Methylene Blue removal from Aqueous Solutions by using Rice Husk Ash (RHA) and Peanut Shell Ash (PSA)

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Abstract

Methylene blue (MB) adsoption study using Rice husk ash (RHA) and Peanut Shell ash (PSA) were investigated The effect of different parameters such as initial pH, contact time, adsorbent dose, dye concentration were studied. The adsorption % efficiencies of Methylene Blue on RHA and PSA were 84.5 % and 83.5 % respectively (in 120 minutes on 0.2 g adsorbent). The results further revealed that adsorption of MB on PSA and RHA occur by both physisorption and chemisorptions processes. The comparative studies revealed that both the adsorbents have similar removal efficiencies in 120 minutes. However, RHA has faster rate of adsorption as compared with PSA. Therefore, it is concluded that both the RHA and PSA are good adsorbents for the removal of MB in water.

***Keywords*:** Methylene blue, Rice husk ash, Peanut shell ash, water

1. Introduction

The dyes can adversely affect many forms of life therefore their presence in the effluents is of great concern. They are hazardous to both aquatic organisms and human. Therefore, it is indeed important to remove these coloured contaminants from waste water [1].

The conventional methods for the treatment of dye are physical, chemical and biological treatments namely reverse osmosis, electrolysis, coagulation and flocculation. Mostly they are not applicable on large scale because of the disposal problems as large amount of sludge is been generated. Furthermore, these conventional methods are not cost effective [1, 2]. This technique can handle fairly large flow rates, producing a high quality effluent that does not result in the formation of harmful substances, such as ozone and free radicals [3]. It is reported that the adsorption techniques are more efficient than other physical and chemical treatments [3, 4]. Additionally, this process can

remove different types of pollutants and has a wider applicability in pollution control. Presently, the trend has been shifted to the use of naturally available materials as adsorbents at the tertiary stage of effluent's treatment. Agricultural by products and waste materials have been used for removal of methylene blue from aqueous solution include yellow passion fruit waste [5], rice husk [6], hazelnut shell [7], garlic peel [8], mango seed kernel powder [9], and peanut hull [10].

Previous research efforts have focused on the adsorption technology for the dye remediation from wastewater [11]. Adsorption process is quite simple and highly efficient. It has found to be an effective method for removal of dye from wastewater. Basic dyes are cationic in nature. Therefore, they have affinity towards materials with negatively charged functional groups. Methylene blue (MB) is a cationic dye used for dying cotton, paper, hair colorant and wool [4]. A number of low cost adsorbents such as, rice Husk, rice hull ash, date pit, Neem leaf powder leaf and cotton fiber have been used for the removal of Methylene Blue from aqueous solutions [1, 12].

This paper aims to study the effectiveness of Removal of Methylene blue (Cationic dye) by using RHA and PSA. Many low cost adsorbents have been reported in literature for the removal of Methylene Blue including Raw rice husk, rice husk ash and Peanut shell [1, 4, 6, 12, 13]. To the best of our knowledge PSA has not been previously used to study the removal of MB. This study will help to compared to different types of materials and to understand the mechanism of adsorption of MB on both materials. Chemically, RHA is rich in silica content [14] while PSA has low silica content [15]. Therefore, while comparing the adsorption process at different pH values and relating to their point of zero charges, this study may provide useful information of adsorption processes on two different types of adsorbents.

Experimental

1.1. Materials and Reagents

Methylene blue used in this work was obtained from May & Baker, U.K. All the chemicals were of analytical grade and were used without further purification. 0.1 N HCl and NaOH were used for the adjustment of pH of solutions. Ultrapure deionised water was used throughout the study. The Rice Husk and peanut shells were purchased from the local market.

1.2. Preparation of Ashes

The rice husk and peanut shell obtained from a local market were washed with distilled water and were dried in air for 48 hrs. After washing and drying it was placed in a furnace at 600^{o}C for 6 hrs. The powered material obtained was dipped in 0.1 M nitric acid for 24 hrs. It was then filtered by using suction filtration assembly and was washed thoroughly with deionised water until a constant pH was

obtained [14] and the solution becomes colourless. It was then dried in an oven at 110^{o}C overnight.

