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Adsorptive removal of methylene blue dye from soapnut shell & pineapple waste derived activated carbon

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Abstract

The methylene blue (MB) adsorption from the aqueous solution on activated charcoal from soapnut shell & pineapple waste were studied in batch mode. The influence of a major parameter determining the efficiency of the process, such as the initial concentration, the adsorbent dose and the contact time on the removal process, was studied. Experimental studies have shown that the adsorption capacity of methylene blue increases with the increase of the adsorbent dose and decreases with the increase of the initial concentration. The equilibrium time of 120 min was observed. The considered optimal dose for removing methylene blue from aqueous solutions from soapnut shell & pineapple waste were 0.6 g & 1g respectively. The equilibrium data corresponds precisely to the Langmuir isotherm.

Keywords: adsorption, methylene blue, soapnut shell, pineapple waste, langmuir isotherm

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1. Introduction

Polluting effluents by various chemical industries like the textile, color dye, cosmetic & beauty product, paper and pulp and food processing industries contains significant amount of coloring agent and these harmful coloring agents transported to surface water streams that can cause various environmental and ecological problems (Singh, Mohan, Sinha, Tondon, & Gosh, 2003). “Water is life” but over the time water is also become source of various problems because of anthropogenic activities. Day by day more and more pollutant increasing in water resources, pollution condition become worsen when it comes to developing countries.

Dye is one of toxic pollutant and it needs to remove from wastewater before it discharges in water resources (Öden & R, 2014). Dyes cause carcinogenic effects on human body due to their toxicity. Ecological system of aquatic biota is highly sensitive to sunlight reaching up to plants inside the aquatic body and we know even very low amount of dyes can cause huge difference in strength of light passing through it. For example, less than 1ppm concentration of methylene blue dye can reduce light up to that limit where photosynthesis can be prohibited, so this is very important to remove dyes from wastewater before it discharges to water bodies (Patil, Renukdas, & Patel, 2011; Singh et al., 2003). Many methods and advanced technologies are developed in last few decades for wastewater treatment such as chemical precipitation, various filtration technology, technologies based on ion

exchanges, reverse osmosis and many more but these technologies have own limitations for dyes removal and cost effectiveness. Due to high efficiency and easy recovery adsorption is remain as most favorable for the pollutant removal (Patel & Vashi, 2012).
Removal of dyes using activated charcoal highly used in research activities. Biomass wastes such as corncobs, coconut shells, palm skins, apple pulp, chickpea peel, olive and walnut shells, cherry stones, rice bran, oil palm peels, tea wastes, bagasse of sugarcane and waste of palm oil fruit bundles have been found to be appropriate for making activated carbon. It is reported by various researchers that high surface area of activated carbon, high yields and better porous structure is achieved in chemical activation comparing to the physical activation (Sunanda, Tiwari, Sharma, & Raunija, 2013).
In this research activity soapnut shell and pineapple waste being used for making activated carbon, soapnut shell contains high carbon and low inorganic substances which is suitable for chemical activation (Ozer, Imamoglu, Turhan, & Boysan, 2012). Using soapnut shells and pineapple waste together for producing activated carbon is reported very limited in literature.

Among the many reagents proposed for chemical activation zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), aluminum chloride, magnesium chloride, potassium hydroxide (KOH), sodium hydroxide (NaOH) etc. out of which $ZnCl_2$, H_3PO_4, and KOH, are the most commonly used (Gong, Xie, Yang, & Yao, 2013; Kumar, Ramalingam, & Sathish kumar, 2011; Pathania, Sharma, & Singh, 2017).
This research aims to investigate and analyze adsorption efficiency of activated carbon prepared by using soapnut shells and pineapple waste for removal of methylene blue dyes from aqueous solution.

2. Material and Methods

2.1 Material: Soapnut seeds and pineapple waste are purchased from local shop in Kanpur. Synthetic wastewater was prepared from methylene blue dye $C_{16}H_{18}CIN_3S$ (Molar mass: 319.85 g/mol). High grade chemicals were used for experiment such as hydrochloric acid, sodium hydroxide, ortho phosphoric acid, sodium thiosulphate, iodine solution, sulphuric acid, starch, purchased from Thomas Baker.

