Batch Adsorption Study of Methylene Blue in Aqueous Solution using Activated Carbons from Rice Husk and Coconut Shell

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ABSTRACT: The removal efficiency of activated carbons prepared from rice husk and coconut shell in the adsorption of methylene blue (azo dye) from the synthetic industrial wastewater was investigated in a batch system. Rice husk and coconut shell were both processed into activated carbon by carbonizing at 600 ºC and activated with 3.0 M H_3PO_4 at 80 ºC for 3h. Synthetic solutions of methylene blue were prepared and the adsorption process was carried out by varying initial, methylene blue concentration, adsorbent dosage, and contact. The results showed that higher values of adsorbent dosage and contact time favored the adsorption of methylene blue from the simulated waste water. Activated carbon from coconut shell proved a better adsorbent compared to the activated carbon obtained from rice husk as coconut shell has the highest percentage removal for methylene blue.

Synthetic dyes are organic compounds widely used in the textiles, rubber, paper, plastics, cosmetic, and leather industries (Ali *et al.,* 2012; Bhatnagar and Sillanpää, 2010; Yagub *et al.,* 2014). Dye as an organic compounds has the tendency to stick to surfaces of any materials such as fabrics to impact colour (Bouasla *et al.,* 2012). The use of synthetic chemical dyes in for different industrial applications has increased considerably over the years resulting in dye-containing industrial effluent discharged into aquatic ecosystems (Ahmad *et al.,* 2015; Aksu, 2005; Brillas, and Martínez-Huitle, 2015). Due to the recalcitrant and toxic nature of most dyes, discharging them into water bodies often results in environmental pollution (Pagga *et al.,* 1986). The addition of dyes into water bodies often lead to unpleasant colouration of the water surface which usually hinders penetrations of sun lights needed for photochemical and biological activities by the aquatic life (Ertugay and Acar, 2017; Mittal et al., 2014). Hence, it is expedients for the proper treatment of industrial wastewater containing dyes prior to discharging them into water bodies in order abate environmental pollution.

In the past decades, serious research efforts on how to efficiently remove dyes from industrial effluents have resulted in the investigations of methods such as adsorption, advanced oxidation, and membrane separations (Ahmad *et al*., 2015; Yagup *et al*., 2014). Reports have shown that these techniques proved to be effective and displayed varying degree of dye removal from the industrial wastewater (Kyzas et al., 2015; Yagub *et al.,* 2015). However, amongst the techniques, adsorption has been established as the most effective with applications in the industries for the removal of recalcitrant pollutants from the effluents prior to discharge into water bodies (Kyzas *et al.,* 2015). Recently, there is a growing attention on the treatment of these dye-containing effluent using cost-effective means by employing activated carbon produced from agriculture waste and industrial as an adsorbent for the removal of these recalcitrants organic compounds (Mohan *et al.,* 2014; Regti *et al*., 2017). Reports have shown that activated carbon has been obtained from industrial and agricultural waste rich in carbonaceous materials such as nutshells, coconut shell, rice husk, peat, wood, coir, lignite, and coal (Aljeboree *et al*., 2017; Mullick *et al*., 2018). This study therefore focuses on the comparative analysis of the performance of activated carbon produced from two industrial waste namely rice husk and coconut shell modified with H_2PO_4 used for the adsorption of methylene blue from a synthesized industrial wastewater in a batch system.

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MATERIALS AND METHODS

Preparation of Activated Carbon: The Rice Husk was obtained from a local milling factory at Niger state, Nigeria. The Coconut Shell was obtained from local coconut candy seller at ring road market, Benin City, Nigeria. The coconut shell and rice husk were initially washed thoroughly with potable water to remove dust, colour, and impurities then rinsed with distilled water and oven dried at 110 ºC for 3 h. Thereafter, both the dried coconut shell and the rise husk were separately grind, carbonated and activated with H_3PO_4. The carbonization of the dried rice husk and coconut shell were performed in a muffle furnace. Each of the two sample were kept in crucible and heated separately from ambient temperature to the carbonization temperature of 600 ºC for 1h. 200 g each of the carbonized samples were activated using in 400ml of 3 M H_3PO_4 for 4 h. Thereafter, the mixtures were filtered and the pH was checked and adjusted to pH. Subsequently, each of the samples were sieved using a 35mesh sized sieve to obtain a particle size of 0.45mm and stored separately in a sealable airtight plastics.