Materials characterization

The surface morphology of RHA and PSA was studied by using Scanning electron microscope (SEM), Model, JSM-6010LA. The point of zero charge of catalyst was determined by mass transfer method [16].

2.3 Batch experiments

The adsorption experiments of MB were conducted in 100mL glass-stopper Erlenmeyer flask, to which 100mL of MB solution (20mg/L) was added. Weighted amount of adsorbent was added in the flask. The pH of the solutions was adjusted by using 0.1 N HCl and NaOH. The flask was placed in an orbital shaker (PA-16250, Pamico Technologies). The experiments were performed with an agitation speed of 130 rpm. The temperature was kept constant for all experiments (30^{o}C). For this purpose the orbital shaker was placed in an incubator (Memmert 854, Schwabach, Germany).

The MB Removal efficiency was determined by using following formula

Removal efficiency % = $100*(A_o - A_t)/A_o$

Where A_o = Absorbance at time 0

A_t = Absorbance at time t

2.4. Analytical procedures

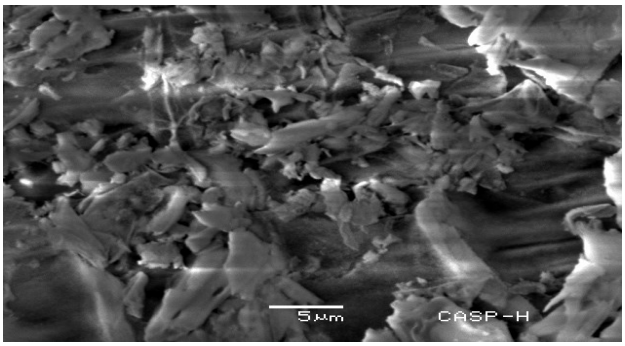
2.4.1. Methylene blue concentration

Concentrations of Methylene blue were determined by UV-Vis spectrophotometer (UV-1201, Shimadzu). The λ_{max} was determined before the analysis and was found to be 664 nm. It is important to mention here that calibration curves were prepared before analysis, both the intraday and inter-day validations were studied.

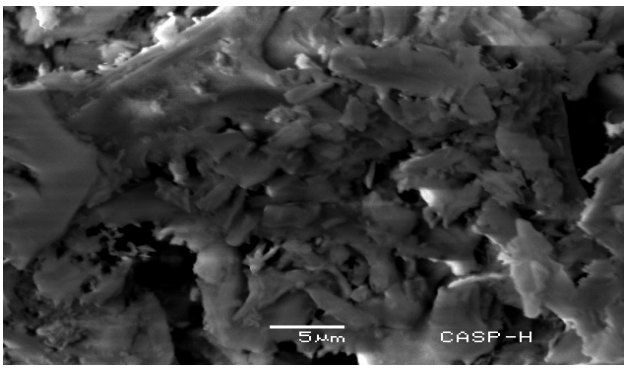
Results and discussion

3.1. Adsorbent characterisation

The point of zero charge was determined by mass transfer method and was found to be 3.3 for RSA and 9.1 for PSA. The SEM images of Both RHA and PSA (Fig 1a,b) have been taken. This indicates the porous nature of RHA and PSA.



(a)



(b)

Figure 1 SEM images of (a) RHA (b) PSA

3.2. Effect of various Parameters

3.2.1. Effect of pH

In order to study the effect of initial pH on the removal efficiency of adsorbents, solutions of various initial pH values (2, 4, 6, 8, 10) were prepared. The effect of solution pH on the removal efficiency using PSA and RHA are shown in Figure 2.