2.2 Feed preparation: The seeds are broken manually in a traditional iron mortar-pestle. The internal flexible part from the soapnut is discarded because its adsorption capacity may be low and hard shell of the seed used for preparation of activated carbon. After washing the shell and pineapple waste with double-distilled water and at 105 °C it is dried in a laboratory hot air oven for 24 hrs. The shells of dried soapnut shell and pineapple waste were grinded in smaller size.

2.3 Activated carbon preparation: The coarse soapnut shell and pineapple waste are mixed with phosphoric acid (H_3PO_4) in the 1:1 w/v ratio and kept for digestion in hot air oven at 100 °C for 3 hours. Now this mixture is kept in muffle furnace at 500 °C for 1 hour 30 minutes. After carbonization the treated material is removed from the muffle furnace and place in desiccator for cool down to the room temperature. The material is washed several times with double-distilled water to eradicate the hints of free acid until it attains the pH value of 6. After that activated carbon is dried in laboratory hot air oven for 5 hours at 105 °C. The produced activated carbon is crushed, sieved and stored in moisture proof container.

3. Results and Discussion

3.1 Proximate analysis: The proximate analysis of the samples is done with standard method and yielded the following results shown in Table 1:

Table 1. Proximate analysis

S.N.	Content	Amount , %	
		Soapnut Shell	Pineapple Waste
1	Moisture	5.08	2.31
2	Ash	11.37	4.48
3	Volatile Matter	58.43	77.35
4	Fixed Carbon	25.12	15.56

Proximate analysis aids us to evaluate the amount of moisture, volatile, ash content and residual carbon present in the sample (Kurniawan & Ismadji, 2011). Result shows that the amount of moisture in soapnut shell is significantly high while ash and volatile content are low. The fixed carbon content in soapnut shell is high as comparison to pineapple waste.

3.2 Yield and characterization of activated carbon: The various characterization data is shown in Table 2 such as BET, pH, bulk density, yield of activated carbon etc. There is significant changes in data for both precursor i.e. soapnut shell and pineapple waste.

Table 2. Different properties of activated carbon

S.N.	Properties	Soapnut Shell	Pineapple Waste
1	Activated Carbon Yield,%	40.97	35.48
2	Bulk density, g/mL	0.383	0.417
3	Iodine number, mg/g	1248.93	785.85
4	pH	6.76	6.28
5	BET surface area, m^2/g	1287.770	987.890
6	Average pore radius ,Å	1.39×10^{1}	1.31×10^{1}
7	Total pore volume, cc/g	8.9×10^{-1}	8.3×10^{-1}

3.3 SEM analysis: The scanning electron microscopy (SEM) analysis was used to observe surface morphology of activated carbon. Figure 1 clearly shows that widespread variety of pores and fibrous structure are present in activated carbon.

