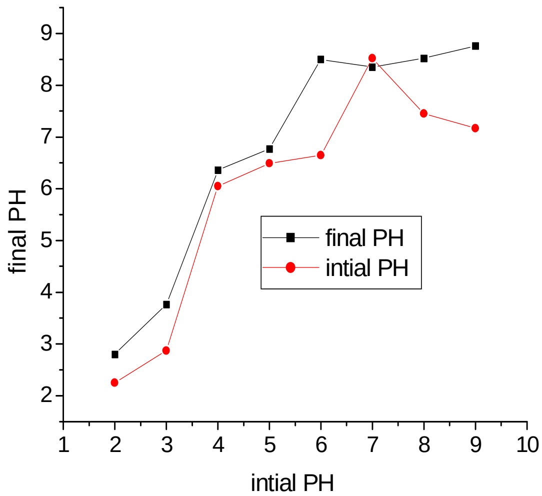

Fig.1. pH of zero point charge of activated rice husk carbon (ARHC)

3.2 SURFACE AREA ANALYSIS RICE HUSK CARBON (RHC)

The surface area of prepared carbon was determined using Sear’s method. Surface area per gram of the ARHC and ARHC-Fe adsorbent was found to be 615 and 679 m^2/g respectively. The surface area of the carbon after adsorption was decreased as the concentration of dye increase. This may be due to the tendency of formation of polymerized end products at high initial concentration.

3.3 EFFECT OF OPERATING CONDITIONS

Effects of initial dye Concentration: The effect of initial concentration on the removal efficiency of activated rice husk carbon was investigated over wide range of MB concentration. The results are presented in fig.2 and 3. As it can be seen in the figure, uptake of MB was rapid at lower concentration (10-15 mg/L) and as concentration increase the amount of MB adsorbed was decreased. Percentage sorption decreased (from 99.959 to 99.128) but the amount of MB adsorbed per unit mass of adsorbent increased (from 0.5 to 1.49 mg/g) with increase in MB concentration from 10 to 30ppm. On the other hand, when all the sites are occupied, this concentration adsorbed becomes nearly constant. This suggests that formation of monolayer on carbon surface. In fact, the more concentrated the solution, the better the adsorption capacity of ARHC as noted [15] With respect to the two active carbons the carbon impregnated with iron has higher sorption capacity of MB due to high porosity of adsorbent.

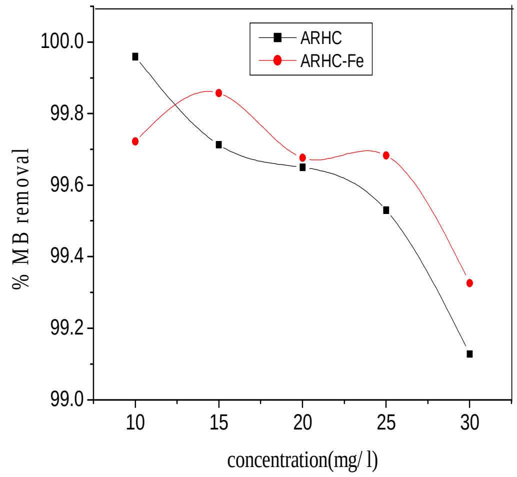

Fig.2. Effect of initial concentration the removal efficiency Methylene blue using treated rice husk carbon Conditions: pH = 8, t= 120 minutes, W_{AC}= 1g, and T= 25 ±2°C.

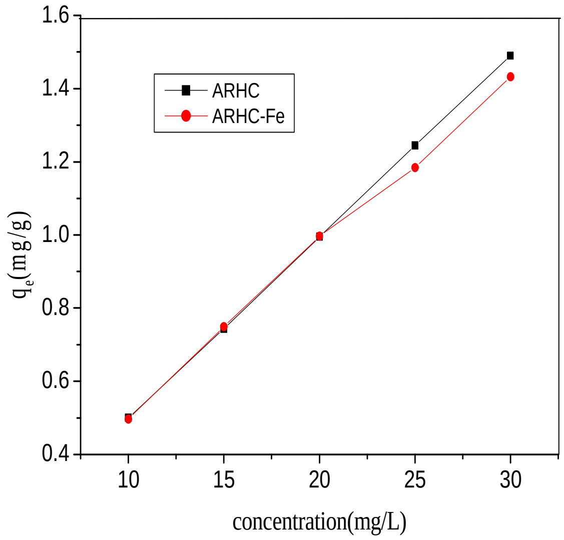

Fig.3. Effect of initial concentration on adsorption capacity of Methylene Blue using rice husk Carbon at 30 ppm. Conditions: pH = 8; t=120 minutes W_{AC}= 1g and T= 25 ±2°C.

Effect of Adsorbent Dosage: The effect of adsorbent mass on the adsorption of Methylene Blue dye was investigated. To this end, a series of adsorption experiment was carried out with different adsorbent dosages at initial dye concentration of 30 ppm. Fig. 4 and 5 presents the effect of adsorbent dosage on the removal of Methylene blue using ARHC and ARHC-Fe.