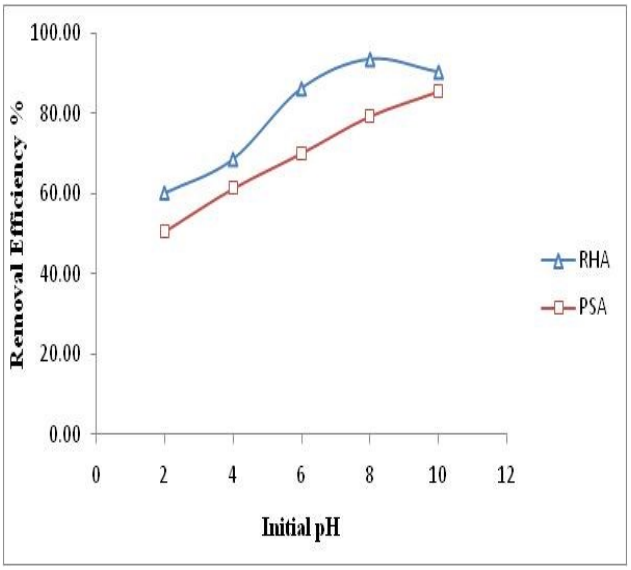


Figure 2 Effect of initial pH on the removal of methylene blue ($C_{o\ (MB)}$ =20 mg/L; T = 30^{o}C; pH= 2, 4, 6, 8, 10; V = 100 mL; Time = 60 minutes; adsorbent dose = 0.2 mg/L)

The result indicates that the removal of MB increased with the increase of pH of the solution. For example at pH 2.0, the removal of MB was found to be 50.45% and 60.21% for RHA and PSA respectively in 60 minutes and it was 79.12% for PSA and 93.39% with RHA. It is important to mention here that RHA has higher adsorption % efficiency (60 minutes) as compared with PHA. This may be due to the quick adsorption on negatively charged silica (RHA) [6]. With the further increase in pH of solution the process of adsorption slows down in the case of PSA and while in the case of RHA slight decrease in adsorption was observed, this may be due to the influence of hydroxide ions in the solution [6]. It is hypothesised that at higher pH values hydroxide ions may solvate the positively charged MB. Therefore, adsorption on negatively charged alumina may be lower. Therefore, pH 8 was considered as optimum pH value is selected as 8.

3.2.2. Effect of Contact Time

The results presented in Figure 3 clearly suggests that the adsorption efficiency of MB on both the adsorbents increases with time and rate of adsorption was rapid at initial stages and becomes slow with the increase in time, till saturation occurred. The results further indicate that equilibrium can be assumed to be achieved after 1 hour (60 min) for RHA and more than 120 minutes for PSA. This shows that adsorption on RHA may be a quick process as compared with peanut shell ash. This may be attributed due to the different chemical nature of adsorbents. As RHA may have strong electrostatic forces of attraction between the positively charged MB and negatively charged RHA at studied pH. While PSA has low silica content as compared with RHA [15]. Silica content may accelerate the adsorption process as this may be due to the surface charge on silica at studied pH. At studied pH the surface of silica

will be negatively charged and it may adsorb more positively charged dye through electrostatic forces of interactions [15].

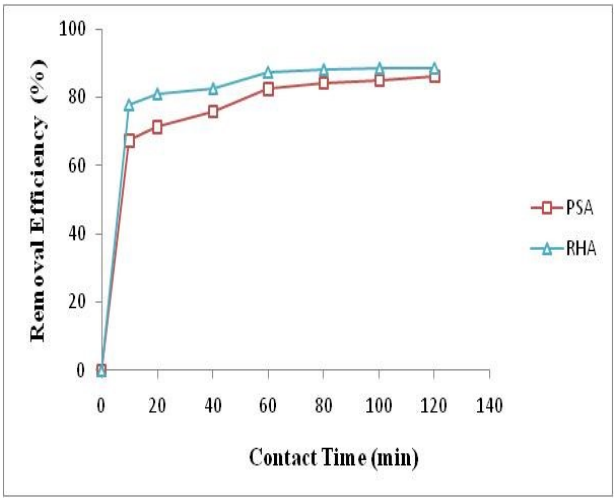


Figure 3 Effect of contact Time ($C_{o\ (MB)}$ =20 mg/L; T = 30°C; pH= 8.0; V = 100 mL Time=20, 40, 60, 80,100,120 minutes; adsorbent dose 0.2 mg/L)

3.2.3 Effect of Adsorbent dose

The adsorbent dose affects the amount of dye adsorbed on the surface of the adsorbent [10]. The results presented in figure 4 shows that the adsorption % efficiency of MB increases with the increase in adsorbent dose for both adsorbents, this is because of the increased availability of active sites for the adsorption of MB [6]. However, after 0.4 g adsorbent the rate of adsorption slows down. This may be due to the lesser availability of MB in the solution [6]. As with the increase in adsorbent dosage most of the MB in solution was adsorbed in first few minutes and lesser MB may be available in solution to adsorb on adsorbent [6].