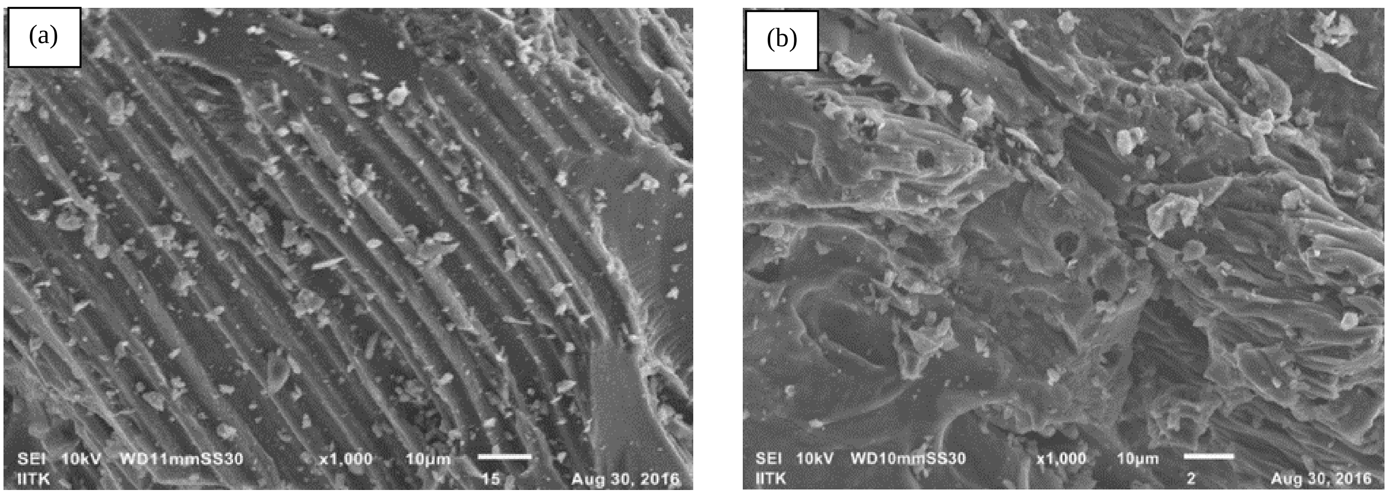

Figure 1. SEM Images of (a) Soapnut shell (b) Pineapple waste

3.4 Calibration curve: To obtain the amount, adsorption of methylene blue dye by activated carbon, an absorbance calibration curve versus concentration was drawn. Methylene blue dye was prepared at different concentrations and its absorbance was measured by spectrophotometer. The graphical representation of absorbance versus concentration provided a straight line through the origin as shown in Figure 2. This was used in conjunction with the various absorbance values of 668 nm wavelength light samples.

$$y = 0.0939\,x + 0.0065 \quad (1)$$

By equation 1 we can find the equilibrium concentration of the sample. The percentage color removal is given by Equation (2):

$$\%\ \text{color removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) is the initial and equilibrium concentration of the sample.

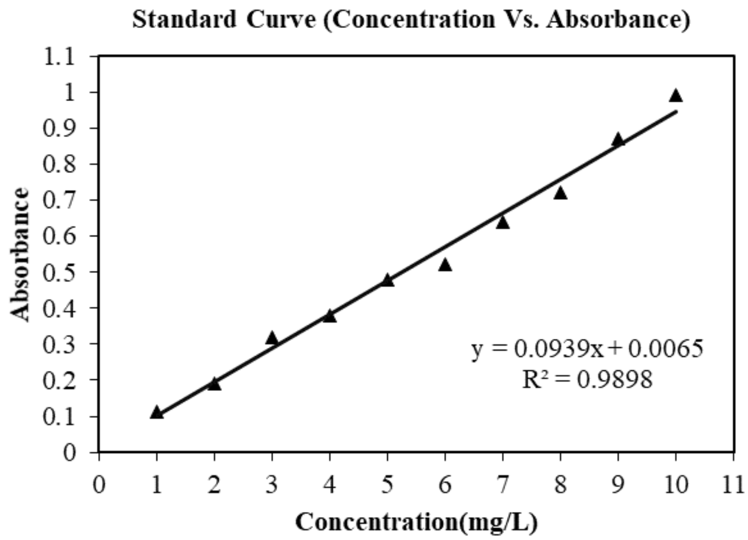

Figure 2. Calibration curve

3.5 Effect of initial concentration on adsorption: Adsorption experiments were carried out in the concentration range (10-50 mg/L) and an adsorbent dose of 0.5g. The amount of adsorbed MB decreases with increasing initial concentration, while maximum adsorption is obtained at the lowest concentration. The initial concentration of MB was plotted against the adsorption percentage of MB (Figure 3). The observed trend shows that it is higher in soapnut shell in comparison to pineapple waste. The amount of dye adsorbed per unit mass by adsorbent highly dependent on initial concentration of dye, at lower concentration it possesses maximum removal of MB (Mahapatra, Ramteke, & Paliwal, 2012; Yang & Qiu, 2010).