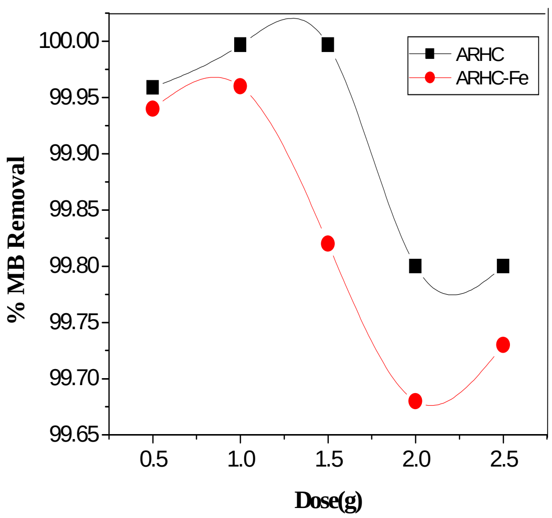

Fig. 4: Effect of adsorbent dosage on the adsorption efficiency of Methylene blue using ARHC and ARHC-Fe, at Co=30ppm. PH = 8, t=120 min, T= 25 ±2°C.

The results follow the expected pattern, in which the percentage sorption increased with the increased in adsorbent dosage until it reaches the equilibrium dosage (1g). On reaching equilibrium the percentage removal is decreased with increasing the amount of rice husk carbon. Several investigation demonstrated that although, increasing of adsorbent dosage leads to increase of active sites for adsorption, but this phenomenon may not lead to high adsorption capacity and adsorption efficiency of adsorbent due to the over load of the carbon area is decreased [17],[18]. It can be seen in fig. 5 that the adsorption efficiency of ARHC-Fe was lower than the ARHC. Increase of adsorbent dosage leads to increase iron content in active site so the iron may block the adsorption site of the activated carbon [19].

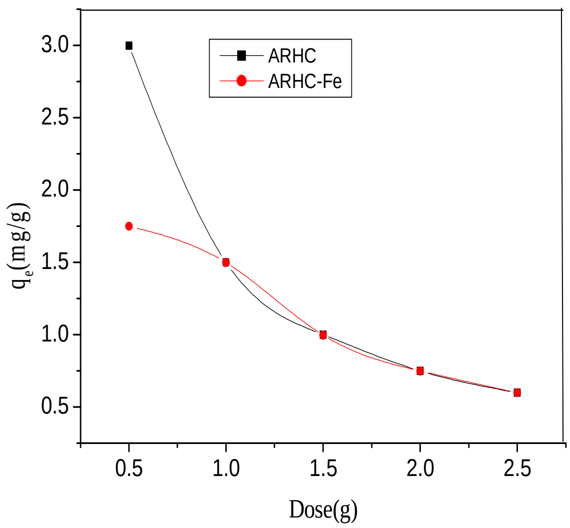

Fig.5. Effect of adsorbent dosage on the adsorption capacity of Methylene blue using ARHC and ARHC-Fe Conditions at Co=30ppm. pH = 8, t=120 min, T= 25 ±2°C.

Effect of contact time: The effect of contact time on the amount of dye adsorbed on the RHC is investigated at initial concentration of 30 ppm and temperature of 25°C. The system was subjected to an agitation speed of 200 rpm at different contact time. The result obtained is presented in fig. 6. As it can be seen a rapid adsorption of Methylene blue dye on ARHC and ARHC-Fe was observed at the initial stages of the adsorption and equilibrium is attained within about 120 min. Such uptake indicates high degree of affinity towards dye molecules via chemisorptions. After the rapid uptake, the capacity of the adsorbent became exhausted and the adsorption would be replaced by the transportation of dye from the external sites to the internal sites of the adsorbent particles. Similar results were reported elsewhere [14], [20].

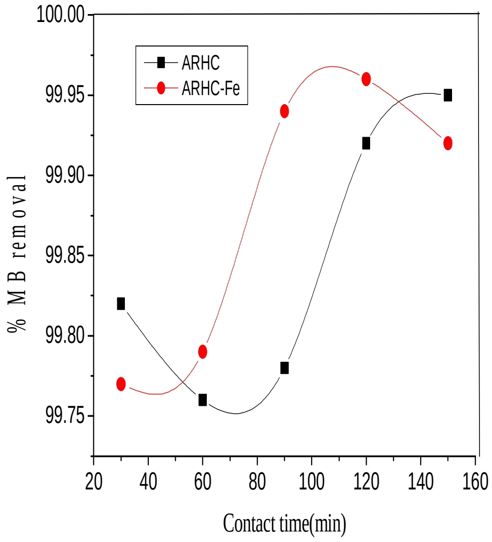

Fig. 6. Effect of contact time on the adsorption efficiency of Methylene blue using ARHC and ARHC-Fe Conditions: C_0=30 ppm, PH =8, D= 25 ±2°C, W_{AC}=1g

Effect of pH: Studies were carried out to see the effect of pH on adsorption MB on ARHC in the pH range of 2-10. The pH of the solution was maintained by adding hydrochloric acid or sodium hydroxide. The result obtained at 30 ppm initial concentration using ARHC and ARHC-Fe is shown in Fig.7. As it can be seen in figure 7, the removal of Methylene blue increased with increasing of pH of mother solution. Lower adsorption of Methylene blue at low pH is probably due to the presence of H^+ ions competing with the cations groups on the MB for adsorption sites, there by inhibiting the adsorption of dye.