Preparation of Aqueous solution of Methylene Blue: Methylene blue solution of different concentration was prepared by dissolving an appropriate amount of methylene blue in a 1000 ml volumetric flask containing distilled water. The final methylene blue concentration was determined by using absorbance values measured at 668 nm after the treatment with visible spectrometer (Nwabanne and mordi, 2009).

Batch Experimental Studies: The batch experimental studies were conduction by mixing 100 ml of methylene blue with varying initial concentration and 2 g of the adsorbent in a set of 250 ml Erlenmeyer flasks (Hameed et al., 2008). The mixture was agitated maintaining a speed of 120 rpm at room temperature. At interval of 20 min, a known solution was taken from the mixture to measure the concentration of the methylene blue.

In order to ensure a clear solution, the sample was initially filtered to remove any activated carbon residues that might interfere with the reading. UV-Vis spectrophotometer was employed to measure the concentration of the methylene blue in the supernatant solution. The amount of methylene blue adsorbed by a unit mass of an adsorbent at equilibrium (Q_e), the amount of MB absorbed at any time and the adsorption percentage (%R) were calculated using the Equations (1)-(3), respectively (Abechi et al, 2011).

$$Q_e = \frac{C_o - C_e}{m} V \qquad (1)$$

$$Q_t = \frac{C_O - C_t}{m} V \qquad (2)$$

$$\text{Percent removal} = \frac{C_o - C_t}{C_o} 100 \qquad (3)$$

RESULTS AND DISCUSSION

Effect of Initial Methylene Blue Concentration: The influence of the initial methylene blue concentration (50, 100, 150, 200, 250, 300) mg/l on the adsorption rate using the adsorbents from rice husk and coconut shell were investiagted. The experiment was carried out using a constant adsorbent dosage of 2 g, at room temperature (26±1 °C). The effect of the initial methylene blue concentration on its removal efficiency is depicted in Figure 1.

It can be seen that the percentage removal of methylene blue decreases from 38% to 6% as the concentration increases from 50 to 300 mg/l. The trends observed for the removal of the methylene blue using adsorbent derived from rice husk revealed that the adsorption of methylene blue at room temperature is favoured at a higher concentration (Hameed et al., 2008). Moreover, the trend observed could be attributed to the fact that increase in concentration increases the number of methylene blue molecules with the limited adsorbent particle to attach to, and therefore the rate at which methylene blue molecule passes from the bulk solution to the adsorbent surface was highly reduced. A similar trend was also observed for the removal of methylene blue using adsorbent obtained from coconut shell. However, the percentage methylene blue removal of coconut shell adsorbent is higher compared to that of rice husk adsorbent because coconut shell is more porous and contain more active sites than rice husk (Aksu, 2005).
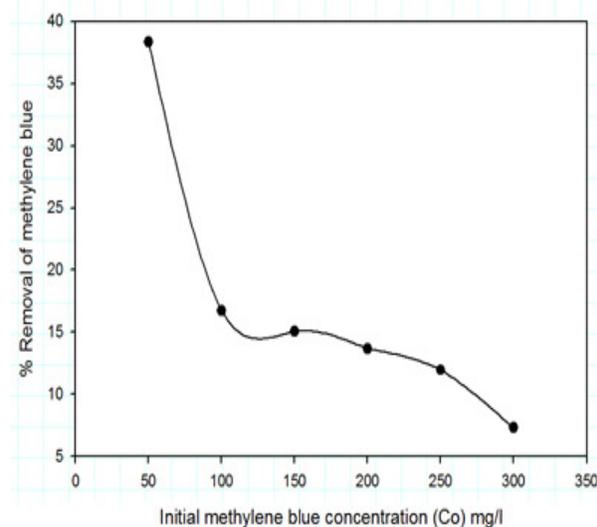