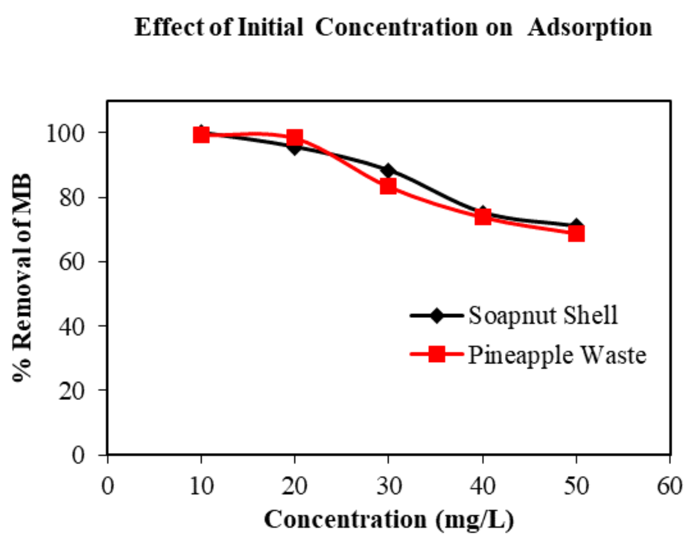

Figure 3. % Removal of MB vs Initial concentration by Soapnut shell and Pineapple waste (Amount of adsorbent = 0.5g, Adsorption time = 2 hr, Volume of adsorbate = 100ml)

3.6 Effect of adsorbent dose on adsorption: Effect of various amount of adsorbent is studied at constant time to investigate minimum amount of adsorbent required to achieve ~100% adsorption, 0.2,0.4,0.6,0.8,1.0 g of absorbent is used respectively, concentration of MB dyes is taken 100ppm (sample volume 100 ml). As expected, increase of absorbent amount increases the adsorption of MB dye, 0.6g of soapnut activated carbon is achieved nearly 100% adsorption and for same amount of adsorption 1g of pineapple waste activated carbon utilized. Above analysis concluded that 1g and 0.6 g are respectively amount of pineapple waste activated carbon and soapnut activated carbon for removing 100ppm MB dyes solution of 100ml. for economical point of view soapnut activated carbon finds to be more feasible for dye removal (Dargo, Gabbiye, & Ayalew, 2015; Mohammed MA, Shitu A, & Ibrahim A, 2014).

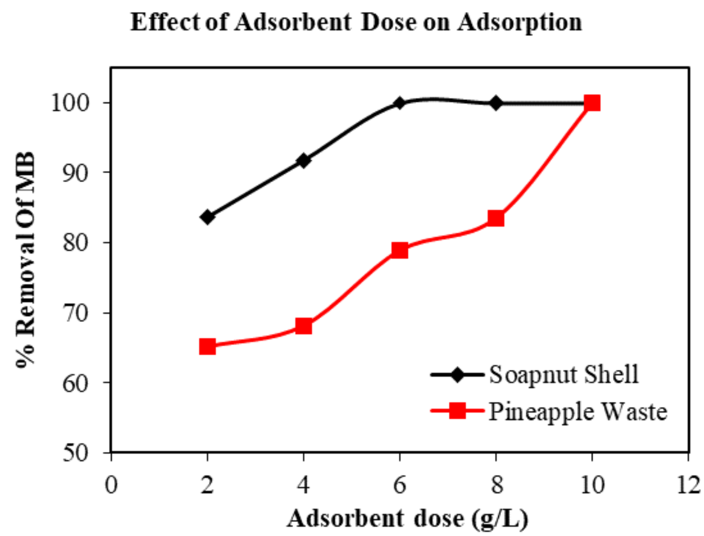

Figure 4. % Removal of MB vs Adsorbent dose by Soapnut Shell & Pineapple waste (Concentration of adsorbate = 100ppm, Volume of adsorbate = 100 ml, Adsorption time = 60 min)

3.7 Effect of contact time on adsorption: Figure 5 shows that, at 100 ppm concentration equilibrium contact time achieved within 120 min for MB after that removal efficiency become constant. Firstly, the percentage removal for MB was rapid up to 80 min thereafter it proceeds at a slower rate and finally attains saturation (Ibrahim, Haruna, & Ibrahim, 2012; Sugumaran, Susan, Ravichandran, & Seshadri, 2012). Generally, the contact time for adsorption is a crucial step to understand how the MB (adsorbate) approach to the adsorbent surface. The removal of the adsorbate is higher in the beginning due to the availability of high surface area after that it is saturated due to few active sites present on the adsorbent.