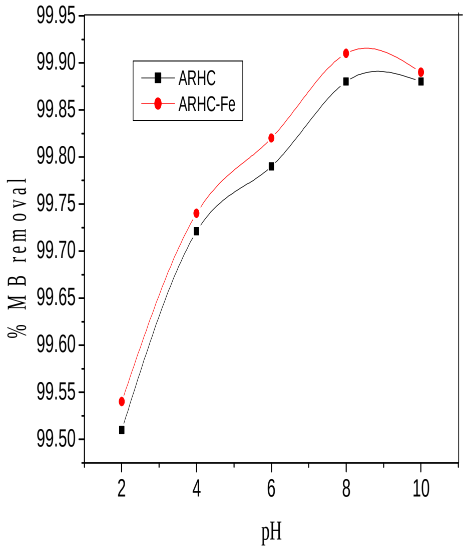

Fig.7. Effect of pH solution on the adsorption efficiency Methylene blue using treated ARHC and RHC-$FeCl_3$ at Co=30 ppm. , W_{AC} = 1g, t=120 minutes and T= 25±2°C.

As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged Metheylene blue and the surface of the activated carbon is lowered; this may result in an increase in the rate of adsorption as reported [21],[22].

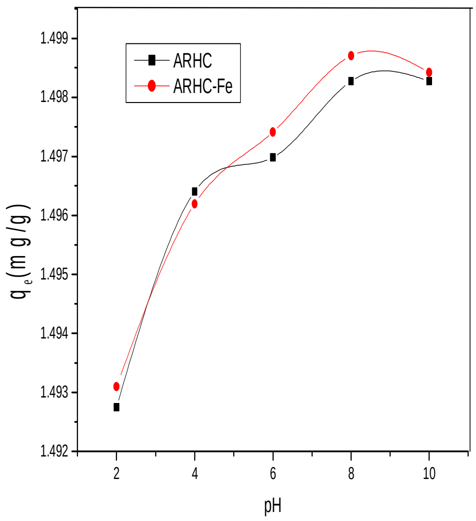

Fig. 8. Effect of pH solution on the adsorption capacity Methylene blue using treated ARHC and RHC-FeCl$_3$ at Co=30 ppm. , W$_{AC}$ = 1g, t=120 minutes and T= 25±2°C.

Effect of temperature: To study the effect of temperature on the adsorption of dye over RHC, several experiments were performed at temperatures of 10 ^{0}C, 20^{0}C, 30^{0}C, 40^{0}C and 50^{0}C. Fig.9 presents the influence of temperature on the adsorption of dye onto RHCs. As it can be seen in fig.9, removal of MB decreases with increasing temperature. This suggests that the adsorption of MB on ARHC follows exothermic process. A similar result was reported elsewhere [23].

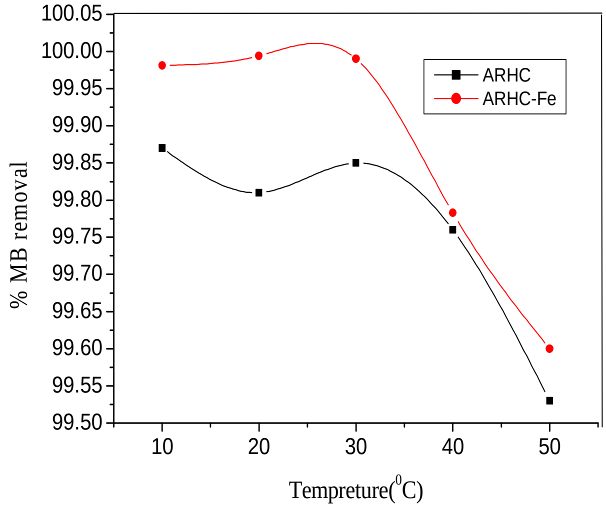

Figure 9: Effect temperature on the adsorption efficiency Methylene blue using treated ARHC and ARHC-Fe at Co=30 ppm. , W$_{AC}$ = 1g, t=120 minutes and PH = 8.

4 CONCLUSION

In this study, ARHC with and without iron impregnated was tested and evaluated as a possible adsorbent for removal of Methylene blue dye from its aqueous solution in a batch adsorption experiment. The adsorption experiments were conducted for a wide range of solution pH, adsorbent dosage, temperature, initial concentration and contact time. It was observed that the percentage removal of Methylene blue dye decreased with an increase initial concentration, adsorbent dose and temperature while it increased with increase in solution pH and contact time. To this end, over 99% removal efficiency of Methylene blue dye was achieved at solution pH around 8. This suggests that both ARHC and ARHC-Fe can be used in the removal of dyes from textile waste water.

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