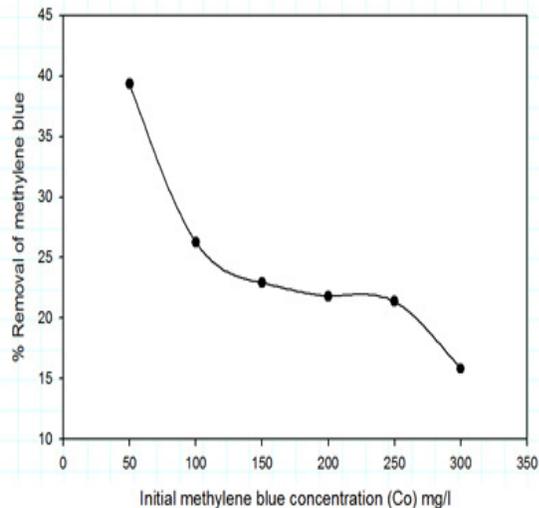**Figure 1**. Effect of initial dye concentration on the removal of methylene blue using adsorbents from rice husk.

Figure 2. Effect of initial dye concentration on the removal of methylene blue using adsorbents from rice husk.
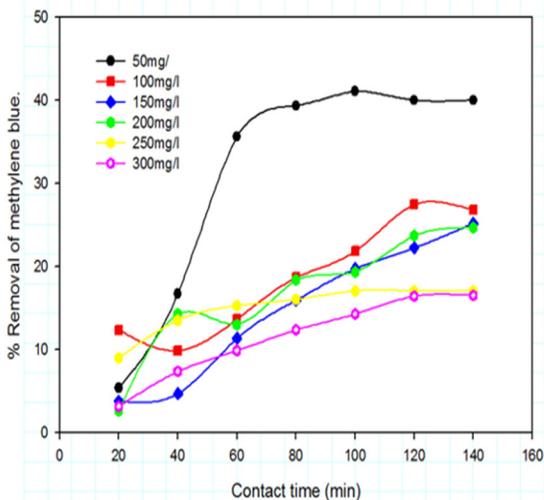

Figure 3: Effect of Contact time and initial methylene concentration on the removal of methylene blue using Coconut shell-based adsorbent.

Effect of Contact Time and Initial Methylene Concentration on the Removal Efficiency of the Methylene blue: The effect of contact time and the initial methylene concentration on the removal efficiency of the methylene blue using the two adsorbents from coconut shell and rice husks are depicted in Figure 3 and 4, respectively. It can be seen that the contact time for agitating the mixture of the adsorbents and the methylene blue solutions at varying initial methylene concentration had significant effect on the removal efficiency of the methylene by the two adsorbents. The increase in the contact time from 20 to 140 min resulted in corresponding increase in the amount of methylene blue removed from the solution. This could be attributed to the increase rate of mass transfer and molecular diffusion from the bulk solution

to the adsorbent (Weng and Pan, 2003). Moreover, the contact time seems to have more impact on the percentage methylene removal at higher initial methylene concentration. The adsorption of methylene blue by rice husk and coconut shell increased steadily throughout the 140 min contact time. The fast kinetics process observed at the initial stage can be attributed to the abundant availability of active binding site on the adsorbent which are later occupied as the process proceeds (Mavi et al., 2004). In the long run it was observe that coconut shell has a better adsorption capacity to rice husk