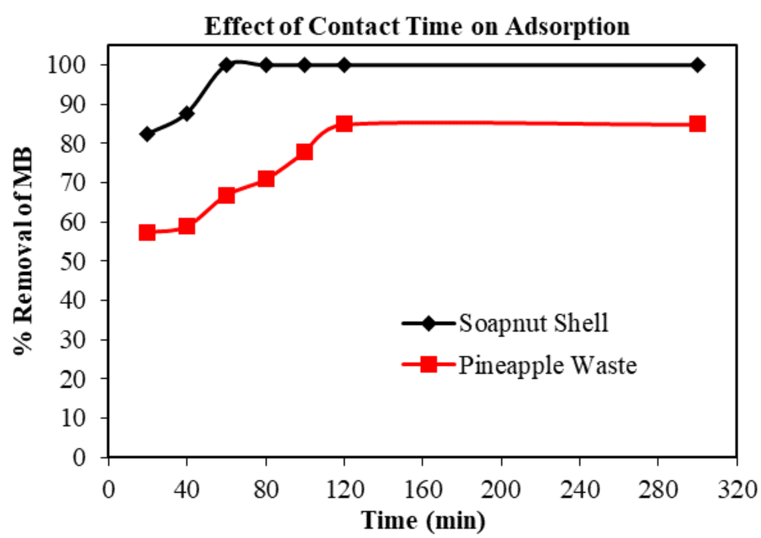

Figure 5. % Removal of MB vs Contact time by Soapnut Shell & Pineapple waste (Amount of adsorbent = 0.6g, Volume of adsorbate = 100ml, Concentration of adsorbate = 100ppm)

3.8 Adsorption isotherm study: Langmuir isotherm study is carried out to understand adsorption occurring on surface of both adsorbent, Langmuir isotherm is appropriate for homogeneous (Mahamad, Zaini, & Zakaria, 2015; Malik, 2004; Selvanathan & Subki, 2015). In Langmuir sorption, each molecule of sorbate which is adsorb on surface of adsorbent has identical activation energy. Langmuir isotherm is represented by following Equation (3):

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{3}$$

In Equation (3) q_e represent the concentration solid phase sorbate at equilibrium condition, both K_L and a_L are constants.
Equation (4) is the linear form of Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (4)$$

In this analysis linear form of equation is used for analysis of Langmuir isotherm, value of Ce /qe vs Ce are almost linear which show reasonable fitting of Langmuir isotherm. Values of Langmuir isotherm is given in Table 3. Freundlich isotherm is used for multilayer adsorption isotherm (Hameed, Din, & Ahmad, 2007; Joshi, Bansal, & Purwar, 2004), represented by Equation (5):

$$q_e = K_F C_e^{1/n} \quad (5)$$

where, K_F is Freundlich constant. Calculated values are best fitted with Langmuir isotherm and it is shown in Table 3**.**

Table 3. Different properties of activated carbon

Isotherm Parameters	**Soapnut shell**	**Pineapple waste**
Langmuir		
K_L(L/g)	9.9701	9.6154
a_L(L/mol)	1.4138	1.4192
R^2	0.9851	0.9823
Freundlich		
N	7.9114	5.2002
K_F	4.52	3.9243
R^2	0.9618	0.9218

4. Conclusions

The current study present that activated carbon derived from soapnut shell and pineapple waste is an effective adsorbent for methylene blue (MB) removal from the synthetic wastewater. The adsorption efficiency depends on process parameter like run time, initial concentration, pollutants type etc. The adsorption capacity of soapnut shell is much greater than that of pineapple waste derived activated carbon. The soapnut shell possess high surface area and require lower adsorbent dose for the removal of methylene blue dye i.e. 0.6g, the adsorption isotherm data fits well with langmuir isotherm. The dye removal is about 99% & 96% from soapnut shell & pineapple waste respectively. Overall soapnut shell and pineapple waste-based adsorbent can play vital role in environmental remediation.

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