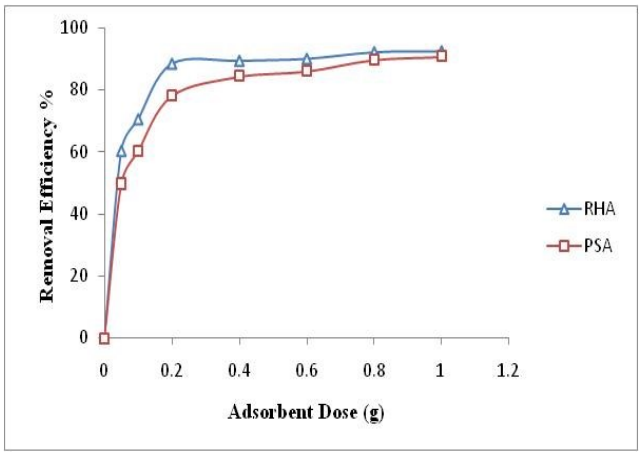


Figure 4 Effect of Adsorbent Dose ($C_{o\ (MB)}$ =20 mg/L; T = 30°C; pH= 8.0; V = 100 mL Time=60 minutes; adsorbent dose 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1 mg/l)

3.2.4 Effect of Initial Dye Concentration

The adsorption rate also depends upon the concentration of dye present in the solution [6, 17]. Experiments have been carried out with different concentrations of dyes from 10-200 mg/lit in order to understand the relationship between the removal efficiency and initial dye concentration. It is clear from the figure 5 that with the increase in dye concentration the removal efficiency increases. Similar trend has been observed in the case of PSA (Fig 5). Previous studies on MB removal using RHA also show similar results [6].

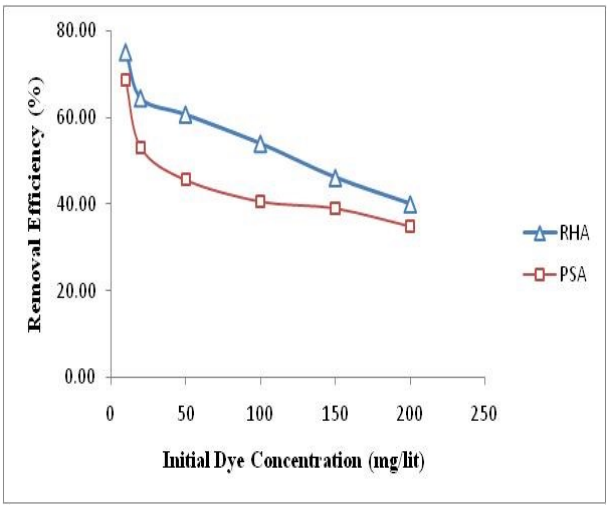


Figure 5 Effect of Initial Dye concentration ($C_{o\ (MB)}$ =10, 20, 50,100,150,200 mg/L; T = 30°C; pH= 8.0; V = 100 mL Time=60 minutes; adsorbent dose 0.2 mg/L)

3.2.5 Adsorption Isotherms

Langmuir adsorption isotherm graph is plotted. The linear regression was conducted using plot l/qe v/s 1/Ce, it was found that R^2 values are closer to 1 but Langmuir adsorption isotherm is best fit for PSA as compare to RHA.

Freundlich adsorption isotherm graph is plotted. The linear regression was conducted using plot log q v/s log C. It is clear from the figure and linear regression value that Freundlich adsorption isotherm is best fit for the data of RHA as the R^2 value is more.