Effect of Adsorbent Dosage: The effect of the adsorbent dosage (0.5, 1, 1.5, 2, 2.5, and 3 g) on the percentage removal of methylene blue using rice husk- and coconut shell-based adsorbent are depicted in Figures 5 and 6, respectively. The effect of adsorbent dosage on the removal of the methylene blue from the solution was used to investigated to determine the capacity of adsorbent for a given initial adsorbate concentration and binding site available for adsorption. It can be seen that as the adsorbent dosage of the coconut shell-and rice husk-based adsorbent were increased from 0.5 to 3.0 g, there was a corresponding increase in the percentage removal of the methylene blue from the solution. This is an indication that the increase in the adsorbent dosage increases the methylene blue uptake as a result of the increase in the population of active site (Ho et al., 1995). For rice husk and coconut shell the maximum removal of methylene blue was observed at an adsorbent dosage of 3 g.
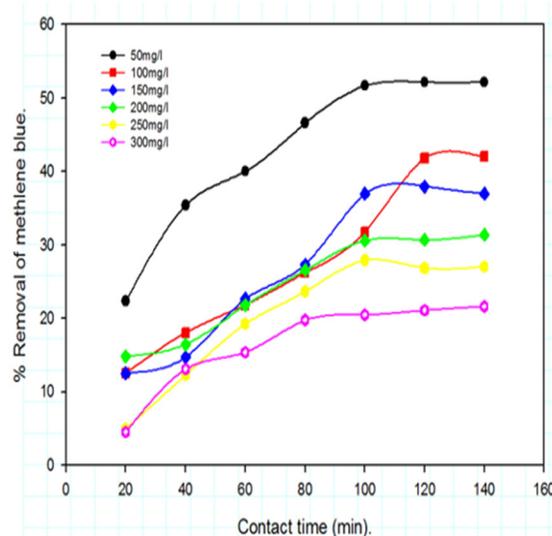

Figure 4: Effect of Contact time and initial methylene concentration on the removal of methylene blue using rice husk-based adsorbent.
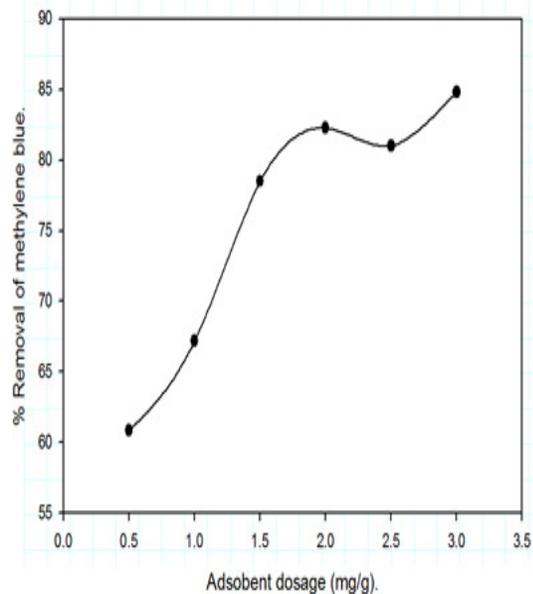
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Figure 5: Effect of adsorbent dosage of rice husk on the removal of methylene blue
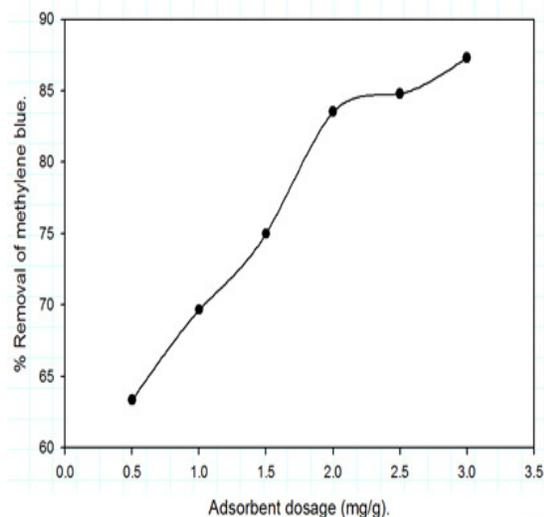

Figure 6: Effect of adsorbent dosage of rice husk on the removal of methylene blue

Conclusion: The present study has investigated the comparative analysis of methylene blue removal from synthetic waste water using adsorbent derived from coconut shell and rice husk. It can be inferred from the study that the parameters investigated significantly influenced the uptake of methylene blue from the simulated waste water on to the adsorbents. In all cases, for both coconut shell-and rice husk-based adsorbent, the percentage removal of the methylene blue from the solution increases with initial methylene concentrations, contact time and the adsorbent dosage. The activated carbon from coconut shell proved a better adsorbent compared to the activated carbon of rice husk.

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