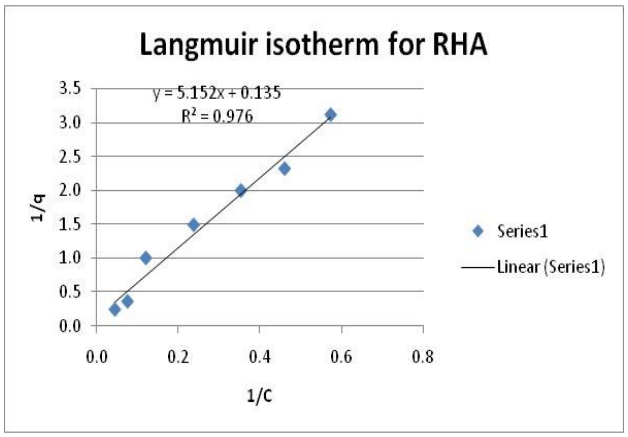


Figure 6 Langmuir isotherm for RHA

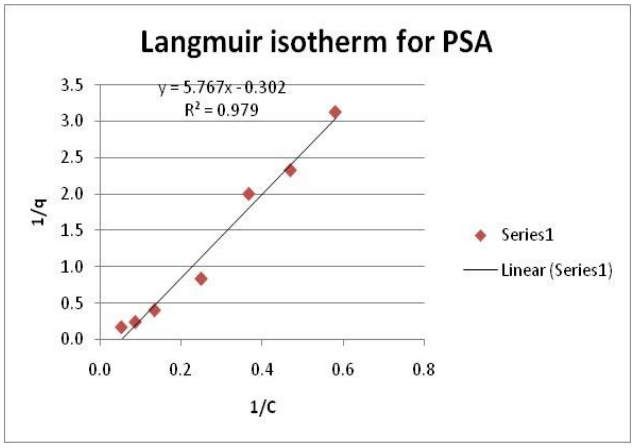


Figure 7 Langmuir isotherm for PSA

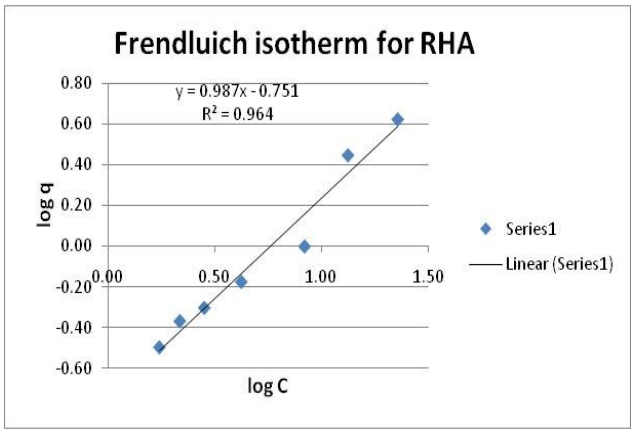


Figure 8 Frendluich isotherm for RHA

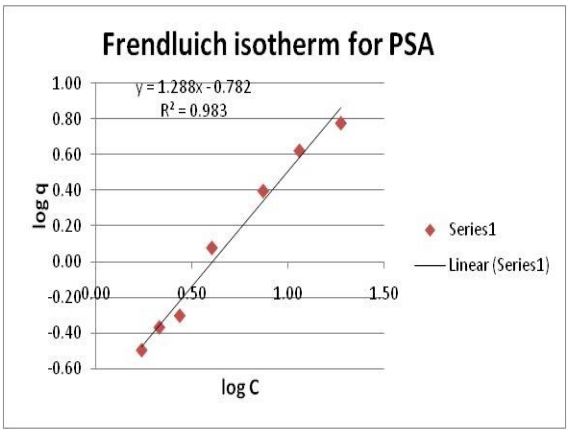


Figure 9 Frendluich isotherm for PSA

4. Conclusions

1. Both the rice husk and peanut shell ash are good adsorbents for Methylene blue removal. The adsorption of Methylene blue is a pH dependent process on both adsorbents and is increases with the increase in pH. Furthermore, it was observed that RHA also shows good efficiency in less time than that of PSA. Langmuir isotherm model is found to best fit to the experimental data of PSA and Freundlich isotherm model is best fit to RHA.

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